Investigation of Organic Contaminants in the Kopeopeo Canal

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Cover Photo: Kope Canal below Shaw Road looking down to Site 6 and 5.

Executive Summary

A previous investigation of potential environmental contamination from historic wood waste dumps in the Whakatane area of the Bay of Plenty in November and December 2004 found most sites to have little impact with the apparent exception of the lower Kopeopeo and Orini Canals. In particular the sampling site in the lower Kopeopeo Canal had significant amounts of dioxin present in the sediments and eels. In this current study further sampling has been undertaken to investigate the extent of dioxin contamination in sediments and eels.

Results showed that sediments of the Kopeopeo Canal are extensively and heavily contaminated with dioxins and dioxin-like compounds. Data suggest however, that rather than leaching or spilling from the wood waste dumps, the high degree of contamination is predominantly a legacy of the past stormwater discharge from the Pinex sawmill. The historic stormwater outfall was located just above Site 5. It is probable that PCP levels and dioxin levels in eel flesh are also highest in this area.

The sediment dioxin contamination at Site 5 WHO-TEQ 295 pg/g dw (DR-Calux - TEQ 710 pg/g dw) is higher than any previous sample taken from an open water way in New Zealand's receiving environment and is comparable to the range of values listed by Ministry for Environment for soils (urban/industrial) from overseas (1998) and from estuaries (1999). All other samples taken from the Kopeopeo Canal range from 13 – 100 TEQ pg/g dw (DR-Calux) which means even the lowest may exceed over sea's dioxin sediment guideline of 10 TEQ pg/g dw for the protection of aquatic life. The Site 4 DR-Calux result is much higher (TEQ 2,300) but validation of the result is being undertaken. One positive point is that the contamination is not being actively transported from the site.

The previous study highlighted the human health risk from dioxins associated with consumption of eels from Site 2 in Kopeopeo Canal. The medium WHO-TEQ value of 3.56 for eel flesh means that an average adult male could only eat around 343 g of eel flesh per month without exceeding the guidelines. Results indicate that this risk is likely to be even higher at Site 5/4 and that 1 km further up stream at Site 6 the risk is substantially lower. At Site 7, 2 km above Site 5, there is very little if any risk from eel consumption. Previous results from the Orini Canal show that the dioxin impact on eels declines rapidly with distance in this connected water way. Also previous studies show that the shellfish and sediments in the estuary have not been impacted.

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Chapter 1: Introduction

1.1 Scope

This report presents the results of an investigation of the possible environmental impact of historic wood waste sites in the Whakatane area on the Kopeopeo Canal. It is a follow-up investigation to determine the extent of contamination found in both sediment and biota (eels), after the findings of an earlier wider survey highlighting contamination problems at this location (Park & Futter 2005). The investigation sought to assess;

- The level of dioxin contamination in sediments in terms of toxicity
- Bioaccumulation of dioxins in eels
- Assess the spatial extent and source of contamination
- Provide data to indicate levels of risk to human health regarding consumption of biota such as eels

1.2 Background

A number of properties within the Whakatane district received wastes between 1950 and 1989 from both the former Pinex sawmill and the board mill. During its 39 year period of operation, the Pinex sawmill discharged stormwater from its timber treatment area to the Kopeopeo Canal (just above Site 5 in this study).

Preliminary information on the whereabouts of these sites was provided to Whakatane District Council (WDC) and Environment Bay of Plenty by “SWAP” (Sawmills Workers against Poisons). SWAP members comprised of persons who were former employees of NZ Forest Products Ltd, former owners of both sawmill and board mill and other interested parties. This information was used to conduct a preliminary screening survey titled “Contaminated Site Screening Whakatane Board Mill Wastes” by Gwilym Environmental Services Ltd (GES). This report confirmed the existence of wastes at the majority of sites. GES sampled fifteen sites at random and analysed for pentachlorophenol (PCP). Samples from ten of these sites were analysed for dioxins using a screening method (hepta-chloro dibenzo-dioxin and octo-chloro dibenzo-dioxin).

Review of this report made it clear that further investigation was required to determine the risk at individual sites included in the screening report. In summary, the GES investigation program was conducted to confirm the general existence of the sites and to procure a generic understanding of the levels of PCP’s and dioxin related contaminants that may have been disposed of in any one of the sites that received waste.

Individual sites were investigated by Gulf Resource Management Ltd (GRM) to assess the risk associated with those generic levels between March 2003 and December 2003. The findings of the individual site risk assessments are summarised in the report titled "The Delineation & Risk Assessment of Mill Waste Disposal Sites Summary Report, February 2004" (GRM 2004). Additional surface water, sediment and biota sampling was recommended at a number of sites. This investigation was conducted in late 2004 and findings reported (Park & Futter 2005).

In general there were very low levels of chlorophenols or dioxin in the water ways into which these contaminated sites drain. There were however, significant levels of dioxin contamination identified in the sediment and biota of the lower Orini Stream and Kopeopeo Canal. Levels found in the Orini Stream, while high, do not appear to pose a significant risk to either biota or human consumption. In contrast those found in the Kopeopeo Canal are high enough to warrant further investigation to determine more accurately human and ecological risks from dioxin. This report covers the findings of the additional sediment and biota sampling.

Chlorophenols

Chlorophenols are found in a variety of environmental media including air, soil, sediment and biota. In the aquatic environment they tend to be mainly bound to sediment and suspended particles in the water. As a result they can often be found at far higher levels in biota than in the water itself. Industries such as pulp mills using chlorine are well known sources of chlorophenols.

The chlorophenol group of chemicals are aromatic organic compounds based on a single benzene ring with a hydroxyl (OH) group attached. Substitution of the hydrogen atoms with 1 – 5 chlorine atoms produces chlorophenols. The best known of these compounds is PCP or pentachlorophenol, which is the most halogenated of the phenols with five chlorine atoms attached. Toxicity of the lower halogenated phenols is low and increases with increasing chlorine substitution. PCP is the most toxic of the group. PCP is relatively non-toxic to birds but can be very toxic to fish. It is not highly accumulated in biota as it can be metabolised and removed from tissues and the blood stream. Toxicity is most often expressed by damage to the liver, kidneys and central nervous system. It has not been proven to be carcinogenic. Many of the toxicity studies have not used pure PCP and many of the effects observed are likely to be the result of other contaminants. Dioxin is a common contaminant of technical grade PCP that has been used extensively in the past for wood treatment.

Dioxins/furans

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are commonly known as dioxins. They are found in a variety of environmental media including air, soil, sediment and biota. The compounds are all very hydrophobic in nature, which means that they do not dissolve well in water. As a result they tend to attach quite strongly to other particulate matter and have a high affinity to bind with fatty compounds. This leads to the compounds being retained strongly by biota and being magnified at each step in a food chain. Their toxicity even at concentrations several orders of magnitude lower than most other chemicals has resulted in a great deal of public concern.

The dioxin and furan group of chemicals are aromatic organic compounds comprising of two benzene rings joined by either one or two oxygen atoms. They are classified as halogenated hydrocarbons due to the attachment of up to eight chlorine atoms. The different amounts of chlorine attachment and the sites at which they attach to the benzene rings results in a total of 75 possible dioxin (PCDD) congeners and 135 possible furan (PCDF) congeners. The most widely studied and known compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin. This congener is the reference compound in

respect of toxicity for deriving Toxicity Equivalency Factors (TEF) of all the other compounds belonging to the dioxin/furan group. TEF's presented in this report use the latest internationally accepted factors as agreed at a 1997 World Health Organization (WHO) consultation (Van den Berg *et al.*, 1998).

Toxicity of these compounds is dependant on the number of chlorine atoms that they contain. Congeners containing one, two or three chlorine atoms are thought to be non-toxic. Congeners with chlorine atoms substituted in the 2,3,7 and 8 positions are thought to pose a high degree of toxicological risk while further increases in substitution from four to eight chlorine atoms generally results in a marked decrease in potency. Table 1 below provides the homologues and the number of possible congeners.

Table 1 Homologues and congeners of the dioxin and furan group of compounds.

Abbreviation	Homologue name	No. possible congeners	No. of possible 2,3,7,8- chlorinated congeners
MCDD	Monochlorodibenzo-p-dioxin	**2**	0
DiCDD	Dichlorodibenzo-p-dioxin	**10**	0
TrCDD	Trichlorodibenzo-p-dioxin	**14**	0
TCDD	Tetrachlorodibenzo-p-dioxin	**22**	1
PeCDD	Pentachlorodibenzo-p-dioxin	14	1
HxCDD	Hexachlorodibenzo-p-dioxin	10	3
HpCDD	Heptachlorodibenzo-p-dioxin	2	1
OCDD	Octachlorodibenzo-p-dioxin	1	1
MCDF	Monochlorodibenzofuran	4	**0**
DiCDF	Dichlorodibenzofuran	16	**0**
TrCDF	Trichlorodibenzofuran	28	**0**
TCDF	Tetrachlorodibenzofuran	38	**1**
PeCDF	Pentachlorodibenzofuran	28	**2**
HxCDF	Hexachlorodibenzofuran	16	**4**
HpCDF	Heptachlorodibenzofuran	4	**2**
OCDF	Octachlorodibenzofuran	1	**1**

Chapter 2: Location and Methods

2.1 Location

Figure 1 Location of sampling sites along the Kopeopeo Canal.

The location of sites at which sampling was conducted is shown in Figure 1 above. Kopeopeo Canal drains water from low lying flat farm lands of the Rangitaiki Plains into the Whakatane Estuary. Water velocities are generally low and even up to Site 8 there is a tidal effect with water backing up during the high tide. There is a large control structure/flood gate on the canal just prior to discharge to the estuary which has been in place since 1969. Prior to its construction however, floods in the Whakatane Estuary would have created considerable water flows back up the canal. Before 1969 a much smaller control structure may have prevented tidal flows back up the canal.

Site 2 is the location of the original sampling site (38) from the previous study (Park & Futter 2005) and is adjacent one of the known wood waste sites. Sediment sampling in this investigation was however conducted mid channel and on the opposite bank to the wood waste dump site. Sites 9 and 10 were selected as reference (clean) sites for the sediment sampling. Site 6 is located downstream of where one of the stormwater drains from the old sawmill site is thought to have discharged. Site 5 is immediately downstream of the main stormwater outfall from the old sawmill site, while Site 4 is approximately another 200 m further downstream. Site 3 is immediately downstream of

the stormwater outfall for the industrial area at Gateway Drive and another of the wood waste dump sites.

The Patuwai Road site was included in this study to check whether there is any contamination from another wood waste site over which there are concerns. Patuwai Road drain is linked but kept separate from the Kopeopeo Canal and drains direct to the Whakatane River. All the wood waste sites and descriptions of them are provided in the GRM (2004) report prepared for Environment Bay of Plenty.

Sediment samples were collected from Sites 1 - 8 on 1st August 2005 and Sites 9 and 10 on the 22nd September 2005. Eels were caught between 1st and 11th August 2005.

2.2 Methods

Chemical analyses were all done by the IANZ accredited laboratory of AgriQuality New Zealand Limited which specialises in ultra low level analysis of organochlorine compounds. Specially prepared sample containers were provided by AgriQuality. All sampling was done using clean sampling methods. Chain of custody procedure was followed for the dispatch of all samples for analysis. All sample preparation areas and implements (stainless steel) used for processing eel and sediment samples were washed down with acetone and rinsed off with hexane prior to use.

Sampling methodology was designed to allow comparison to the MfE Organochlorines Programme and Tasman Mill studies on the levels of dioxins and furans in feral eels from the Tarawera River and other rivers in New Zealand. Eels were collected using baited fyke nets (25 mm mesh) set overnight as close as possible to the same locations from which sediment samples were taken. It was intended to obtain a composite sample of at least 10 small shortfin eels (*Anguilla australis*) <400 mm in length from each site if possible.

Selected eels were killed using an overdose of benzocaine before being measured and weighed. Flesh samples from the eels were comprised of a fillet taken in the mid-section with the skin left on and frozen until sent for analysis. Analysis of dioxins and furans was based on wet weight of eel flesh.

Eels in the desired size range would have been around 6-8 years old on average (Park 1998). Larger eels were not included as they eat different prey items which expose them to different and potentially higher levels of dioxins/furans.

Sediment sampling comprised of ten small surface (2-5 cm deep) replicate grab samples taken near the centre line of the water way at each site. Replicate grab samples were combined and thoroughly mixed to provide a single composite sample for each site. Sediment particle size fractions were determined for each composite sample.

Chapter 3: Results

3.1 Sediments

3.1.1 Physical Sediment Properties

Total organic carbon (TOC) content and the sediment particle size were analysed for all sediment samples as both these parameters influence the capacity to hold contaminants. In general contaminants will have a greater capacity to accumulate in sediments with higher TOC and mud (clay and silts) content.

Results for TOC and mud content of the sediment samples are provided in Table 2 below. Generally the sites above the old sawmill stormwater outfall (sites 6-10) have higher TOC and mud levels in the sediments. There is no obvious reason why TOC levels are lower from Site 5 down, unless contamination has had an effect in slowing biological production.

Table 2 TOC (%dw) and mud content of sediments.

Site	TOC	% Mud
Site 1 (downstream of dumps)	1.36	37.3
Site 2a (adjacent dump – Keepa Rd, Site 38 in previous study)	2.83	36.5
Site 2b (opposite dump – Keepa Rd)	2.33	40.0
Site 3 (downstream industrial area)	0.31	6.4
Site 4 (200m below old sawmill stormwater outfall)	1.12	13.8
Site 5 (directly below old sawmill stormwater outfall)	3.30	48.2
Site 6 (below main road)	5.49	63.8
Site 7 (upstream of all stormwater outfalls – Jones Rd)	7.44	90.1
Site 8 (upstream of all stormwater outfalls – SH30 crossing)	5.88	60.3
Site 9 (Powdrel Rd)	5.74	76.2
Site 10 (1 km above Powdrel Rd)	5.86	88.6
Patuwai Road	5.13	91.9

3.1.2 DR-Calux Toxicity Bioassay

Dioxins, furans and polychlorinated biphenyls (PCBs) show similar toxicity effects and belong to a group of chemicals known as polyhalogenated aromatic hydrocarbons (PHAHs). The **D**ioxin **R**esponsive-**C**hemically **A**ctivated **LU**ciferase e**X**pression (DR-CALUX) assay comprises a genetically modified H4IIE rat hepatoma cell-line, incorporating the firefly luciferase gene coupled to DREs (dioxin responsive enhancers) as a reporter gene for the presence of dioxins and dioxin-like compounds. Cells that are exposed to dioxins or dioxin-like chemicals not only express proteins and enzymes that are under normal circumstances associated to the DRE, but also luciferase. By addition of the appropriate substrate for luciferase, light is emitted. The amount of light is proportional to the amount of ligand-AhR binding which is related to 2,3,7,8-TCDD toxic equivalents (TEQs).

In summary, the DR-Calux assay provides a rapid, repeatable and accurate quantitative bio-assay test which is biologically relevant. It has the same degree of sensitivity in terms of TEQ as the instrumental techniques but tends to produce a higher result, although it can be considered to be roughly equivalent to WHO-TEQ results.

Results from the DR-Calux test on the sediments are presented in Table 3 below. Sites 1, 2b & 3 have lower levels of TEQ while sites 6, 7 & 8 have high levels recorded in the sample. Site 5 and 4 have extremely high results.

Table 3 DR-Calux sediment results providing TEQ pg/g-dw as sampled and standardised to clay/silt (mud) fraction and Total Organic Carbon (TOC) content.

	WHO-TEQ pg/g dw		
Site	**As sampled**	**Std - TOC**	**Std - Mud**
Laboratory blank	0.02-0.06		
Site 1	40	2,941	107
Site 2a*	100	3,534	250
Site 2b	13	558	36
Site 3	15	4,839	234
Site 4	2,300	205,357	16,667
Site 5	710	21,515	1,473
Site 6	84	1,530	132
Site 7	59	793	65
Site 8	53	901	88
Site 9	29	505	38
Site 10	41	700	46
Patuwai Road	12	234	13

* Sampled in previous survey at slightly different location to 2b (Park & Futter 2005)

The DR-Calux TEQ values shown above for samples taken from the Kopeopeo Canal are generally all in excess of the maximum dioxin TEQ values obtained in the Ministry for Environment studies (1998,1999) on New Zealand soils and estuarine sediments. In the MfE studies maximum PCDD and PCDF I-TEQ for soils was 33 pg/g found adjacent to a chemical plant, while the maximum in the estuary samples was 2.71 pg/g.

Standardising the results (Table 3), particularly to the amount of TOC present in the sediments shows more clearly that the contamination levels are highest on the downstream side of the outfall area (Sites 4/5).

A re-analysis of sediment samples from sites 2a and 5 was made to provide a breakdown of the dioxin contribution to TEQ and reveal the proportions of congeners. The results are in Table 4 below.

Table 4 Dioxin/furan analysis results for sediment samples from the Kopeopeo Canal showing homologue concentrations and WHO-TEQ in pg/g - dw.

Parameter	Site 2a	Site 5
2378 TCDD	1.2	2.8
Total TCDF	58	260
Total TCDD	890	250
Total PeCDF	100	570
Total PeCDD	380	480
Total HxCDF	830	3,500
Total HxCDD	1,500	2,900
Total HpCDF	2,800	12,000
Total HpCDD	6,600	25,000
OCDF	5,200	15,000
OCDD	50,000	150,000
Sum of congeners	68,400	210,000
WHO-TEQ - medium	95.4	294
CALUX - TEQ	100	710

The relative proportions of the different homologue groups of dioxins and furans shown above in Table 4 is reasonably typical of that commonly found in New Zealand and overseas. Proportionately there is a far greater amount of the higher chlorinated congeners. The pattern of homologue concentrations is also virtually identical to that observed for PCP formulations where OCDD are the most prevalent, followed by HpCDD then HxCDD congeners (Bright *et al* 1999).

At Site 2a it would appear that most of the TEQ recorded by DR-Calux bioassay can be attributed to the presence of dioxin while at Site 5 it would appear that other chlorinated chemicals may also be having an impact.

3.2 Biota (eels)

3.2.1 Biometric Data

The individual eel biometric data is available in Appendix II. Summarised data providing a comparison between sites is provided in Table 5 below. The number of eels in each sample, the median length weight and condition, plus the lipid content of each sample are given. Most of the eels caught were shortfin eels with only one or two longfin eels caught at each site. There are some morphological differences between the two species, but they are very similar and feed on the same prey items (Sagar *et. al*. 2005).

Table 5 Number, median length, weight, condition and lipid content of eels in each of the eel samples.

Site	(n)	Length (mm)	Weight (g)	condition	Lipid (%)
2	12	395	142	0.22	3.51
6	10	431	176	0.22	3.7
7	10	425	163	0.21	3.08
8	10	442	191	0.22	2.66

The lipid content is a measure of the fat content of the eels which can influence the degree to which some organic compounds such as dioxins are retained and accumulated. Results in Table 4 indicate that eels at all Kopeopeo Canal sites appear to be in good condition. Lipid content of the eels is similar at all sites but near the low end of the expected range. Eels from previous studies have commonly had lipid content around 5% with a very high value of 11% being recorded for eels at SH30 in the Tarawera River in 2002.

3.2.2 Dioxins

Results of the dioxin/furan analyses are summarised and presented in this section. The full results are provided in Appendix IV. Toxicity values (TEQ using World Health Organisation factors) are presented in Table 6 below. Site 6 had a full dioxin analysis conducted and recorded a low/moderate result which is lower than the result previously recorded at Site 2. Eels at Sites 7 and 8 were analysed using the DR-Calux bioassay and show low levels of toxicity with results being similar to the laboratory blank (0.13 pg/g TEQ).

Dioxin and furan congeners detected in the Site 2 and Site 6 samples showed a consistent pattern. 123678-HxCDD was the most abundant congener, followed by OCDD and 1234678 HpCDD. This type of pattern is close to that observed for PCP formulations where OCDD are the most prevalent, followed by HpCDD then HxCDD congeners (Bright *et al* 1999). Accordingly, there is a very high likelihood that the observed dioxin contamination in the eels, originally entered the environment with PCP that was detected at these sites in both this and the previous study (Park & Futter 2005).

A comparison between the results of this study and others which have reported levels of dioxins/furans in eel flesh is provided in Table 6 below. In terms of the MfE (1998a) study of background levels in New Zealand, Sites 2 and 6 are both well above background levels. Sites 7 and 8 only recorded low levels of TEQ and sit at the high end of the background range.

Table 6 *Comparison of toxicity equivalency (medium value) and the sum of dioxin/furan congeners recorded in eel flesh samples (pg/g ww) with other studies. Site 7 & 8 are DR-Calux results.*

Site		TEQ	Sum of congeners
Site 2 (covers a & b sub-sites)		3.56	47.5
Site 6		2.37	29.4
Site 7		0.11	
Site 8		0.14	
Tarawera River	**SH30 1991**	5.67	43.26
	SH30 2002	2.95	13.4
	Matata 2002	0.72	3.87
Canada (in MfE, 1998a)		0.2 – 2.2*	
Germany (in MfE, 1998a)		1.0 – 6.0*	
16 NZ river sites (MfE, 1998a)		0 – 0.38*	0 – 1.61

*TEQ values based on International toxicity equivalency .

Site 2 is higher than the levels measured in the Tarawera River in 2002 at SH30, but below the levels recorded in 1991 which would have been influenced by the previous elemental chlorine bleaching of pulp at the Tasman mill. It is also higher than the range of background levels recorded from Canada, but within the range given for studies in Germany.

Chapter 4: Discussion

Overall the results of this survey highlight extensive sediment contamination with dioxins of the Kopeopeo Canal. The results tend to suggest that rather than spilling or leaching out of the wood waste dumps, the contamination is historical, being centered on and caused by the old storm water discharge from the sawmill (Site 5). The canal has very little sediment movement if any because of the low current speeds. This means that any dioxin settling in the canal is essentially then locked up in the sediment and remains relatively immobile. The findings also show that it is possible that dioxin contamination previously reported in eels and sediment in the lower Orini Stream (Park & Futter 2005) is related to the old sawmill storm water discharge rather than the wood waste sites.

4.1 Sediment Contamination

In the previous study chlorophenols were measured at Site2a ("38") with PCP and the higher chlorinated phenols being prevalent in both the water and sediment samples. The Site 2a sediment PCP concentration of 22 ng/g is well above the New Zealand background levels. Given that Site 5 shows a much higher dioxin TEQ level, it is probable that PCP concentrations could also be much higher than Site 2a. A subsequent analysis of the sample from Site 4 showed that the total chlorophenols levels were higher (43 ng/g) but PCP concentration was 14 ng/g.

In terms of environmental guidelines for protection of aquatic organisms the Netherlands have sediment limit values of 20, 90 and 100 ng/g dw for PCP, TeCP and TCP respectively (in MfE 1999). The British Columbia Ministry of Environment has a suggested maximum PCP concentration in sediments from freshwater systems of 10 ng/g dw (Environment Canada 1988). The value of PCP at Site 2a in the Kopeopeo Canal exceeds both these values while Site 4 exceeds the later.

The DR-Calux bioassay results were a cost effective and biologically relevant means of investigating the potential toxicity of the sediments from dioxins and furans associated with the PCP. Repeatability of DR-Calux on sediments is good (within $\pm$ 22%) but the match with WHO – TEQ is not precise and does tend to be higher. As a method it has been well validated for foods, but in sediments there may be greater variation away from a quantitative result of combining PCBs and dioxin TEQ due to other organic compounds which may also bind to the dioxin receptors.

Most sites showed moderate to very high levels of toxicity equivalence in terms of 2,3,7,8-TCDD (TEQ). Subsequent analysis of two sediment samples for dioxin congeners has shown that at Site 2a, dioxin alone can account for the recorded DR-Calux TEQ. At Site 5 the dioxin analysis produced medium bound WHO-TEQ 294 pg/g dw which is lower than the DR-CALUX result of 710, although the I-TEQ for the same sample from the dioxin analysis was 432 pg/g dw. This highlights how much a result can change by assigning slightly different toxicity equivalency factors (TEF) to the various dioxin congeners. However, the difference is still large enough to open up the

possibility of PCBs or similar chlorinated organic compounds contributing to the observed biological toxicity at Site 5. Site 4 samples are being repeated to verify the DR-Calux/dioxin TEQ results.

There are very few guidelines for 2,3,7,8-TCDD in the aquatic environment. The Canadian Environmental Protection Authority has suggested a sediment TEQ value of 10 pg/g. All sites sampled in the Kopeopeo Canal exceed this if the DR-Calux TEQ were to be considered directly comparable, which they are not. The Patuwai Road Sample indicates that this drain probably does have an impact from dioxins with a TEQ value of 12 pg/g dw which is also marginally above the guideline. It is also possible the contamination results from the sawmill storm water outfall rather than wood waste sites as the drain does link to the Kopeopeo Canal and may have been open to flows from it in the past.

At two of the sites with lower values in the Kopeopeo Canal, there may have been changes which have reduced the recorded TEQ values. At Site 2b there may have been material deposited more recently as it was hard to avoid stones and rocks. Also at Site 3 the sediments were surprisingly very sandy and may indicate that this part of the canal had been dredged in more recent years. However it is also possible that biological production of organic material has been inhibited. When the results are viewed on the basis of standardizing for TOC, Site 3 has the third highest value.

Sites 7 – 10, which are 2 - 6 km respectively above the historic storm water outfall (Site 5) from the Pinex sawmill, had higher contamination levels in the sediments than expected. The reason for this may be that between 1950 when the sawmill started and 1969 when the Orini floodgate structure was built on the canal, that floods in the Whakatane Estuary caused regular backflow. This would have dispersed the storm water from the sawmill back up past these sites over a period of 19 years at times when site runoff was highest.

Overall the Kopeopeo Canal has elevated levels of toxicity in sediments from Site 10 – 1 with DR-Calux results ranging from 13 – 2,300 pg/g TEQ dw. Those samples for which a dioxin analysis has been done are well above New Zealand background levels and is similar to the high values reported by Ministry of Environment (1998, 1999) for industrialized areas of the world. A similar investigation of dioxin contamination of sediments in the Puarenga Stream near Rotorua as a result of sawmill operations (Gifford et al. 1993) found elevated levels with 32.3 pg/g TEQ dw. The recent investigation of the impact of the DOW chemical plant at New Plymouth on soils from air deposition (MfE 2002) showed dioxin levels highest adjacent the plant with a maximum TEQ pg/g dw of around 98.6. In that same study levels generally fell away quite quickly, with most values being less than 12 TEQ pg/g dw.

Comparative results from sediment samples collected from the Waioho Stream and 5 km up the Orini Stream show very low background levels of contamination (Park & Futter 2005). All these comparisons highlight the severe extent of contamination in the Kopeopeo Canal.

4.2 Biota Contamination

Previously an eel flesh sample obtained at Site 2, and in this study another three sites were established further up the Kopeopeo Canal and samples analyzed for dioxins and furans. These compounds are highly hydrophobic (do not dissolve in water) and bioaccumulate strongly in the food chain. As such the eels being further up the food chain provide a good indicator of the presence of dioxins and furans in the environment.

TEQ (2.37 pg/g ww) measured at Site 6 was less than Site 2 (3.56 pg/g ww). Site 6 is about 1km above the old storm water outfall at Site 5, while Site 2 is around 1.3 km below it. The DR-Calux TEQ values from eels at sites 7 & 8 were very low despite some sediment contamination recorded at these sites (see Figure 2 below). Site 8 is a total of around 3 km above the historic storm water outfall at Site 5. It appears that eels may be accumulating dioxin most readily near Site 5/4. Also it is probable that TEQ values peak just downstream from Site 5 and would be higher than the levels recorded at Site 2.

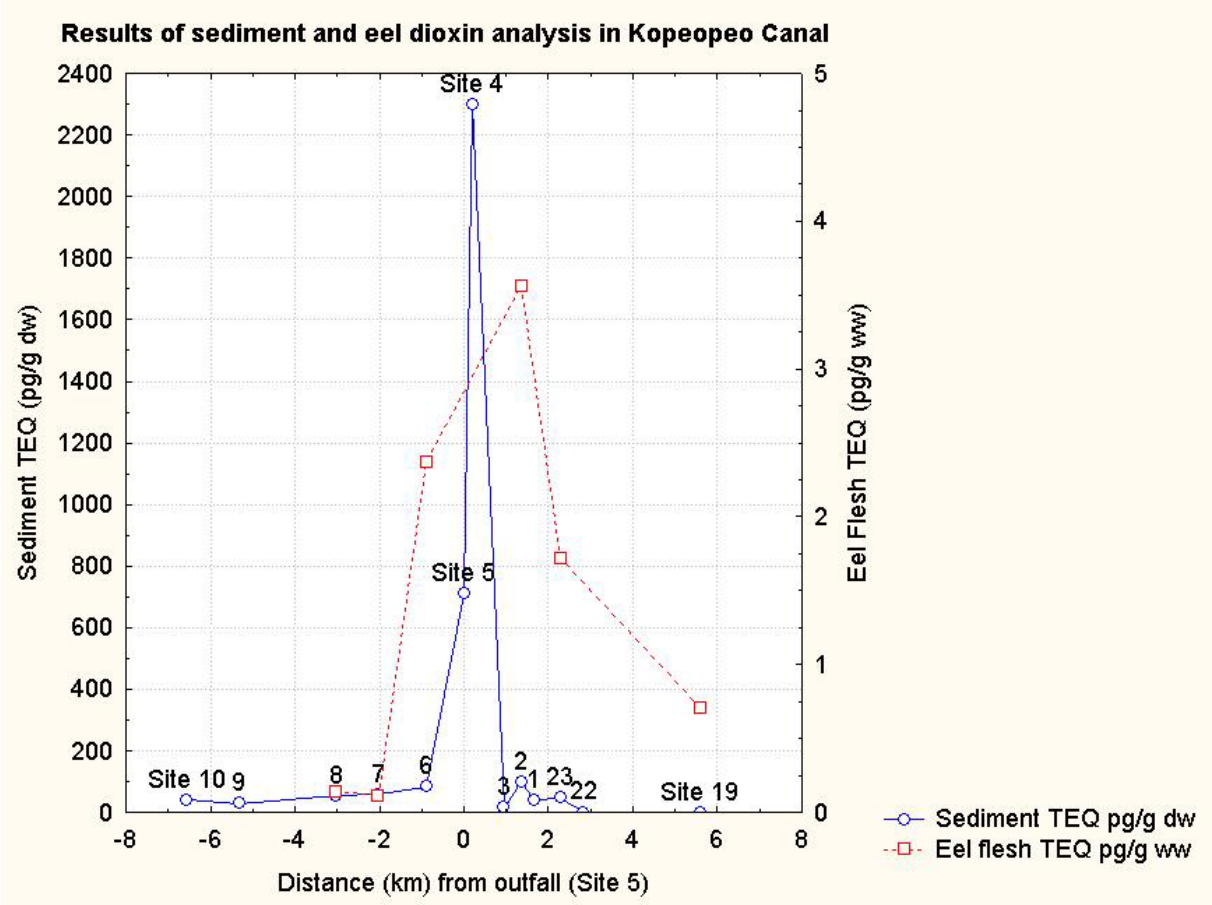

Figure 2 *Relationship between sediment (DR-Calux TEQ) and eel flesh contamination moving away from the historic storm water outfall point in Kopeopeo Canal (-ve is upstream, +ve is down stream and into the Orini Stream).*

The previous study which sampled eels in the Orini Stream which is connected shows that dioxin contamination declines with distance from Site 5. In that study a site 2.3 km away had an eel flesh TEQ value of 1.72 pg/g ww and at 5.6 km TEQ was 0.71 pg/g ww. These results are included in Figure 2 above.

Consumption of food containing dioxins and furans is thought to pose a high degree of health risk even when these compounds are present at very low levels. The Ministry of Health has a recommended Interim Maximum Monthly Intake guideline of 30 pg TEQ/kg of body weight/month. For a 70kg person this is 2,100 pg TEQ/month, or 544g of eel flesh based on the maximum possible concentration in eels from Site 2. The small eels of 400 mm length weighed around 140g each which means that this figure could be reached by consuming 4 small eels in a month.

Taking into account other dietary sources would reduce this number further. Median background exposure values for New Zealand adult male dietary intake were estimated to be 11.1 pg TEQ/kg bw/month, or for a 70kg male 777 pg TEQ/month. This would then mean only 2.5 small eels (343 g flesh) consumed in a month from Site 2 could put a person at risk of exceeding the guideline. Sample data suggests that the risk is even higher near Site 5 and then reduces again going up the canal. From Site 7 and above the risk appears to be low. To accurately identify risk, a local study would need to be conducted.

It should be noted that the health guidelines for consumption of dioxins and furans are based on lifetime exposures. There are large safety margins built in the guidelines as it is a very controversial and complex issue.

Previous studies have been done in Whakatane Estuary to investigate levels of dioxins and furans in the sediments and shellfish. These studies included a sediment sample from the estuarine receiving environment of the Orini Stream and Kopeopeo Canal. Dioxin result were low and suggest that the estuary is not currently being impacted. The Orini Stream and Kopeopeo Canal provide a very low energy environment in which contaminants can settle and accumulate with low risk of being transported elsewhere.

Results from this study also indicate that little transfer and bioaccumulation of dioxin in sediments by eels appears to be occurring in that part of the canal which is only moderately impacted. At Sites 7 and 8 sediment DR-Calux TEQs were 59 and 53 pg/g dw respectively, but eel flesh levels were similar to low background results found in non-impacted areas. Dioxin accumulation in the food chain appears to be occurring mainly around the old sawmill storm water outfall where sediment levels of dioxin are very high.

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Appendices

Appendix I Site locations

Appendix II Eel biometric data

Appendix III Dioxins/furans & DR-Calux - Sediment

Appendix IV Dioxins/furans & DR-Calux - Eels

Appendix 1 – Site Locations

Locations (NZMS260) of the samplings sites used in this study.

Site 1:	2859940 6354170	Sample #	05/4482
Site 2a:	2859550 6353870	Sample #	04/6838
Site 2b:	2859510 6353850	Sample #	05/4481
Site 3:	2859200 6353600	Sample #	05/4483
Site 4:	2858460 6353630	Sample #	05/5442
Site 5:	2858340 6353640	Sample #	05/4484
Site 6:	2857490 6353670	Sample #	05/4485, 05/4489
Site 7:	2856440 6353130	Sample #	05/4486, 05/4490
Site 8:	2855410 6353400	Sample #	05/4487, 05/4491
Site 9:	2853300 6353960	Sample #	05/5443
Site 10:	2852170 6354260	Sample #	05/5444

Appendix 2 –Eel Data

Biometric data for eels caught at sampling sites in Kopeopeo Canal.

Site	Species	length mm	weight g	Condition
1	shortfin	440	195	0.228916
1	shortfin	430	172	0.216333
1	shortfin	480	225	0.203451
1	shortfin	380	131	0.238737
1	shortfin	400	143	0.223438
1	shortfin	480	239	0.21611
1	shortfin	390	141	0.237698
1	shortfin	385	127	0.222547
1	shortfin	385	137	0.24007
1	shortfin	340	83	0.211174
1	shortfin	380	122	0.222336
1	longfin	445	147	0.166816
5	shortfin	520	331	0.235406
5	shortfin	458	242	0.251895
5	shortfin	492	294	0.246861
5	shortfin	444	212	0.242207
5	shortfin	461	201	0.20516
5	shortfin	417	148	0.204105
5	shortfin	411	150	0.216056
5	shortfin	406	146	0.21816
5	shortfin	360	87	0.186471
5	shortfin	390	124	0.209039
6	longfin	385	169	0.296145
6	longfin	424	199	0.261069
6	shortfin	409	138	0.201702
6	shortfin	430	157	0.197467
6	shortfin	385	108	0.189252
6	shortfin	426	138	0.178505
6	shortfin	400	134	0.209375
6	shortfin	485	272	0.238421
6	shortfin	482	225	0.200928
6	shortfin	555	365	0.213508
7	longfin	550	376	0.225995
7	shortfin	560	448	0.255102
7	shortfin	435	184	0.223537
7	shortfin	448	197	0.219095
7	shortfin	520	375	0.266699
7	shortfin	350	85	0.198251
7	shortfin	362	94	0.198154
7	shortfin	470	228	0.219605
7	shortfin	390	134	0.225897
7	shortfin	364	114	0.236375

Appendix 3 – Dioxins/Furans and DR-Calux – Sediment

AgriQuality Limited
Huarangi

Wellington Office
P.O. Box 31 242
1B Bell Road, Lower Hutt

Phone: 64 4 5708800
Facsimile: 64 4 5708176

15 September 2005

Certificate of Analysis

AgriQuality

Client:	Environment B.O.P PO Box 364 Whakatane
Attention:	Stephen Park
Date Received:	12 Aug 2005
AgriQuality Lab. Reference:	7080
Sample Type:	Soil
Analysis:	**Calux(R) Bioassay**

Method:

The sample was homogenised and extracted with organic solvent. The toxic equivalence (TEQ) of the extract was measured using the DR-Calux® Bioassay. The concentration of dioxin-like compounds in the samples are given in units of pg/g (ng/kg) total TEQ, on a dry weight basis to two significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Lawrence Porter
Authorised Signatory
AgriQuality Limited

15 September 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7080-1
Sample Identification: 05/4481 Kope Canal 1

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**13**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-2
Sample Identification: 05/4482 Kope Canal 2

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**40**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-3
Sample Identification: 05/4483 Kope Canal 3

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**15**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-4
Sample Identification: 05/4484 Kope Canal 4

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 13 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**710**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

15 September 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7080-5
Sample Identification: 05/4485 Kope Canal 5

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	84

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-6
Sample Identification: 05/4486 Kope Canal 6

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	59

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-7
Sample Identification: 05/4487 Kope Canal 7

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	53

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Amended Report Ref: 306235 THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY Page 6 of 10

15 September 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7080-8
Sample Identification: 05/4488 Patuwai Rd Drain

Date Received: 12 Aug 2005
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**12**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

15 September 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7080/BLANK-1
Sample Identification: Laboratory Blank

Date Received: Not applicable
Date Extracted: 25 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**0.060**

† = Results are calculated using the average weight of samples in this batch.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Certificate of Analysis

AgriQuality

Client:	Environment B.O.P PO Box 364 Whakatane
Attention:	Stephen Park
Date Received:	27 Sep 2005
AgriQuality Lab. Reference:	7755
Sample Type:	Soil
Analysis:	**Calux(R) Bioassay**

Method:

The sample was homogenised and extracted with organic solvent. The toxic equivalence (TEQ) of the extract was measured using the DR-Calux® Bioassay. The concentration of dioxin-like compounds in the samples are given in units of pg/g (ng/kg) total TEQ, on a dry weight basis to two significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Lawrence Porter
Authorised Signatory
AgriQuality Limited

Final Report Ref: 306734 THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY Page 1 of 5

17 October 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7755-1
Sample Identification: 05/5442 Kopeopeo Canal 200m from SW O

Date Received: 27 Sep 2005
Date Extracted: 29 Sep 2005
Date Analysed: 11 Oct 2005

Analyte	Conc.† (pg/g)
Teq	**2300**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Laboratory Reference: 7755-2
Sample Identification: 05/5443 Kopeopeo Canal Powdrel Rd

Date Received: 27 Sep 2005
Date Extracted: 29 Sep 2005
Date Analysed: 11 Oct 2005

Analyte	Conc.† (pg/g)
Teq	**29**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Laboratory Reference: 7755-3
Sample Identification: 05/5444 Kopeopeo Canal 1km Upstream fro

Date Received: 27 Sep 2005
Date Extracted: 29 Sep 2005
Date Analysed: 11 Oct 2005

Analyte	Conc.† (pg/g)
Teq	**41**

† = Results are reported on a dry weight basis.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Laboratory Reference: 7755 BLANK
Sample Identification: Laboratory Blank

Date Received: Not applicable
Date Extracted: 29 Sep 2005
Date Analysed: 11 Oct 2005

Analyte	Conc.† (pg/g)
Teq	**0.020**

† = Results are calculated using the average weight of samples in this batch.
< = Less than limit of detection.

Lab Analyst: TM Data Analyst: MV Authorised: Lawrence Porter

Certificate of Analysis

AgriQuality

Client:	Environment B.O.P Quay Street Whakatane
Attention:	Stephen Park
Date Received:	03 Dec 2004
AgriQuality Lab. Reference:	4563
Sample Type:	Sediment
Analysis:	**Polychlorinated dibenzo-p-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures as a lower, medium, and upper bound.

The total toxic equivalence (TEQ) was calculated for each sample using both WHO toxic equivalency factors (WHO-TEFs) and international toxic equivalency (I-TEFs). The total WHO-TEQ and I-TEQ level is reported as a lower, medium, and upper bound to three significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Mike Valentine
Authorised Signatory
AgriQuality Limited

NATA

laboratory

International Accreditation New Zealand (IANZ) has a Mutual Recognition Agreement (MRA) with the National Association of Testing Authorities (NATA), Australia, such that both organisations recognise accreditations by IANZ and NATA as being equivalent. Users of test reports/certificates are recommended to accept test reports/certificates in the name of either accrediting body.

Results: USEPA Method 1613B

Laboratory Reference: **4563-8**

Sample Identification: **04/6838 Site 26a/38**

Date Received: 03 Dec 2004 Date Analysed U2: 15 Apr 2005

Date Extracted: 13 Apr 2005 Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	ND	8		162	24 - 169	
Total TCDF	58					
2378 TCDD			1.2	72	25 - 164	
Total TCDD			890			
37Cl TCDD				95	35 - 197	
12378 PeCDF	ND	10		79	24 - 185	
23478 PeCDF	3.2			73	21 - 178	
Total PeCDF	100					
12378 PeCDD	5.9			109	25 - 181	
Total PeCDD	380					
123478 HxCDF	ND	60		109	26 - 152	
123678 HxCDF	18			114	26 - 123	
234678 HxCDF	12			119	28 - 136	
123789 HxCDF	ND	4		107	29 - 147	
Total HxCDF	830					
123478 HxCDD	ND	50		107	32 - 141	
123678 HxCDD	230			111	28 - 130	
123789 HxCDD	38					
Total HxCDD	1500					
1234678 HpCDF	640			86	28 - 143	
1234789 HpCDF	63			91	26 - 138	
Total HpCDF			2800			
1234678 HpCDD	3800			113	23 - 140	
Total HpCDD	6600					
OCDF	5200					
OCDD	50000			71	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	68400	68400	68400	pg/g
Total I-TEQ:	136	142	148	pg/g
Total WHO-TEQ:	89.1	95.4	102	pg/g

† = Results are reported on a dry weight basis

ND = Not Detected

DL: Sample Specific Estimated Detection Limit

EMPC: Estimated Maximum Possible Concentratio

^{13}C %RE: Labelled Compound Recovery

LCL-UCL: Lower Control Limit - Upper Control Limit

$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: MP Data Analyst: PB Authorised: Mike Valentine

Results: USEPA Method 1613B

Laboratory Reference: **4563 BLANK**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 13 Apr 2005
Date Analysed U2: 15 Apr 2005
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.4		136	24 - 169	
Total TCDF	ND	0.4				
2378 TCDD	ND	0.7		88	25 - 164	
Total TCDD	ND	0.7				
37Cl TCDD				111	35 - 197	
12378 PeCDF	0.35			76	24 - 185	
23478 PeCDF	0.35			80	21 - 178	
Total PeCDF	0.69					
12378 PeCDD	0.40			107	25 - 181	
Total PeCDD	0.40					
123478 HxCDF	0.43			107	26 - 152	
123678 HxCDF	ND	0.4		106	26 - 123	
234678 HxCDF	ND	0.4		126	28 - 136	
123789 HxCDF	ND	0.6		106	29 - 147	
Total HxCDF	0.43					
123478 HxCDD	ND	0.5		105	32 - 141	
123678 HxCDD	ND	0.5		103	28 - 130	
123789 HxCDD	ND	0.5				
Total HxCDD	ND	0.5				
1234678 HpCDF	ND	0.7		76	28 - 143	
1234789 HpCDF	ND	0.8		84	26 - 138	
Total HpCDF	ND	0.8				
1234678 HpCDD	0.50			92	23 - 140	
Total HpCDD	0.50					
OCDF	ND	1				
OCDD	1.4			46	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	3.42	5.12	6.82	pg/g
Total I-TEQ:	0.442	0.965	1.49	pg/g
Total WHO-TEQ:	0.641	1.16	1.69	pg/g

† = Results are calculated using the average weight of samples in this batch

ND = Not Detected

DL: Sample Specific Estimated Detection Limit
EMPC: Estimated Maximum Possible Concentratio
^{13}C %RE: Labelled Compound Recovery
LCL-UCL: Lower Control Limit - Upper Control Limit
$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: MP Data Analyst: PB Authorised: Mike Valentine

Certificate of Analysis

AgriQuality

Client:	Environment B.O.P PO Box 364 Whakatane
Attention:	Stephen Park
Date Received:	12 Aug 2005
AgriQuality Lab. Reference:	7080
Sample Type:	Soil
Analysis:	**Polychlorinated dibenzo-p-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures as a lower, medium, and upper bound.

The total toxic equivalence (TEQ) was calculated for each sample using both WHO toxic equivalency factors (WHO-TEFs) and international toxic equivalency (I-TEFs). The total WHO-TEQ and I-TEQ level is reported as a lower, medium, and upper bound to three significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Mike Valentine
Authorised Signatory
AgriQuality Limited

NATA

new zealand accredited laboratory

International Accreditation New Zealand (IANZ) has a Mutual Recognition Agreement (MRA) with the National Association of Testing Authorities (NATA), Australia, such that both organisations recognise accreditations by IANZ and NATA as being equivalent. Users of test reports/certificates are

Results: USEPA Method 1613B

Laboratory Reference: **7080-4**

Sample Identification: **05/4484 Kope Canal 4**

Date Received: 12 Aug 2005 Date Analysed U2: 26 Sep 2005

Date Extracted: 21 Sep 2005 Date Analysed SP2331: 27 Sep 2005

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	2.8			72	24 - 169	
Total TCDF	260					
2378 TCDD	6.7			71	25 - 164	
Total TCDD	250					
37Cl TCDD				71	35 - 197	
12378 PeCDF	12			86	24 - 185	
23478 PeCDF	9.6			87	21 - 178	
Total PeCDF	570					
12378 PeCDD	20			81	25 - 181	
Total PeCDD	480					
123478 HxCDF	120			86	26 - 152	
123678 HxCDF	51			89	26 - 123	
234678 HxCDF	ND	10		97	28 - 136	
123789 HxCDF	ND	20		85	29 - 147	
Total HxCDF	3500					
123478 HxCDD	39			95	32 - 141	
123678 HxCDD	550			89	28 - 130	
123789 HxCDD	100					
Total HxCDD	2900					
1234678 HpCDF	2400			81	28 - 143	
1234789 HpCDF	320			89	26 - 138	
Total HpCDF			12000			
1234678 HpCDD	13000			98	23 - 140	
Total HpCDD	25000					
OCDF	15000					
OCDD	150000			108	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	210000	210000	210000	pg/g
Total I-TEQ:	431	432	434	pg/g
Total WHO-TEQ:	292	294	295	pg/g

† = Results are reported on a dry weight basis

ND = Not Detected

DL: Sample Specific Estimated Detection Limit

EMPC: Estimated Maximum Possible Concentratio

^{13}C %RE: Labelled Compound Recovery

LCL-UCL: Lower Control Limit - Upper Control Limit

$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: TG Data Analyst: AP Authorised: Mike Valentine

Results: USEPA Method 1613B

Laboratory Reference: **7080/BLANK-A**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable — Date Analysed U2: 26 Sep 2005

Date Extracted: 21 Sep 2005 — Date Analysed SP2331: 27 Sep 2005

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.7		75	24 - 169	
Total TCDF	ND	0.7				
2378 TCDD	ND	1		74	25 - 164	
Total TCDD	ND	1				
37Cl TCDD				76	35 - 197	
12378 PeCDF	ND	0.5		102	24 - 185	
23478 PeCDF	ND	0.5		103	21 - 178	
Total PeCDF	ND	0.5				
12378 PeCDD	ND	1		98	25 - 181	
Total PeCDD	ND	1				
123478 HxCDF	ND	0.6		96	26 - 152	
123678 HxCDF	ND	0.6		101	26 - 123	
234678 HxCDF	ND	0.6		104	28 - 136	
123789 HxCDF	ND	0.9		94	29 - 147	
Total HxCDF	ND	0.9				
123478 HxCDD	ND	2		98	32 - 141	
123678 HxCDD	ND	2		100	28 - 130	
123789 HxCDD	ND	2				
Total HxCDD	ND	2				
1234678 HpCDF	ND	1		89	28 - 143	
1234789 HpCDF	ND	1		101	26 - 138	
Total HpCDF	ND	1				
1234678 HpCDD	ND	2		96	23 - 140	
Total HpCDD	ND	2				
OCDF	ND	3				
OCDD	ND	2		80	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	0	7.05	14.1	pg/g
Total I-TEQ:	0	1.38	2.76	pg/g
Total WHO-TEQ:	0	1.63	3.26	pg/g

† = Results are calculated using the average weight of samples in this batch

ND = Not Detected

DL: Sample Specific Estimated Detection Limit

EMPC: Estimated Maximum Possible Concentratio

^{13}C %RE: Labelled Compound Recovery

LCL-UCL: Lower Control Limit - Upper Control Limit

$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: TG Data Analyst: AP Authorised: Mike Valentine

Appendix 4 – Dioxins/Furans and Calux – Eels

AgriQuality Limited
Hoarangi

Wellington Office
P.O. Box 31 242
1B Bell Road, Lower Hutt

Phone: 64 4 5708800
Facsimile: 64 4 5708176

07 September 2005

Certificate of Analysis

Client:	Environment B.O.P PO Box 364 Whakatane
Attention:	Stephen Park
Date Received:	12 Aug 2005
AgriQuality Lab. Reference:	7080
Sample Type:	Biota
Analysis:	**Polychlorinated dibenzo-p-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a wet weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures.

The total toxic equivalence (TEQ) was calculated for each sample using both WHO toxic equivalency factors (WHO-TEFs) and international toxic equivalency (I-TEFs). The total WHO-TEQ and I-TEQ level is reported as a lower, medium, and upper bound to three significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Mike Valentine
Authorised Signatory
AgriQuality Limited

07 September 2005

Results: USEPA Method 1613B

Laboratory Reference: **7080-9**

Sample Identification: **05/4489 Kope Canal 5 Eel Flesh**

Date Received: 12 Aug 2005 Date Analysed U2: 31 Aug 2005

Date Extracted: 26 Aug 2005 Date Analysed SP2331: 31 Aug 2005

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.2		58	24 - 169	
Total TCDF	1.4					
2378 TCDD	0.18			61	25 - 164	
Total TCDD	1.0					
37Cl TCDD				72	35 - 197	
12378 PeCDF	ND	3		77	24 - 185	
23478 PeCDF	0.17			76	21 - 178	
Total PeCDF	2.1					
12378 PeCDD	0.87			77	25 - 181	
Total PeCDD	1.6					
123478 HxCDF	ND	0.2		81	26 - 152	
123678 HxCDF	ND	0.2		85	26 - 123	
234678 HxCDF	ND	0.2		87	28 - 136	
123789 HxCDF	ND	0.3		81	29 - 147	
Total HxCDF	1.1					
123478 HxCDD	ND	0.4		81	32 - 141	
123678 HxCDD	10			83	28 - 130	
123789 HxCDD	0.42					
Total HxCDD	11					
1234678 HpCDF	0.36			66	28 - 143	
1234789 HpCDF	ND	0.3		81	26 - 138	
Total HpCDF	2.6					
1234678 HpCDD	3.5			75	23 - 140	
Total HpCDD	4.6					
OCDF	ND	0.5				
OCDD	3.7			34	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	29.1	29.4	29.6	pg/g
Total I-TEQ:	1.78	1.94	2.09	pg/g
Total WHO-TEQ:	2.22	2.37	2.52	pg/g

† = Results are reported on a wet weight basis

ND = Not Detected

DL: Sample Specific Estimated Detection Limit

EMPC: Estimated Maximum Possible Concentratio

^{13}C %RE: Labelled Compound Recovery

LCL-UCL: Lower Control Limit - Upper Control Limit

$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: TR Data Analyst: AP Authorised: Mike Valentine

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07 September 2005

Results: USEPA Method 1613B

Laboratory Reference: **7080/BLANK-B**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable — Date Analysed U2: 31 Aug 2005

Date Extracted: 26 Aug 2005 — Date Analysed SP2331: 31 Aug 2005

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C%RE	LCL-UCL	Qualifiers
2378 TCDF	0.033			70	24 - 169	
Total TCDF	0.062					
2378 TCDD	ND	0.03		73	25 - 164	
Total TCDD	ND	0.03				
37Cl TCDD				73	35 - 197	
12378 PeCDF	ND	0.03		91	24 - 185	
23478 PeCDF	ND	0.03		89	21 - 178	
Total PeCDF	ND	0.03				
12378 PeCDD	ND	0.05		93	25 - 181	
Total PeCDD	ND	0.05				
123478 HxCDF	ND	0.04		86	26 - 152	
123678 HxCDF	ND	0.04		97	26 - 123	
234678 HxCDF	ND	0.04		98	28 - 136	
123789 HxCDF	ND	0.05		87	29 - 147	
Total HxCDF	ND	0.05				
123478 HxCDD	ND	0.04		98	32 - 141	
123678 HxCDD	ND	0.04		103	28 - 130	
123789 HxCDD	ND	0.04				
Total HxCDD	ND	0.04				
1234678 HpCDF	ND	0.02		78	28 - 143	
1234789 HpCDF	ND	0.03		85	26 - 138	
Total HpCDF	ND	0.03				
1234678 HpCDD	0.045			83	23 - 140	
Total HpCDD	0.045					
OCDF	ND	0.1				
OCDD	0.11			53	17 - 157	

	Lower Bound	Medium Bound	Upper Bound	Units
Sum of congeners:	0.217	0.382	0.547	pg/g
Total I-TEQ:	0.00386	0.0544	0.105	pg/g
Total WHO-TEQ:	0.00376	0.0668	0.130	pg/g

† = Results are calculated using the average weight of samples in this batch

ND = Not Detected

DL: Sample Specific Estimated Detection Limit

EMPC: Estimated Maximum Possible Concentratio

^{13}C %RE: Labelled Compound Recovery

LCL-UCL: Lower Control Limit - Upper Control Limit

$^{37}CL_4$ TCDD: Clean-up recovery spike

Lab Analyst: TR Data Analyst: AP Authorised: Mike Valentine

Final Report Ref: 306119 THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY Page 3 of 3

AgriQuality Limited
Huarangi

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P.O. Box 31 242
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Phone: 64 4 5708800
Facsimile: 64 4 5708176

15 September 2005

Certificate of Analysis

Client: Environment B.O.P
PO Box 364
Whakatane

Attention: Stephen Park

Date Received: 12 Aug 2005

AgriQuality Lab. Reference: 7080

Sample Type: Biota

Analysis: **Calux(R) Bioassay**

Method:

The sample was homogenised and extracted with organic solvent. The toxic equivalence (TEQ) of the extract was measured using the DR-Calux® Bioassay. The concentration of dioxin-like compounds in the samples are given in units of pg/g (ng/kg) total TEQ, on an as received basis to two significant figures.

Unless requested, samples will be disposed of three months from the date of this report.

Lawrence Porter
Authorised Signatory
AgriQuality Limited

Amended Report Ref: 306235

15 September 2005

Results: DR-Calux Bioassay

Laboratory Reference: 7080-10
Sample Identification: 05/4490 Kope Canal 6 Eel Flesh

Date Received: 12 Aug 2005
Date Extracted: 26 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**0.11**

† = Results are reported on an as received basis.
< = Less than limit of detection.

Lab Analyst: TR Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080-11
Sample Identification: 05/4491 Kope Canal 7 Eel Flesh

Date Received: 12 Aug 2005
Date Extracted: 26 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**0.14**

† = Results are reported on an as received basis.
< = Less than limit of detection.

Lab Analyst: TR Data Analyst: MV Authorised: Lawrence Porter

Results: DR-Calux Bioassay

Laboratory Reference: 7080/BLANK-E
Sample Identification: Laboratory Blank

Date Received: Not applicable
Date Extracted: 26 Aug 2005
Date Analysed: 06 Sep 2005

Analyte	Conc.† (pg/g)
Teq	**0.13**

† = Results are calculated using the average weight of samples in this batch.
< = Less than limit of detection.

Lab Analyst: TR Data Analyst: MV Authorised: Lawrence Porter

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