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RISK ASSESSMENT OF SEDIMENT DISPLACED IN THE WAITANGI CATCHMENT FOLLOWING CYCLONE GABRIELLE

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RISK ASSESSMENT OF SEDIMENT DISPLACED IN THE WAITANGI CATCHMENT FOLLOWING CYCLONE GABRIELLE

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EXECUTIVE SUMMARY

In February 2023, the Hawke's Bay Region was heavily impacted by Cyclone Gabrielle, experiencing intense weather conditions with more than 180 mm of rainfall in a day. Rivers and streams surged beyond their banks, carrying significant amounts of sediment in their flow. The suburb of Awatoto, south of Napier, where the sewage treatment plant and a variety of industries are located, was heavily impacted, and contaminants were potentially spread across the land.

The aim of this study was to investigate the risk of displaced sediments that were deposited throughout the Waitangi catchment, south of Napier City, using a combination bioassays and chemical analysis. Sediment samples were collected from three locations between the coastline and Waitangi Stream (Sites 4679, 4680 and 4681, from north to south), and toxicity was assessed using a series of bioassays. Chemicals present in the samples were subjected to targeted analysis for specific analytes and a more rapid comprehensive chemical analysis method based on an automated identification and quantification system linked to a database. The toxicity of sediments was assessed on chemical extracts or elutriates with four different bioassays. The yeast two-hybrid assays provide insights into the presence of organic chemicals, including dioxin-like chemicals. The Microtox® and blue mussel embryo-larval development assays provide indication on the general toxicity of the extracts to bacteria and invertebrates.

The *in vitro* assay (yeast two-hybrid), with the human ligand-activated transcription factors involved in xenobiotic metabolism, detected high activity levels in two of the three samples (4679 and 4681). The Microtox® and blue mussel embryo-larval development (survival) bioassays detected significant inhibitory activities for samples 4679 and 4680.

The targeted and comprehensive analyses both detected the presence of insecticides in sediments.

The most toxic sediment elutriate was found at the site 4679 with the blue mussel test, but variation in pH could have been a confounding factor affecting the survival of the embryos.

Overall, the results from this study suggest that the toxicity and chemicals detected are what would be expected from a typical agricultural soil. The risk posed by the displaced sediment in the Waitangi catchment can be considered low. Nonetheless, some caution is warranted for handling and disposing of the sediment material.

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1. INTRODUCTION

On 14 February 2023, Tropical Cyclone Gabrielle impacted Hawke's Bay Region, depositing more than 180 mm of rainfall in a day at Napier's Hawke's Bay Airport (Figure 1) and generating strong winds, resulting in widespread damage and flooding. Rivers burst their banks, flooding homes and businesses. The Awatoto suburb south of Napier City was completely inundated, including the wastewater treatment plant, the surrounding industrial area (Napier City Council 2023) and the Waitangi Stream catchment (Figure 2), and contaminants were potentially spread across the land.



Figure 1. Daily precipitation at Hawke's Bay Airport from January to the end of February 2023. Data source: National Institute of Water and Atmospheric Research.





Figure 2. Before (A) and after (B) Cyclone Gabrielle hit the Awatoto suburb of Napier in the vicinity of Waitangi Stream. Imagery source: Toitū Te Whenua – Land Information New Zealand.

There were concerns over the potential risk posed by the silt and sediment that were displaced and covered the Waitangi Stream during the cyclone event. Staff from Hawke's Bay Regional Council (HBRC) contracted Cawthron Institute (Cawthron) to conduct an investigation to assess the risk of contamination associated with the displaced sediment.

The aims of this study were to assess the toxicity of sediment samples from the Waitangi Stream to provide an indication of chemical contamination and using a series of bioassays. Chemical contamination was assessed using a rapid comprehensive chemical analysis method and a targeted chemical analysis. For bioassays, we used bacteria and mussel embryo development standard tests to assess the general toxicity of the sediment samples. Two yeast-based assays were used to determine the presence of chemicals commonly found in urban environments based on their biological activities. The aryl hydrocarbon receptor (AhR) and the constitutive androstane receptor (CAR) are ligand-activated transcription factors involved in xenobiotic metabolism. Dioxin-like compounds are the ligands of the AhR and include molecules such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). CAR has a low specificity for ligands and is implicated in hepatic detoxification of endogenous molecules, xenobiotics and environmental contaminants. Both AhR and CAR yeast assays have detected these biological activities for many chemicals (Kamata et al. 2018; Shiraishi et al. 2018).

2. MATERIAL AND METHODS

2.1. Sediment sampling

Sediment samples were collected by HBRC staff on 13 May 2023 at three locations (Figure 3):

- Waitangi Stream opposite 32 Waitangi Road (Site 4679) (latitude -39.54070, longitude 176.91752)
- Waitangi Stream D/S BioRich driveway (Site 4680) (latitude -39.55579, longitude 176.92030)
- Waitangi Stream D/S stopbank receiving environment (Site 4681) (latitude -39.55939, longitude 176.92128).



Figure 3. Sediment sampling sites in the Awatoto suburb south of Napier City in Hawke's Bay.

The sediment samples were double-bagged and kept refrigerated at 4 °C until they were sent to Cawthron, where they were received on 20 May 2023 and stored in the dark at 4 °C until use.

2.2. Toxicity testing

2.2.1. Elutriates and sediment extract preparations

Sediment samples were mixed with the dilution water corresponding to each test at a ratio of 1:4 sediment:dilution water (ASTM International 2014). Two water types – including a solution of 2% sodium chloride (NaCl) filtered at 0.22 μ m and reconstituted seawater filtered at 0.45 μ m – were used to dilute the test solutions for the Microtox® and the blue mussel embryo-larval tests, respectively.

The mixture of sediment / diluent was mixed in a rotating block for 1 hour in the dark at 4 °C. It was then centrifuged for 2× 3 minutes at 1,500 g to achieve a clear supernatant without any coloration or obvious suspended particles. The alternative method of letting sediment settle to achieve a clear supernatant took too long (> 1 hour), likely due to the fine silt.

Supernatants were then used immediately to generate the dilution series for the assays with their respective diluents. Tests were carried out within 1–4 hours after elutriates were prepared. Elutriates were diluted two-fold to a range of concentrations (Table 4).

For the non-targeted chemical analysis, 20 g of sediment (wet weight) sample was first extracted with 20 mL of acetone by shaking and sonication for 10 minutes. It was further extracted with a 20 mL solution of acetone and dichloromethane (DCM) (1:1) using the same method, and the resulting extracts were then combined (40 mL in total). Of the total 40 mL, a volume of 20 mL consisting of 5 mL of DCM and 15 mL of acetone was used as the analysis sample. Then, 100 mL of pure water and 3 g of NaCl were added to 20 mL volume, and 5 mL of DCM was recovered after shaking at 2,700 rpm for 10 minutes. The DCM was dried under a nitrogen stream and redissolved in 1 mL n-hexane. The internal standard (10 μ L) for NAGINATA was added to a 100 μ L sample to prepare a sample for AIQS-GC analysis (Omagari et al. 2022). NAGINATA is one of the software of AIQS-GC (Nishikawa Keisoku Co., Ltd) that can identify and quantify chemicals using AIQS-database.

In parallel, moisture content of the sediment samples was determined following a recognised standard protocol (ASTM International 1998), where a known weight of sediment was dried at 105 °C until constant weight was reached to estimate dry weight.

2.2.2. Assays

The potential sediment toxicity was assessed using a combination of *in vitro* and whole organism assays. The *in vitro* assays provide insights into the presence and bioavailability of chemical contamination that was translocated in the soil during the flood event, while the whole organisms' assays provide a general toxicity indication of the contaminants from the sediments that could be resuspended in water

In vitro yeast two-hybrid assay

Yeast two-hybrid (Y2H) assays with yeast cells (*Saccharomyces cerevisiae* Y190) incorporating human CAR and AhR were previously developed and described (Shiraishi et al. 2000; Kamata et al. 2018). CAR and AhR are ligand-activated transcription factors involved in xenobiotic metabolism. Y2H is a genetically modified assay incorporating the chemiluminescent reporter gene (for β -galactosidase) as a marker of activity in 96-well culture plates.

CAR binding assay

Yeast cells were pre-incubated at 30 °C for 24 hours with shaking in the medium (Table 1), and the cell density was adjusted to an absorbance of 1.75–1.85 at 595 nm. The medium (60 μ L) was added to each well of the first row of a black 96-well culture plate for chemiluminescence measurement.

The medium (60 μ L) was added to the wells in all cells. Sediment extracts (in DMSO, 20 μ L) were added to the medium (480 μ L), and aliquots of this mixture (60 μ L) were also added to the wells of the first row of the plate. The test solution was serially diluted from rows 1–7 (each 2), then the yeast cell suspension (60 μ L) was added to each well (including those in row 8, which served as the blank control).

After adding the yeast suspension and vortexing, the plates were incubated at 30 °C under high humidity for 4 hours. Next, 50 μ L of lysis solution (zymolyase 100T/Z buffer [2.9 mg/10 mL]) was added to each well, mixed and left at 37 °C for 1 hour. The solution (80 μ L) for inducing chemiluminescence from released β -galactosidase, consisting of a reaction buffer (Table 2) containing enhancer (Sapphire-II, Applied Biosystems, Japan) and substrate (Galacton-Star, Applied Biosystems, Japan), was added to each well. The plate was incubated on a hotplate set at 30 °C for 10 minutes and then placed in a 96-well plate luminometer (Luminescencer JNRAB2100, Atto Corporation, Tokyo, Japan). Agonist activity was evaluated as EC_{x10}, defined as the concentration of test solution producing a chemiluminescent signal 10 times that of the solvent control. 4-tertoctyl-phenol (4op) was used in the positive control of the Y2H for CAR. The sample's activity was calculated by converting it into each positive control equivalent concentration, compared with the 4op activity on that day. The activity was calculated as wet weight (ww) and converted to dry weight (dw) using the moisture content of each sediment sample.

AhR binding assay

Yeast cells for AhR were pre-incubated with shaking for 24 hours at 30 °C in medium (Table 1) supplemented at 1% with filter-sterilised leucine aqueous solution (1.76 mg/100 mL).

After measuring the cell density of the bacteria at 595 nm, the yeast suspension was centrifuged to precipitate it and the supernatant was decanted. Cell density was adjusted to an absorbance of 1.75–1.85 using the reaction solution medium (Table 2).

The next stage in the procedure was similar to that applied for CAR. Final composition of the medium for the assay is reported in Table 3.

AhR activity values were calculated using β -naphthoflavone (β na) as a positive control.

Yeast nitrogen base w/o amino acids		5.8 g
Dextrose		8.8 g
Dropout solution		
L-isoleucine	300 mg	
L-valine	1,500 mg	
L-adenine hemisulfate salt	200 mg	
L-arginine HCI	200 mg	
L-histidine HCI monohydrate	200 mg	174 ml
L-lysine HCI	300 mg	17 4 111
L-methionine	200 mg	
L-phenylalanine	500 mg	
L-threonine	2,000 mg	
L-tyrosine	300 mg	
L-uracil	200 mg	
Purified water		final 1,000 ml

 Table 1.
 Composition of medium for pre-incubation and CAR final assay.

Table 2. Components of the reaction solution.

Solution A 200 µL	Galacton-Star (100× concentrated)	
	100 mM sodium phosphate buffer (pH 7.4)	100 ml
Solution B 10 mL	MgCl · 6H ₂ O	0.02 g
-	Sapphire-II	174 ml

Table 3. Composition of medium for AhR final assay.

Yeast nitrogen base w/o amino acids	5.8 g
Galactose	15 g
Dropout solution (-Trp)	174 ml
Purified water	final 1,000 ml

Microtox® (Aliivibrio fischeri) bioluminescence inhibition

Microtox® determines the acute toxicity of aqueous solutions by measuring the changes of light naturally produced by the bioluminescent bacterium *Aliivibrio fischeri* under standard conditions when exposed to a test sample (Johnson 2005). The test was conducted according to the relevant International Organization for Standardization standard (ISO 1999). Briefly, freeze-dried bacteria in a vial were revived in a 5 °C aqueous suspension and added at 1% in the test solution. Luminescence in test samples was measured after 5, 15 and 30 minutes at 15 °C, with the measured effect, light reduction, relating to the control. A summary of the test conditions is presented in Table 4.

Blue mussel (Mytilus galloprovincialis) embryo-larval development / survival

Adult blue mussels were collected from Pelorus Sound / Te Hoiere. Animals were kept in a recirculatory system at 13 °C until use. The test was conducted according to the ASTM standard (ASTM International 2021). A summary of the test conditions is presented in Table 4.

The survival of mussel larvae was determined by the yield of normal D-larvae characterised under the microscope. The number of abnormal D-larvae in a test solution provides an indication of embryo toxicity in early life stage development. Survival at each concentration is compared to survival in the control to assess the ecotoxicological parameters (10%, 25% and median lethal concentration).

Table 4.	Summary of test conditions for Microtox® and blue mussel embryo-larval bioassays.

	Microtox®	Mussel test
Test start to end dates	7 June2023	14–16 June 2023
Standard	ISO 11348-3 (2007)	ASTM E724-21 (2021) ETX 4
Test species	Aliivibrio fischeri	Mytilus galloprovincialis
Source	BioLight Aqua-Science (Lot 10641121)	Pelorus Sound / Te Hoiere
Density, number per test container	n/a	~400
Type of test container	5 mL glass tube	6-well plate (10 mL/well)
Exposure time (hours)	0.08, 0.25, 0.5	48
Concentrations tested (%)	0, 0.2–50	0, 0.2–100
Replicates	2	5 for controls, 5 for treatments
Temperature (°C)	15	16.5 ±1.2
Dissolved oxygen (at the beginning of the test) (mg/L)	n/m	8.8 (109%)
рН	n/m	8.1
Dilution water	Type I with NaCl 2%	Reconstituted seawater
Aeration	None	None
Salinity (at the beginning of the test, PSU)	20	34.2
Endpoint	Luminescence	Survival
Sensitivity (EC ₅₀ with 95%	1.15(0.96–1.12) mg Zn ²⁺ /L	0.148 (0.144–0.153) mg
confidence interval)	(15 minutes)	Zn ²⁺ /L
Control quality for consitivity (moon	$1.27(0.08, 1.56)$ mg $7n^{2+1/2}$	0.174 (0.115–0.233) mg
+2x standard doviation)	(n - 3) (15 minutes)	Zn ²⁺ /L
	(n = 3) (13 minutes)	(<i>n</i> = 8)
Test acceptability (in controls)	Yes	No
		< 60% D-yield
		Collection date:
Note	_	13 June 2023
	—	Spawning method: thermal
		stimulation

2.3. Chemical analysis

2.3.1. Rapid comprehensive chemical analysis

Sediment extracts from each sediment sample were analysed using AIQS-GC methods as previously described (Omagari et al. 2022). Information on retention times (RTs), retention indexes (RIs), mass spectra and calibration curves were registered in the AIQS database (AIQS-DB). A chemical was identified by comparing RTs or RIs and the mass spectrum in the sample with the AIQS-DB. The chemical analyses

presented here used AIQS-GC for the identification of each chemical in the environmental sample.

Chemicals identified in the AIQS-GC were allocated between one and five stars based on the identification accuracy using the star-based scoring conditions presented in Table 5. Target concentrations below the method of detection limits were treated as zero.

Table 5.Conditions of scoring in AIQS-GC. The number of asterisks (*) indicates the accuracy of
identification. RI = retention index; MS hit rate = similarity of MS spectrum between
AIQS-DB and samples; QT ratio = qualifier ion / target ion. These are calculated from the
difference between actual results in the sample and predicted results in AIQS-DB. When
the targets are evaluated for scoring, the ignored index is not considered.

Score	RI	MS hit rate (%)	QT ratio
****	-10 to +10	> 25	Not considered
****	-20 to +20	> 25	Not considered
***	-10 to +10	< 25	0.9 to 1.1
**	-20 to +20	< 25	0.8 to 1.2
*	-20 to +20	< 25	< 0.8 or > 1.2

2.3.2. Targeted chemical analysis

Sediments collected by HBRC staff were sent to Hills Laboratory Ltd for analysis for a suite of metals and metalloids, and an extensive suite of organic chemicals (heavy metals, pesticides, polychlorobiphenyls, ethers, hydrocarbons (polycyclic aromatic and total petroleum), phenols, plasticisers and halogenated compounds. Details are provided in Appendix 1. For the organic chemicals, results of measured concentrations in sediment samples were normalised to 1% total organic carbon to allow comparison with the available default guideline values (ANZG 2018).

2.4. Statistical analysis

Model-based ecotoxicological parameters (LC₁₀ and LC₅₀ with associated 95% confidence intervals (CI), and no effect (significant) concentration (N(S)EC) were calculated using R (R Core Team 2023) with the drc (Ritz et al. 2015) and bayesnec (Fisher et al. 2023) packages, respectively. Hypothesis testing (no effect and lowest effect observed concentrations (NOEC and LOEC) (at level of statistical significance of P < 0.05) were determined with the Statistica software (TIBCO Software Inc., 2020).

3. **RESULTS**

The sediment samples were homogenous in colour and texture. They can be classified as 'mud' (mix of silt and clay, with a majority of sediment grain size < 63 μ m – see Appendix 1; Valentine 2019). No dark colour, which is typically characteristic of anoxic conditions, was observed. Moisture content of the three sediment samples used for bioassays was 47%, 43% and 47% for 4679, 4680 and 4681, respectively (similar to the dry matter reported in Appendix 1).

3.1. AhR and CAR

The results from the AhR and CAR binding activity using Y2H reporter gene assays are summarised in Table 6. AhR- and CAR-mediated activities were detected in all sediment sample extracts tested. The AhR activities were higher than those reported for sediment samples displaced by floods caused by Typhoon Hagibis in Japan in October 2019 (Omagari et al. 2022). The CAR activities detected were also higher than those reported for the sediment samples from Typhoon Hagibis, indicating the presence of 4-tertoctyl-phenol-type substances.

Table 6.	AhR- and CAR-mediated activities in the sediment extracts using the Y2H reporter gene
	assays.

Site	AhR	CAR
	(μg-βna eq./kg-dw)	(µg-4op eq./kg-dw)
4679	427	140
4680	349	34
4681	502	145

3.2. Microtox®

Results of the Microtox® test are presented in Figure 4, with raw data reported in Appendix 3. Only measurements after 15 minutes of exposure are shown in the figure as these best represent the trend. Measurements after 5 minutes and 30 minutes are reported in Appendix 3. Elutriates from sediment samples from Site 4679 and Site 4680 inhibited light emission in bacteria at lowest concentration but stimulated it at the highest concentration. Elutriate from sediment samples from Site 4681 showed stimulation of light emission from the bacteria at all concentrations. No significant toxicity of the elutriates was detected (P < 0.05).



Figure 4. Mean effect (\pm standard deviation) on bacterial luminescence of the three tested elutriates.

3.3. Blue mussel embryo-larval development assay

The conditions of the assays (salinity, oxygen saturation, dissolved oxygen concentration [DO], pH) were measured at the highest elutriate concentrations and are presented in Appendix 4 (Table A4.1). The survival of larvae in the controls was below the required 60%, and therefore did not comply with test validity requirements. Sensitivity of test, assessed with the response to the reference toxicant (0.148 (0.144–0.153) mg Zn²⁺/L), was within the required limits of ±2 standard deviations of historical data ([0.115–0.233] mg Zn²⁺/L, n = 8). In this case, the ecotoxicity parameters can be misestimated, but they still can allow comparison between the effects of the elutriates.

Blue mussel larvae survival in relation to elutriate concentration is reported in Figure 5. Ecotoxicity parameters are reported in Table 7. The ecotoxicity parameters associated with sediment elutriate from Site 4679 were the lowest compared to the two other sites, indicating the strongest toxic effects on mussel larvae development. The sediment elutriate with the least toxicity was from Site 4681; this had the highest ecotoxicity parameters, indicating the least impact on mussel larvae development. The sediment elutriate from Site 4680 had an intermediate impact. The raw data for the embryo-larval development assay are reported in Appendix 4 (Table A4.2).



- Figure 5. Mean and standard deviation (whiskers) of the blue mussel larvae survival (D-yield) in the range of concentration of elutriates from the three sediment samples (a same letter indicates a statistical non-significance, P < 0.05).
- Table 7.
 Ecotoxicity parameters for the blue mussel 48-hour embryo-larval development assay after exposure to the elutriates of the three sediment samples.

Site	LC ₁₀ (%) (95%Cl)	LC ₂₅ (%) (95%Cl)	LC ₅₀ (%) (95%Cl)	N(S)EC (%) (95%Cl)	NOEC	LOEC
4679	5.5	7.5	9.7	10.7	6 25	12.5
4075	(4.4–6.6)	(6.5–8.4)	(9.0–10.4)	(7.9–12.2)	0.20	12.0
4680	9.6	11.9	14.4	12.3	6 25	12.5
	(8.6–10.7)	(11.3–12.6)	(13.7–15.2)	(11.4–22.4)	0.25	
4681	42.6	53.0	64.1	58.9	50	100
	(38.3–47.0)	(49.1–56.9)	(60.5–67.7)	(46.2–95.7)	50	100

3.4. Chemical analysis

3.4.1. Rapid comprehensive chemical analysis

The number of compounds detected in sediment extracts were 52, 46 and 55 for the samples from Sites 4679, 4680 and 4681, respectively. Details of the detected compounds are presented in Appendix 2. The most abundant chemicals found in the three sediment extracts were phytosterols, sterols and 'paraffins' (Figure 6). Sterols found were cholesterol and its metabolites. 'Paraffins' are long carbon chains and can be found in oil, lubricant, fuel and plant products. The extract from Site 4679 showed the highest concentration of pesticides, or chemicals used in the manufacture / formulation of pesticides and sterols. The extract from Site 4680 showed the highest

concentration of phytosterol. The extract from Site 4681 had the highest concentration of flame retardants, PAHs, plasticisers, stabilisers and plant products (Figure 6). The rapid comprehensive chemical analysis detected the presence of DDT metabolites at highest concentrations in Site 4681, followed by Site 4680. The lowest concentrations were found in the Site 4679 sample extract.



Figure 6. Main categories of chemicals detected and their relative abundances in the three sediment extracts.

3.4.2. Targeted analysis

Full details of the detected compounds and their concentrations are presented in Appendix 1. Metal and metalloid concentrations in sediments were all below the Australia and New Zealand default guideline values (DGVs) for sediment (ANZG 2018) (Table 8). The total organic carbon content in sediments was 1.82%, 1.45% and 2.4% for the samples from Sites 4679, 4680 and 4681, respectively. A limited number of organic chemicals (DDT and its metabolites, bifenthrin and dieldrin) were detected. Their concentrations were normalised to a carbon content of sample to 1% for comparison against the DGVs. The chemicals and their concentrations are reported in Table 9, along with the related DGVs. Site 4680 had the highest concentration of DDT metabolites (DDD and DDE) above the DGV high. Site 4679 had the lowest concentration of DDT and metabolites (only the DDE concentration was above DGV). Site 4680 was intermediate. Bifenthrin was detected above the Environmental Quality Standards for Priority Substances under the European Water Framework Directive (SCHEER 2022) (no Australia and New Zealand DGV available) for Site 4679 and, at a lesser concentration, at Site 4681.

Table 8.Concentrations of total recoverable metals and metalloids (mg/kg dry weight) in the three
sediment samples and their related default guideline values (DGVs).

Metal / metalloid	Site 4679	Site 4680	Site 4681	DGV	DGV high
Arsenic	6.3	6.8	8.8	20	70
Cadmium	0.127	0.187	1.09	1.5	10
Chromium	21	20	22	80	370
Copper	10.4	8.7	15.9	65	270
Lead	13	13.3	12.4	50	220
Mercury	0.07	0.07	0.1	0.15	1
Nickel	14.7	15.4	14.2	21	52
Zinc	149	70	128	200	410

Table 9. Measured (Meas.) and normalised (Norm.) (at 1% TOC; Norm.) concentrations of organic contaminants (μ g/kg dry weight) detected in the three sediment samples, and their related default guideline values (DGVs).

	Site 4679		Site	Site 4680		Site 4681		DGV
	Meas.	Norm.	Meas.	Norm.	Meas.	Norm.	DGV	high
Bifenthrin	33	18.1	< 6		6	2.5	0.11 ¹	
2,4'-DDD	< 1		22	15.2	28	11.7		
4,4'-DDD	4.4	2.4	12.9	8.9	111	46.3		
2,4'- + 4,4'-DDD	4.4	2.4	34.9	24.1	139	57.9	3.5	9
4,4'-DDE	4.2	2.3	25	17.2	20	8.3	1.4	7
2,4'-DDT	< 1	-	1.6	1.1	< 1	-		
4,4'-DDT	2.7	1.5	14.8	10.2	6.9	2.9		
Total DDT	2.7	1.5	16.4	11.3	6.9	2.9	1.2	5
Total DDT Isomers	12	6.6	56	38.6	230	95.8		
Dieldrin	< 1	_	1.3	0.9	< 1	_	2.8	7

Numbers in bold indicate concentration value above DGV – comparisons with DGV are made with the normalised concentration value at 1% TOC.

4. **DISCUSSION**

In recent years, there has been an increase in the number of severe weather events globally that can result in the remobilisation of pollutants (Crawford et al. 2022). Flood events can redistribute sediment-bound chemicals, and robust risk assessment processes are required to inform communities and develop effective remediation management actions. The approach of this study to characterise the risk of the relocated sediment in the Waitangi catchment has been used successfully to assess the risk of the aftermath of Typhoon Hagibis in Japan (Omagari et al. 2022). The combination of bioassays and chemical analysis can characterise the toxicity and identify the likely chemicals responsible for the biological activities.

The Microtox® and mussel embryo-larval development assays provide insights into the general toxicity of a sample. The AhR and CAR binding assays provide more specific information about the presence of chemicals with specific mechanisms of toxicity through binding to these receptors. The Microtox® results suggest low overall toxicity in the elutriates from the three sediment samples. Elutriates from sediments from Site 4679 and Site 4680 were slightly toxic, while those from Site 4681 stimulated bacterial growth and therefore may have contained nutrients beneficial to Aliivibrio fischeri. It has been reported that some substances can stimulate the growth of bacteria and modulate the response to toxicants (Cerro-Gálvez et al. 2019; Vila-Costa et al. 2019). The results of the mussel embryo-larval development assay agreed with the Microtox® results, with the elutriate from the Site 4681 sediment sample being the least toxic, followed by Site 4680 and with Site 4679 being the most toxic. It should be noted that pH values were lower at higher elutriate concentrations, which could be a confounding factor for the toxicity observed in the embryo-larval test. The sediment elutriate dilutions for which the pH fell below 7 were 25%, 50% and 100% for the elutriates from Site 4679, 4680 and 4681 sediment samples, respectively.

The AhR- and CAR-mediated activities were the highest in the sediment sample from Site 4681, followed by that from Site 4679. This finding was opposite to the results from the Microtox® and mussel embryo-larval development assays, where the Site 4681 sample had the lowest toxicity. It is important to note that the yeast tests were carried out on chemically extracted sediment samples, which means that they contained hydrophobic chemicals that are likely absent from the elutriate samples. As such, they complement the results obtained from the tested elutriates, which provide insights into the more water-soluble chemicals present in the sediment. The results mean that there are more toxic hydrophobic chemicals that can bind to the AhR receptor in samples from Sites 4679 and 4681 compared to the Site 4680 sample.

The chemical analysis detected low DDT concentrations in the sediment samples but some of its metabolites were high (above DGVs; Table 9). This suggests a historical contamination, where legacy DDT has degraded. It has been reported that agricultural

soils in Aotearoa New Zealand where DDT was applied to pasture contain persistent residues (Boul et al. 1994). The half-life of DDT in soil is 2–10 years, and DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethylene) are the two main metabolites resulting from its degradation (Boul 1995). DDT is primarily degraded to DDE by a dechlorination reaction, and DDE can further be degraded to DDD by another dechlorination reaction. DDE and DDD are less toxic than DDT but remain persistent in the environment (Corona-Cruz et al. 1999; Cutright and Erdem 2012).

Bifenthrin is the other pesticide that was measured in the sediment samples at concentrations above its DGV (Table 9). Bifenthrin is a pyrethroid insecticide that affects the nervous system of the insects it targets. It has a broad range of activities used against foliar pests, including Coleoptera, Diptera, Heteroptera, Lepidoptera, Homoptera and Orthoptera, among others. It is allowed for use, with controls, in Aotearoa New Zealand in various formulations² to control insects in commercial and residential applications. It has a moderate to high persistence in soil, with a half-life of 7 days to 8 months (Mukherjee et al. 2010).

The most prevalent category of chemicals detected with the rapid comprehensive chemical analysis was the sterols, most of which have a plant origin (phystosterol). However, other sterols such as coprostanol, epicoprostanol, cholesterol, 3-cholestanone and cholestanol are of faecal origin (Islam et al. 2023) and found in mammalians (Prost et al. 2017). The other prevalent group detected by the rapid comprehensive chemical analysis was the alkanes ('paraffins'). The alkanes detected (C₁₅ to C₃₃) can either be produced by plants (Maffei et al. 2004) or from oil refining to make waxes, anticorrosive agents and lubricating oils (Morrison and Boyd 1992).

² New Zealand Environmental Protection Authority, HSNO application register. <u>https://epa.govt.nz/database-search/approved-hazardous-substances-with-controls/DatabaseSearchForm/?SiteDatabaseSearchFilters=34&Keyword=bifenthrin&DatabaseType=AHSC</u>

5. CONCLUSION

Overall, the results from the toxicity bioassays did not suggest high risk in relation to the displaced sediment in the Waitangi catchment. We tested elutriates which are a complex mixture of chemicals that are water soluble and indicate bioavailability. The Microtox® bioassay results showed some bacterial growth stimulation which suggest that some components in the elutriate samples were beneficial nutrients. The most toxic sediment elutriate was found at the site 4679 with the blue mussel test, but the variation in pH could have been an influencing factor on the survival of the embryos. The yeast assays showed activities similar to what has been reported in Japan after the event of Typhoon Hagibis.

The rapid comprehensive chemical analysis is a qualitative method to provide information on the presence of molecules, while the targeted analysis allows the quantification, but only for the specific chemicals for which a reference is used. Both methods highlighted the presence of a historical contamination by DDT and its metabolites DDE and DDD. These chemicals can, in part, be contributing to the effects in the AhR bioassay. The concentrations of metals and metalloids tested were all below the Australia and New Zealand DGVs. There was also indication of mammalian faecal contamination, likely from farm animals.

Overall, the results from this study suggest that the risk of the displaced sediment in the Waitangi catchment is low. However, some caution is warranted for handling and disposing of the sediment material.

6. ACKNOWLEDGEMENTS

We thank Joshua Fitzgerald for extracting the sediment samples, and Juliette Butler and Tanja Wiles for assisting with the bioassays. This study was funded with Envirolink grant '2346-HBRC271 Waitangi stream post-inundation toxicity advice' CAWX2212.

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8. APPENDICES

Appendix 1. Targeted analysis

X	Hi	l La	abs P	J Hill Laboratories Limited 3 Duke Street Frankton 3204 rivate Bag 3205 amilton 3240 New Zealand	 So 0508 HILL LAB (44 555 22) So +64 7 858 2000 ☑ mail@hill-labs.co.nz ⓓ www.hill-labs.co.nz
C e r t i	ficate of	Analy	sis		Page 1 of 10
Client: Contact:	:: Hawkes Bay Regional Council Inct: Hannah Ludlow C/- Hawkes Bay Regional Council Private Bag 6006 Napier 4142			Lab No:328Date Received:19-Date Reported:17-Quote No:122Order No:PNClient Reference:WaSubmitted By:Ha	30937 SPv3 May-2023 Jul-2023 2691 00018761 itangi Sediment nnah Ludlow
Sample Ty	/pe: Sediment				
	Sa	ample Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681 18-May-2023 3:00 pm
		Lab Number:	3280937.1	3280937.2	3280937.3
Individual Te	ests				
Dry Matter		g/100g as rcvd	49	59	56
Total Recove	erable Phosphorus	mg/kg dry wt	780	970	3,500
Total Recove	erable Rubidium	mg/kg dry wt	17.8	17.7	14.8
Total Recove	erable Silver	mg/kg dry wt	0.04	0.04	0.04
Total Cyanid	e*	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Total Nitroge	n*	g/100g dry wt	0.16	0.11	0.13
Total Organi	c Carbon*	g/100g dry wt	1.82	1.45	2.4
Heavy metal	s, trace As,Cd,Cr,C	u,Ni,Pb,Zn,Hg			
Total Recove	erable Arsenic	mg/kg dry wt	6.3	6.8	8.8
Total Recove	erable Cadmium	mg/kg dry wt	0.127	0.187	1.09
Total Recove	erable Chromium	mg/kg dry wt	21	20	22
Total Recove	erable Copper	mg/kg dry wt	10.4	8.7	15.9
Total Recove	erable Lead	mg/kg dry wt	13.0	13.3	12.4
Total Recove	erable Mercury	mg/kg dry wt	0.07	0.07	0.10
Total Recove	erable Nickel	mg/kg dry wt	14.7	15.4	14.2
Total Recove	erable Zinc	mg/kg dry wt	149	70	128
7 Grain Size	s Profile as received	j*			
Dry Matter of	Sieved Sample*	g/100g as rcvd	50	60	48
Fraction >/=	2 mm*	g/100g dry wt	0.2	7.1	0.8
Fraction < 2	mm, >/= 1 mm*	g/100g dry wt	0.2	0.6	1.0
Fraction < 1	mm, >/= 500 µm*	g/100g dry wt	0.1	0.9	1.2
Fraction < 50	00 μm, >/= 250 μm*	g/100g dry wt	0.2	1.1	2.7
Fraction < 25	50 μm, >/= 125 μm*	g/100g dry wt	0.4	3.6	11.6
Fraction < 12	25 μm, >/= 63 μm*	g/100g dry wt	2.2	17.1	29.1
Fraction < 63	3 µm*	g/100g dry wt	96.7	69.7	53.6
Acid Herbici	des Trace in Soil by	LCMSMS*			
Acifluorfen		mg/kg dry wt	< 0.010	< 0.010	< 0.010
Bentazone		mg/kg dry wt	< 0.010	< 0.010	< 0.010
Bromoxynil		mg/kg dry wt	< 0.010	< 0.010	< 0.010
Clopyralid		mg/kg dry wt	< 0.010	< 0.010	< 0.010
Dicamba		mg/kg dry wt	< 0.010	< 0.010	< 0.010
2,4-Dichloro (24D)	phenoxyacetic acid	mg/kg dry wt	< 0.010	< 0.010	< 0.010
2,4-Dichloro (24DB)	ohenoxybutyric acid	mg/kg dry wt	< 0.010	< 0.010	< 0.010
Dichlorprop		mg/kg dry wt	< 0.010	< 0.010	< 0.010



This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised. The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked * or any comments and interpretations, which are not accredited.

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Sample Type: Sediment						
Sar	nple Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681		
I :	ah Numher:	3280937 1	3280937 2	3280937.3		
Acid Herbicides Trace in Soil by L	CMSMS*	0200001.1	0200001.2	02000110		
Fluazifop	ma/ka drv wt	< 0.010	< 0.010	< 0.010		
Fluroxypyr	ma/ka drv wt	< 0.010	< 0.010	< 0.010		
Haloxyfop	ma/ka dry wt	< 0.010	< 0.010	< 0.010		
2-methyl-4-chlorophenoxyacetic	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
acid (MCPA)						
2-methyl-4- chlorophenoxybutanoic acid (MCPB)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Mecoprop (MCPP; 2-methyl-4- chlorophenoxypropionic acid)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Oryzalin	mg/kg dry wt	< 0.02	< 0.02	< 0.02		
Pentachlorophenol (PCP)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Picloram	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Quizalofop	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
2,3,4,6-Tetrachlorophenol (TCP)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
2,4,5-trichlorophenoxypropionic acid (245TP,Fenoprop, Silvex)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
2,4,5-Trichlorophenoxyacetic acid (245T)	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Triclopyr*	mg/kg dry wt	< 0.010	< 0.010	< 0.010		
Multiresidue Pesticides in Sedime	ent samples by (GCMS				
Acetochlor	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Alachlor	mg/kg dry wt	< 0.007	< 0.006	< 0.006		
Atrazine	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Atrazine-desethyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Atrazine-desisopropyl	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
Azaconazole	mg/kg dry wt	< 0.007	< 0.006	< 0.006		
Azinphos-methyl	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
Benalaxyl	mg/kg dry wt	< 0.007	< 0.006	< 0.006		
Bendiocarb	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Benodanil	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
Bifenthrin	mg/kg dry wt	0.033	< 0.006	0.006		
Bitertanol	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
Bromacil	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Bromophos-ethyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Bromopropylate	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Bupirimate	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Buprofezin	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Butachlor	mg/kg dry wt	< 0.014	< 0.011	< 0.12		
Captafol	mg/kg dry wt	< 0.07	< 0.06	< 0.06		
Captan	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
Carbaryl	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Carbofenothion	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Carbofuran	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Chlorfenvinphos	mg/kg dry wt	< 0.019	< 0.016	< 0.017		
Chlorfluazuron	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Chiorothalonil	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Chiorpropham	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
Chiorpyritos-methyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012		
	mg/kg dry wt	< 0.03	< 0.03	< 0.03		
	mg/кg dry wt	< 0.014	< 0.011	< 0.12		
Coumapnos	mg/kg ary wt	< 0.03	< 0.03	< 0.03		
Cydridzine	mg/kg dry wt	< 0.014	< 0.011	5 U. 12		
Cynuthrin	mg/kg ary wt	< 0.016	< 0.014	< 0.015		

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Sample Type: Sedime	nt			
	Sample Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681
	Lab Numbor	3280037 1	3280037.2	18-May-2023 3:00 pm
Multiresidue Pesticides in Se	ediment samples by (3200937.1	3200337.2	5200357.5
Cyhalothrin	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Cynermethrin	mg/kg dry wt	< 0.04	< 0.03	< 0.012
Cypermetinin	mg/kg dry wt	< 0.04	< 0.03	< 0.03
Cyproconazole	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Deltamethrin (including	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Diazinon	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Dichlobenil	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Dichlofenthion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Dichlofluanid	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Dichloran	mg/kg dry wt	< 0.04	< 0.03	< 0.03
Dichlorvos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Dicofol	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Dicrotophos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Difenoconazole	mg/kg dry wt	< 0.019	< 0.016	< 0.017
Dimethoate	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Dinocap	mg/kg dry wt	< 0.15	< 0.13	< 0.13
Diphenylamine	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Diuron	mg/kg dry wt	< 0.014	< 0.011	< 0.012
EPN	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Ethion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Etrimfos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Famphur	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fenarimol	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fenitrothion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fenpropathrin	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fenpropimorph	mg/kg dry wt	< 0.014	< 0.011	< 0.12
Fensulfothion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fenvalerate (including Esfenvalerate)	mg/kg dry wt	< 0.019	< 0.016	< 0.017
Fluazifop-butyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fluometuron	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Flusilazole	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Fluvalinate	mg/kg dry wt	< 0.010	< 0.008	< 0.009
Folpet	mg/kg dry wt	< 0.03	< 0.03	< 0.3
Furalaxyl	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Haloxyfop-methyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Hexaconazole	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Hexazinone	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Hexythiazox	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Imazalil	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Indoxacarb	mg/kg dry wt	< 0.014	< 0.011	< 0.012
lodofenphos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
IPBC (3-lodo-2-propynyl-n- butylcarbamate)	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Isazophos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Isofenphos	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Kresoxim-methyl	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Leptophos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Linuron	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Malathion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Metalaxyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Methacrifos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Methamidophos	mg/kg dry wt	< 0.07	< 0.06	< 0.06

Sample Type: Sediment				
Sa	mple Name:	102127 - Waitangi Stream	102129 - Waitangi Stream D/S	102128 - Waitangi Stream D/S
		opposite 32 Waitangi Rd: 4679	BioRich driveway: 4680	stopbank receiving
		10-101ay-2023 1.30 pm	10-way-2025 2.50 pm	18-May-2023 3:00 pm
Ľ	ab Number:	3280937.1	3280937.2	3280937.3
Multiresidue Pesticides in Sedime	ent samples by (GCMS		
Methidathion	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Methiocarb	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Metolachlor	ma/ka drv wt	< 0.007	< 0.006	< 0.06
Metribuzin	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Mevinphos	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Molinate	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Myclobutanil	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Naled	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Nitrofen	ma/ka drv wt	< 0.03	< 0.03	< 0.03
Nitrothal-isopropyl	ma/ka drv wt	< 0.014	< 0.011	< 0.012
Norflurazon	ma/ka drv wt	< 0.03	< 0.03	< 0.03
Omethoate	ma/ka drv wt	< 0.07	< 0.06	< 0.06
Oxadiazon	ma/ka drv wt	< 0.014	< 0.011	< 0.012
Oxychlordane	mg/ka drv wt	< 0.007	< 0.006	< 0.006
Oxvfluorfen	ma/ka drv wt	< 0.007	< 0.006	< 0,006
Paclobutrazol	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Parathion-ethyl	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Parathion-methyl	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Penconazole	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Pendimethalin	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Permethrin	ma/ka dry wt	0.40	< 0.004	< 0.004
Phosmet	mg/kg dry wt	< 0.014	< 0.004	< 0.004
Phosphamidon	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Pirimicarb	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Pirimiphos-methyl	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Prochloraz	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Procymidone	mg/kg dry wt	< 0.014	< 0.00	< 0.12
Prometryn	mg/kg dry wt	< 0.017	< 0.006	< 0.02
Propachlor	mg/kg dry wt	< 0.007	< 0.011	< 0.012
Propanil	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Propazine	mg/kg dry wt	< 0.007	< 0.00	< 0.00
Propetamphos	mg/kg dry wt	< 0.007	< 0.011	< 0.012
Propham	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Propiconazole	mg/kg dry wt	< 0.014	< 0.008	< 0.012
Prothiofos	mg/kg dry wt	< 0.010	< 0.000	< 0.000
Pyrazonhos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Pyrifenox	ma/ka dry wt	< 0.019	< 0.016	< 0.17
Pyrimethanil	mg/kg dry wt	< 0.013	< 0.010	< 0.17
Pyriproxyfen	ma/ka dry wt	< 0.014	< 0.011	< 0.012
	mg/kg dry wt	< 0.03	< 0.01	< 0.012
	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Simazine	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Simetryn	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Sulfentrazone	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Sulfatan	mg/kg dry wt	< 0.01	< 0.00	< 0.00
TCMTB [2-(thiocyanomethylthio) benzothiazole,Busan]	mg/kg dry wt	< 0.03	< 0.03	< 0.03
Tebuconazole	mg/kg drv wt	< 0.014	< 0.011	< 0.012
Tebufenpyrad	mg/kg drv wt	< 0.007	< 0.006	< 0.006
Terbacil	mg/ka drv wt	< 0.014	< 0.011	< 0.012
Terbumeton	ma/ka drv wt	< 0.014	< 0.011	< 0.012
Terbuthvlazine	mg/ka drv wt	< 0.007	< 0.006	< 0.006
Terbuthylazine-desethyl	mg/ka drv wt	< 0.014	< 0.011	< 0.012
Terbutryn	mg/kg dry wt	< 0.014	< 0.011	< 0.12

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Sample Type: Sedime	ent			
	Sample Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681 18-May-2023 3:00 pm
	Lah Number:	3280937 1	3280937 2	3280937.3
Multiresidue Pesticides in S	ediment samples by	GCMS		020000110
Tetrachlorvinnhos	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Thiabendazole	mg/kg dry wt	< 0.07	< 0.06	< 0.06
Thiobencarb	mg/kg dry wt	< 0.014	< 0.011	< 0.12
Tolvlfluanid	mg/kg dry wt	< 0.007	< 0.006	< 0.006
Triadimefon	ma/ka dry wt	< 0.014	< 0.011	< 0.012
Triazophos	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Trifluralin	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Vinclozolin	mg/kg dry wt	< 0.014	< 0.011	< 0.012
Organochlorine Pesticides 1	Frace in Soil			
Aldrin	ma/ka drv wt	< 0.0010	< 0.0010	< 0.0010
alpha-BHC	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
beta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
delta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
gamma-BHC (Lindane)	ma/ka dry wt	< 0.0010	< 0.0010	< 0.0010
cis-Chlordane	ma/ka dry wt	< 0.0010	< 0.0010	< 0.0010
trans-Chlordane	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
2.4'-DDD	mg/kg dry wt	< 0.0010	0.0022	0.028
4,4'-DDD	mg/kg dry wt	0.0044	0.0129	0.111
2,4'-DDE	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
4,4'-DDE	mg/kg dry wt	0.0042	0.025	0.020
2,4'-DDT	mg/kg dry wt	< 0.0010	0.0016	< 0.0010
4,4'-DDT	mg/kg dry wt	0.0027	0.0148	0.069
Total DDT Isomers	mg/kg dry wt	0.012	0.056	0.23
Dieldrin	mg/kg dry wt	< 0.0010	0.0013	< 0.0010
Endosulfan I	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Endosulfan II	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Endosulfan sulphate	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Endrin	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Endrin aldehyde	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Endrin ketone	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Heptachlor	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Heptachlor epoxide	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Hexachlorobenzene	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Methoxychlor	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Polychlorinated Biphenyls T	race in Soil*			
PCB-18	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-28	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-31	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-44	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-49	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-52	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-60	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-77	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-81	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-86	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-101	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-105	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-110	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-114	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-118	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-121	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-123	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-126	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010

Sample Type: Sedime	nt			
	Sample Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681
				18-May-2023 3:00 pm
	Lab Number:	3280937.1	3280937.2	3280937.3
Polychiorinated Biphenyis T	race in Soll"	0.0010		
PCB-128	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-138	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-141	mg/kg ary wt	< 0.0010	< 0.0010	< 0.0010
PCB-149	mg/kg ary wt	< 0.0010	< 0.0010	< 0.0010
PCB-151	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-153	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-156	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-157	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-159	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-167	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-169	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-170	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-180	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-189	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-194	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-206	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
PCB-209	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010
Equivalence (TEF)*	mg/kg dry wt	< 0.0000003	< 0.0000003	< 0.0000003
Equivalence (TEF)*	mg/kg dry wt	< 0.0002	< 0.0002	< 0.0002
Total PCB (Sum of 35 congeners)	mg/kg dry wt	< 0.035	< 0.035	< 0.035
Haloethers Trace in SVOC S	Soil Samples by GC-	MS		
Bis(2-chloroethoxy) methane	e mg/kg dry wt	< 0.12	< 0.10	< 0.11
Bis(2-chloroethyl)ether	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Bis(2-chloroisopropyl)ether	mg/kg dry wt	< 0.12	< 0.10	< 0.11
4-Bromophenyl phenyl ether	mg/kg dry wt	< 0.12	< 0.10	< 0.11
4-Chlorophenyl phenyl ether	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Nitrogen containing compou	nds Trace in SVOC	Soil Samples, GC-MS		
N-Nitrosodiphenylamine + Diphenylamine	mg/kg dry wt	< 0.3	< 0.2	< 0.3
2,4-Dinitrotoluene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
2,6-Dinitrotoluene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Nitrobenzene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
N-Nitrosodi-n-propylamine	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Organochlorine Pesticides T	race in SVOC Soil S	amples by GC-MS		
Aldrin	mg/kg dry wt	< 0.12	< 0.10	< 0.11
alpha-BHC	mg/kg dry wt	< 0.12	< 0.10	< 0.11
beta-BHC	mg/kg dry wt	< 0.12	< 0.10	< 0.11
delta-BHC	mg/kg dry wt	< 0.12	< 0.10	< 0.11
gamma-BHC (Lindane)	mg/kg dry wt	< 0.12	< 0.10	< 0.11
4,4'-DDD	mg/kg dry wt	< 0.12	< 0.10	< 0.11
4,4'-DDE	mg/kg dry wt	< 0.12	< 0.10	< 0.11
4,4'-DDT	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Dieldrin	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Endosulfan I	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Endosulfan II	mg/kg dry wt	< 0.5	< 0.5	< 0.5
Endosulfan sulphate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Endrin	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Endrin ketone	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Heptachlor	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Heptachlor epoxide	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Hexachlorobenzene	mg/kg dry wt	< 0.12	< 0.10	< 0.11

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Sample Type: Sediment				
Sa	mple Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681 18-May-2023 3:00 pm
	ah Number	3280937 1	3280937 2	3280937.3
Polycyclic Aromatic Hydrocarbon	s Trace in SVO	C Soil Samples*	0200001.2	020001.0
	ma/ka day wt	< 0.10	< 0.10	< 0.10
	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Active	mg/kg dry wt	< 0.10	< 0.10	< 0.10
	mg/kg dry wt	< 0.10	< 0.10	< 0.10
	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Benzolajpyrene (BAP)	mg/kg dry wt	< 0.12	< 0.10	< 0.11
fluoranthene	mg/kg ary wt	< 0.12	< 0.10	< 0.11
Benzo[g,h,i]perylene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Benzo[k]fluoranthene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
1&2-Chloronaphthalene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Chrysene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Fluoranthene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Fluorene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
2-Methylnaphthalene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Naphthalene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Phenanthrene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Pyrene	mg/kg dry wt	< 0.10	< 0.10	< 0.10
Benzo[a]pyrene Potency Equivalency Factor (PEF) NES*	mg/kg dry wt	< 0.29	< 0.25	< 0.26
Benzo[a]pyrene Toxic Equivalence (TEF)*	mg/kg dry wt	< 0.29	< 0.25	< 0.25
Phenols Trace in SVOC Soil San	nples by GC-MS	3		
4-Chloro-3-methylphenol	mg/kg dry wt	< 0.5	< 0.5	< 0.5
2-Chlorophenol	mg/kg dry wt	< 0.2	< 0.2	< 0.2
2,4-Dichlorophenol	mg/kg dry wt	< 0.2	< 0.2	< 0.2
2,4-Dimethylphenol	mg/kg dry wt	< 0.4	< 0.4	< 0.4
3 & 4-Methylphenol (m- + p- cresol)	mg/kg dry wt	< 0.4	< 0.4	< 0.4
2-Methylphenol (o-cresol)	mg/kg dry wt	< 0.2	< 0.2	< 0.2
2-Nitrophenol	mg/kg dry wt	< 0.4	< 0.4	< 0.4
Pentachlorophenol (PCP)	mg/kg dry wt	< 6	< 6	< 6
Phenol	mg/kg dry wt	< 0.3	< 0.2	< 0.3
2,4,5-Trichlorophenol	mg/kg dry wt	< 0.3	< 0.2	< 0.3
2,4,6-Trichlorophenol	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Plasticisers Trace in SVOC Soil	Samples by GC·	-MS		
Bis(2-ethylhexyl)phthalate	mg/kg dry wt	1.3	< 0.5	< 0.5
Butylbenzylphthalate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Di(2-ethylhexyl)adipate	mg/kg dry wt	< 0.2	< 0.2	< 0.2
Diethylphthalate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Dimethylphthalate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Di-n-butylphthalate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Di-n-octylphthalate	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Other Halogenated compounds T	race in SVOC S	oil Samples by GC-MS		
1,2-Dichlorobenzene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
1,3-Dichlorobenzene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
1,4-Dichlorobenzene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Hexachlorobutadiene	mg/kg dry wt	< 0.3	< 0.2	< 0.3
Hexachloroethane	mg/kg dry wt	< 0.3	< 0.2	< 0.3
1,2,4-Trichlorobenzene	mg/kg dry wt	< 0.12	< 0.10	< 0.11
Other SVOC Trace in SVOC Soi	I Samples by G	C-MS		
Benzyl alcohol	mg/kg dry wt	< 1.2	< 1.0	< 1.1
Carbazole	mg/kg drv wt	< 0.12	< 0.10	< 0.11
I	5			

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Sample Type: Sediment					
Sa	mple Name:	102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm	102129 - Waitangi Stream D/S BioRich driveway: 4680 18-May-2023 2:30 pm	102128 - Waitangi Stream D/S stopbank receiving environment: 4681 18-May-2023 3:00 pm	
L	_ab Number:	3280937.1	3280937.2	3280937.3	
Other SVOC Trace in SVOC Soil Samples by GC-MS					
Dibenzofuran	mg/kg dry wt	< 0.12	< 0.10	< 0.11	
Isophorone	mg/kg dry wt	< 0.12	< 0.10	< 0.11	
Total Petroleum Hydrocarbons in	Solids				
C7 - C9	mg/kg dry wt	< 30	< 30	< 30	
C10 - C14	mg/kg dry wt	< 30	< 20	< 30	
C15 - C36	mg/kg dry wt	74	< 40	< 50	
Total hydrocarbons (C7 - C36)	mg/kg dry wt	< 100	< 90	< 90	

3280937.1

102127 - Waitangi Stream opposite 32 Waitangi Rd: 4679 18-May-2023 1:30 pm

Client Chromatogram for TPH by FID

Analyst's Comments

It has been noted that the System Monitoring Compounds 2-fluorophenol and phenol-d5 in the SVOC analysis on sample 3280937.3 had lower than expected recoveries. The recoveries were 38% and 38% respectively. Therefore the phenolic compounds may be underestimated.

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 simple 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. A detection limit range indicates the lowest and highest detection limits in the associated suite of analytes. A full listing of compounds and detection limits are available from the laboratory upon request. Unless otherwise indicated, analyses were performed at Hill Labs, 28 Duke Street, Frankton, Hamilton 3204.

Sample Type: Sediment			
Test	Method Description	Default Detection Limit	Sample No
Individual Tests			
Environmental Solids Sample Drying*	Air dried at 35°C Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-3
Environmental Solids Sample Preparation	Air dried at 35°C and sieved, <2mm fraction. Used for sample preparation May contain a residual moisture content of 2-5%.	-	1-3
Soil Prep Dry for Organics, Trace*	Air dried at 35°C Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-3
Dry Matter	Dried at 103°C for 4-22hr (removes 3-5% more water than air dry), gravimetry. (Free water removed before analysis, non-soil objects such as sticks, leaves, grass and stones also removed). US EPA 3550.	0.10 g/100g as rcvd	1-3
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	1-3
Total Cyanide Distillation*	Distillation of sample as received. APHA 4500-CN ⁻ C (modified) 23 rd ed. 2017.	-	1-3

Sample Type: Sediment			
Test	Method Description	Default Detection Limit	Sample No
Total Recoverable Phosphorus	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, screen level. US EPA 200.2.	40 mg/kg dry wt	1-3
Total Recoverable Rubidium	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.02 mg/kg dry wt	1-3
Total Recoverable Silver	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.02 mg/kg dry wt	1-3
Total Cyanide*	Distillation, colorimetry. APHA 4500-CN ⁻ C (modified) 23 rd ed. 2017 & Skalar Method I295-004(+P14). ISO 14403:2012(E).	0.10 mg/kg dry wt	1-3
Total Nitrogen*	Catalytic Combustion (900°C, O2), separation, Thermal Conductivity Detector [Elementar Analyser].	0.05 g/100g dry wt	1-3
Total Organic Carbon*	Acid pretreatment to remove carbonates present followed by Catalytic Combustion (O2), separation, Thermal Conductivity Detector [Elementar Analyser].	0.05 g/100g dry wt	1-3
Heavy metals, trace As,Cd,Cr,Cu,Ni,Pb,Zn,Hg	Dried sample, <2mm fraction. Nitric/Hydrochloric acid digestion, ICP-MS, trace level.	0.010 - 0.8 mg/kg dry wt	1-3
Acid Herbicides Trace in Soil by LCMSMS*	Solvent extraction, LC-MS/MS analysis. Tested on dried sample. In-house.	0.010 - 0.02 mg/kg dry wt	1-3
Multiresidue Pesticides in Sediment samples by GCMS	Sonication extraction, GC-ECD and GC-MS analysis. In-house based on US EPA 8081 and US EPA 8270.	0.0010 - 0.03 mg/kg dry wt	1-3
Polychlorinated Biphenyls Trace in Soil*	Sonication extraction, GC-MS analysis. In-house based on US EPA 8270.	0.00000020 - 0.035 mg/kg dry wt	1-3
Semivolatile Organic Compounds Trace in Soil by GC-MS	Sonication extraction, GC-MS analysis. Tested on as received sample. In-house based on US EPA 8270.	0.10 - 6 mg/kg dry wt	1-3
7 Grain Sizes Profile as received			
Dry Matter for Grainsize samples (sieved as received)*	Drying for 16 hours at 103°C, gravimetry (Free water removed before analysis).	0.10 g/100g as rcvd	1-3
Fraction >/= 2 mm*	Wet sieving with dispersant, as received, 2.00 mm sieve, gravimetry.	0.1 g/100g dry wt	1-3
Fraction < 2 mm, >/= 1 mm*	Wet sieving using dispersant, as received, 2.00 mm and 1.00 mm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Fraction < 1 mm, >/= 500 μm*	Wet sieving using dispersant, as received, 1.00 mm and 500 µm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Fraction < 500 μm, >/= 250 μm*	Wet sieving using dispersant, as received, 500 µm and 250 µm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Fraction < 250 μm, >/= 125 μm*	Wet sieving using dispersant, as received, 250 µm and 125 µm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Fraction < 125 μm, >/= 63 μm*	Wet sieving using dispersant, as received, 125 µm and 63 µm sieves, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Fraction < 63 µm*	Wet sieving with dispersant, as received, 63 µm sieve, gravimetry (calculation by difference).	0.1 g/100g dry wt	1-3
Total Petroleum Hydrocarbons in Solids			
Client Chromatogram for TPH by FID	Small peaks associated with QC compounds may be visible in chromatograms with low TPH concentrations. QC peaks are as follows: one peak in the C12 - 14 band, the C21 - 25 band and the C30 - 36 band. All QC peaks are corrected for in the reported TPH concentrations.	-	1
C7 - C9	Solvent extraction, GC-FID analysis. In-house based on US EPA 8015.	20 mg/kg dry wt	1-3
C10 - C14	Solvent extraction, GC-FID analysis. Tested on as received sample. In-house based on US EPA 8015.	20 mg/kg dry wt	1-3
C15 - C36	Solvent extraction, GC-FID analysis. Tested on as received sample. In-house based on US EPA 8015.	40 mg/kg dry wt	1-3
Total hydrocarbons (C7 - C36)	Calculation: Sum of carbon bands from C7 to C36. In-house based on US EPA 8015.	70 mg/kg dry wt	1-3

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

Testing was completed between 19-May-2023 and 17-Jul-2023. For completion dates of individual analyses please contact the laboratory.

Samples are held at the laboratory after reporting for a length of time based on the stability of the samples and analytes being tested (considering any preservation used), and the storage space available. Once the storage period is completed, the samples are discarded unless otherwise agreed with the customer. Extended storage times may incur additional charges.

This certificate of analysis must not be reproduced, except in full, without the written consent of the signatory.

Ara Heron BSc (Tech) Client Services Manager - Environmental

Appendix 2. Rapid comprehensive chemical analysis

Table A2.1.Concentration of the detected organic compounds by rapid comprehensive analysis in the three sediment samples collected.

Compound name	CAS no.	Concentration (µg/kg-dry wt)			Source / use	
	_	4679	4680	4681		
Benzyl alcohol	100-51-6	4.4		4.4	Solvent	
4-Cymene+	99-87-6		7.1		Solvent	
Isophorone+	78-59-1			6.3	Solvent	
1-Nonanol	143-08-8			5.4	Solvent, fragrance	
3- & 4-Methylphenol+	108-39-4 & 106-44-5	8.4	5.1		Disinfectant, antiseptic, solvent (plastic and resin)	
2-Acetyl-5-methylthiophene+	13679-74-8			6.4	Plant, flavouring agent	
Benzothiazole	95-16-9			3.9	Vulcaniser, antioxidant, dye intermediate, component of some pesticides and pharmaceuticals	
2,6-Dimethylnaphthalene+	581-42-0			111	РАН	
1,3-Dimethylnaphthalene+	575-41-7			6.8	РАН	
a-lonone+	127-41-3			16	Plant, fragrance, flavouring agent	
b-lonone+	14901-07-6			48	Plant, fragrance, detergents, flavouring, intermediate in vitamin A, E and K synthesis	
2,6-Di-tert-butyl-4-benzoquinone+	719-22-2	31	25		Bacterial product, oxidant, polymerisation catalyst	
2-Naphthol	135-19-3	11	17	13	Pigments, fats, oils, insecticides, pharmaceuticals, perfumes, antiseptics, pesticides and antioxidants for rubber, human metabolite (exposure to chlorpyrifos)	
Diethyl phthalate	84-66-2			4.1	Plasticiser	
Diphenylamine	122-39-4	1.7	0.9	12	Stabiliser, pesticide	
4-Nonylphenol+	25154-52-3	258		606	Stabiliser, plasticiser	

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Compound name	CAS no.	Concentration (µg/kg-dry wt)			Source / use	
		4679	4680	4681	-	
Tris(1-chloro-2-propyl)phosphate (TCPP)	13674-84-5	20	17	228	Flame retardant	
Phenanthrene	85-01-8	5.9	6.9		PAH – coal tar constituent	
Diisobutyl phthalate (DIBP)	84-69-5			20	Plasticiser, binding agent	
Methyl palmitate	112-39-0	33	16	59	Intermediate for detergents, stabilisers, resins, lubricants	
Dibutyl phthalate	84-74-2			51	Plasticiser	
2-PhenyInaphthalene+	612-94-2			7.1	PAH	
Linolelaidic acid methyl ester+	2566-97-4		25		Fatty acid	
Methyl stearate	112-61-8	30	21		Lubricant, intermediate for detergents, emulsifiers, stabilisers, plasticisers	
Pyrene	129-00-0	8.2	4.3	26	РАН	
9-Nitrophenanthrene+	954-46-1	120			РАН	
p,p'-DDE	72-55-9	5.5	15.5	24	Pesticide metabolite	
o,p'-DDD	53-19-0		5.3	26	Pesticide	
p,p'-DDD	72-54-8	5.1	14.1	90	Pesticide	
Azamethiphos	35575-96-3	206.4			Pesticide	
Diclomezine+	62865-36-5	310.2			Pesticide	
Tris(2-ethylhexyl)phosphate	78-42-2	57.7			Flame retardant, plasticiser	
Bifenthrin	82657-04-3	36.8			Pesticide	
Butyl benzyl phthalate	85-68-7		15.4		Plasticiser	
Adipic acid, bis-2-ethylhexylester	103-23-1				Plasticiser, solvent	
Benzo(a)anthracene+	56-55-3		6.2		PAH	
Bis(2-ethylhexyl)phthalate	117-81-7	111		1029	Plasticiser	
Permethrin @1	52645-53-1	148			Pesticide	

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Compound name	CAS no.	Co وµ()	ncentration g/kg-dry wt)		Source / use		
-		4679	4680	4681	-		
Permethrin @2	52645-53-1	215			Pesticide		
Perylene+	198-55-0	66	47	98	РАН		
Coprostanol+	360-68-9	575	73	146	Main sterol of the faeces produced by the reduction of cholesterol by intestinal bacteria		
Epicoprostanol+	516-92-7	1307	82	0	Sterol from bile acids and derivatives		
Cholesterol+	57-88-5	3240	1324	982	Main sterol of higher animals found in all body tissues. Emulsifier		
3-Cholestanone	15600-08-5	617		106	Metabolite of cholesterol		
Cholestanol+	80-97-7	965	183	420	Steroid ketone derived from coprostanol		
Indeno(1,2,3-cd)pyrene	193-39-5			28	PAH		
Campesterol+	474-62-4	425	436	540	Phytosterol		
Stigmasterol+	83-48-7	751	843	1243	Phytosterol, used in preparation of progesterone and other steroids		
24-Ethyl coprostanol+	4736-91-8	302	181	376	Phytosterol		
beta-Sitosterol+	83-46-5	2158	2457	2703	Phytosterol, used as emulsifier, stabiliser in cosmetic		
Stigmastanol+	83-45-4	455	435	812	Phytosterol, role in anti-cholesterolemic drug		
n-C12H26(Dodecane)	112-40-3	7.2			Solvent		
n-C14H30(Tetradecane)	629-59-4	35	13	38	Lubricant, stabiliser, solvent, building block for detergents and animal feed		
n-C15H32(Pentadecane)	629-62-9	64	9.2	53	Plant oil, solvent, organic synthesis		
n-C16H34(Hexadecane)	544-76-3	131	16	116	Plant metabolite, component of gasoline, solvent, organic intermediate		
n-C17H36(Heptadecane)	629-78-7	209	29	184	Plant metabolite, paraffin waxes (implies lubricating oil, fuel oil, anticorrosive)		
n-C18H38(Octadecane)	593-45-3	180	8.7	147	Plant, bacteria metabolite, paraffin waxes		
n-C19H40(Nonadecane)	629-92-5	184	26	176	Plant metabolite, paraffin waxes		
n-C20H42(Eicosane)	112-95-8	161	16	144	Plant metabolite, paraffin waxes		

Compound name	CAS no.	Concentration (µg/kg-dry wt)			Source / use	
4679 4680 4681		-				
n-C21H44(Henicosane)	629-94-7	173	41	174	Plant metabolite, pheromone, paraffin waxes	
n-C22H46(Docosane)	629-97-0	129	27	136	Plant metabolite, used in organic synthesis, paraffin waxes	
n-C23H48(Tricosane)	638-67-5	127	38	136	Plant metabolite, paraffin waxes	
n-C24H50(Tetracosane)	646-31-1	95	18	117	Plant metabolite, paraffin waxes	
n-C25H52(Pentacosane)	629-99-2	168	94	189	Plant metabolite, paraffin waxes	
n-C26H54(Hexacosane)	630-01-3	74	46	73	Plant metabolite, paraffin waxes	
n-C27H56(Heptacosane)	593-49-7	284	172	298	Plant metabolite, paraffin waxes	
n-C28H58(Octacosane)	630-02-4	119	64	132	Plant metabolite, paraffin waxes	
n-C29H60(Nonacosane)	630-03-5	486	433	502	Plant metabolite, paraffin waxes	
n-C30H62(Triacontane)	638-68-6		64	121	Natural product (plant, animal), paraffin waxes	
n-C31H64(Hentriacontane)	630-04-6	449	471	458	Natural product (plant, animal), paraffin waxes	
n-C32H66(Dotriacontane)	544-85-4	109	85	163	Plant, paraffin waxes	
n-C33H68(Tritriacontane)	630-05-7	342	304	323	Plant, paraffin waxes	

Source: National Center for Biotechnology Information. 2023. PubChem compound summary. [accessed July 2023]. https://pubchem.ncbi.nlm.nih.gov

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Appendix 3. Microtox® raw data

Table A3.1. Luminescence and gamma measured in the range of concentrations of the three sediment elutriates after 5, 15 and 30 minutes of exposure.

				;	Site 4679						Sit	e 4680		
Elutriate %	10	15	l15	130	G5	G15	G30	10	15	l15	130	G5	G15	G30
0	92	83	76	67	0.9022	0.8261	0.7283	 92	94	93	95	1.0220	1.0110	1.0330
0	78	73	67	60	0.9359	0.8590	0.7692	93	85	91	95	0.9140	0.9785	1.0220
0.20	80	67	64	60	0.0973	0.0531	-0.0016	103	93	95	97	0.0719	0.0784	0.0905
0.20	82	68	64	60	0.1082	0.0794	0.0232	103	92	93	95	0.0835	0.1016	0.1135
0.39	83	67	64	60	0.1385	0.0926	0.0357	101	90	93	95	0.0861	0.0802	0.0919
0.39	79	66	62	59	0.1001	0.0735	0.0025	101	89	91	94	0.0983	0.1040	0.1035
0.78	79	66	64	60	0.1001	0.0400	-0.0141	98	92	95	95	0.0309	0.0260	0.0594
0.78	80	66	60	55	0.1140	0.1234	0.0890	100	90	94	94	0.0754	0.0581	0.0926
1.56	80	67	64	60	0.0973	0.0531	-0.0016	99	91	95	96	0.0529	0.0365	0.0591
1.56	77	67	64	60	0.0562	0.0136	-0.0391	103	91	97	95	0.0954	0.0562	0.1135
3.13	78	70	68	63	0.0240	-0.0335	-0.0729	107	98	101	101	0.0567	0.0537	0.0880
3.13	81	70	67	63	0.0634	0.0185	-0.0373	104	96	102	104	0.0485	0.0141	0.0270
6.25	80	70	67	62	0.0503	0.0060	-0.0338	101	97	101	103	0.0077	-0.0053	0.0071
6.25	82	72	70	64	0.0466	-0.0130	-0.0406	108	98	102	105	0.0666	0.0531	0.0564
12.5	80	70	67	61	0.0503	0.0060	-0.0180	102	101	105	109	-0.0225	-0.0337	-0.0389
12.5	81	73	70	66	0.0197	-0.0250	-0.0810	107	103	107	110	0.0054	-0.0053	-0.0009
25	80	72	67	65	0.0211	0.0060	-0.0784	107	105	111	104	-0.0137	-0.0411	0.0566
25	80	72	69	67	0.0211	-0.0231	-0.1060	107	107	111	106	-0.0321	-0.0411	0.0367
50	82	72	72	71	0.0466	-0.0404	-0.1353	108	110	117	122	-0.0497	-0.0818	-0.0908
50	82	72	72	72	0.0466	-0.0404	-0.1473	 120	133	142	147	-0.1267	-0.1594	-0.1616

	Site 4681								
Elutriate %	10	15	l15	130	G5	G15	G30		
0	92	95	113	127	1.033	1.228	1.38		
0	92	97	117	133	1.054	1.272	1.446		
0.20	85	97	117	135	-0.0856	-0.0918	-0.1103		
0.20	83	97	113	130	-0.1071	-0.0818	-0.0978		
0.39	81	95	114	134	-0.1103	-0.1118	-0.1458		
0.39	89	102	115	127	-0.0895	-0.0326	-0.0097		
0.78	83	94	114	130	-0.0786	-0.0899	-0.0978		
0.78	81	95	111	130	-0.1103	-0.0878	-0.1196		
1.56	84	97	114	137	-0.0963	-0.0789	-0.1336		
1.56	84	100	111	136	-0.1235	-0.054	-0.1272		
3.13	91	104	127	143	-0.0869	-0.1043	-0.1008		
3.13	90	103	123	143	-0.0882	-0.0853	-0.1107		
6.25	89	106	129	145	-0.1239	-0.1376	-0.1327		
6.25	91	108	129	148	-0.1208	-0.1182	-0.1312		
12.5	88	107	132	152	-0.1418	-0.1667	-0.1819		
12.5	87	107	132	155	-0.1516	-0.1761	-0.2069		
25	87	111	138	157	-0.1821	-0.212	-0.217		
25	90	117	142	163	-0.1973	-0.2077	-0.2198		
50	90	121	151	170	-0.2239	-0.255	-0.2519		
50	102	128	156	179	-0.1685	-0.1827	-0.1948		

I0: luminescence before sampleI5, I15, I30: luminescence after 5, 15 and 30 min.

G5, G15, G30: 'gamma'



Figure A3.1. Dose-response of *Aliivibrio fischeri* to an increasing concentration of the reference toxicant.

Appendix 4. Blue mussel embryo-larval development assay

Table A4.1 Physico-chemical parameters of the control and the three sediment elutriate samples at the start of the exposure at the highest tested concentrations.

	Elutriate (%)	Salinity (psu)	Saturation (%)	DO (mg/L)	рН
Control	0	34.2	109	8.8	8.1
4679	3.13	n/m	n/m	n/m	7.9
	6.25	n/m	n/m	n/m	7.7
	12.5	n/m	n/m	n/m	7.4
	25	33.1	83	6.6	6.8
	50	31.3	70	5.5	6.5
	100	27.7	37	2.9	6.3
4680	25	33.4	106	8.2	7.3
	50	31.8	83	6.7	6.9
	100	28.3	58	4.6	6.5
4681	25	32.8	93	7.4	7.6
	50	31.6	86	6.7	7.3
	100	28.1	49	3.9	6.8

Table A4.2 Blue mussel larvae survival	in sediment elutriate samples at a range of
concentrations after 48 hour	s of exposure.

		Survival (%) Site 4679 Site 4680 Site 4681 Cor						
Elutriate (%)	Site 4679	Site 4680	Site 4681	Control				
3.13	47.1	43.7	58.3	59.5				
3.13	48.9	40.6	39.4	46.0				
3.13	51.0	39.6	58.3	50.0				
3.13	51.0	37.6	40.1	45.6				
3.13	49.7	62.3	61.1	57.9				
6.25	43.4	44.1	57.0					
6.25	50.4	36.3	38.1					
6.25	51.6	41.5	53.9					
6.25	40.8	39.8	45.0					
6.25	40.3	65.4	52.2					
12.5	6.1	21.6	40.4					
12.5	21.1	32.0	34.1					
12.5	5.4	23.6	51.5					
12.5	9.1	29.3	40.7					
12.5	9.5	54.8	67.4					
25	0	0	43.3					
25	0	0	28.0					
25	0	0	46.7					
25	0	0	33.3					
25	0	0	65.0					
50	0	0	34.3					
50	0	0	41.3					
50	0	0	46.4					
50	0	0	23.6					
50	0	0	51.4					
100	0	0	0					
100	0	0	0.8					
100	0	0	0					
100	0	0	0					
100	0	0	0					



Figure A4.1 Dose-response (median, with quartiles and maximum / minimum) and fitted model (dashed line) of the blue mussel larvae survival in an increasing concentration of the reference toxicant.

Abbreviations / acronyms							
4op	4-tertoctyl-phenol						
AhR	Aryl hydrocarbon receptor						
AIQS-DB	Automated Identification and Quantification of Chemicals Database						
βna	β-naphthoflavone						
CAR	Constitutive androstane receptor						
CI	Confidence interval						
DCM	Dichloromethane						
DDD	Dichlorodiphenyldichloroethane						
DDE	Dichlorodiphenyldichloroethylene						
DDT	Dichlorodiphenyltrichloroethane						
DGVs	Default guideline values						
DMSO	Dimethyl sulfoxide						
D/S	Downstream						
dw	Dry weight						
EC _x	Effective concentration						
eq.	Equivalent						
g	Gravitational acceleration (9.8 m/s ²)						
GC–MS	Gas chromatography–mass spectrometry						
h	Hour						
HBRC	Hawke's Bay Regional Council						
kg	Kilogram						
L	Litre						
LC	Lethal concentration						
LOEC	Lowest observed effective concentration						
μ m	Micrometre (10 ⁻⁹ m)						
min	Minute						
mL	Millilitre (10 ⁻³ L)						
mm	Millimetre						
MS	Mass spectroscopy						
n	Number of replicates						
NaCl	Sodium chloride						
N(S)EC	No (significant) effect concentration						
NIWA	National Institute of Water and Atmospheric Research						
NOEC	No observed effective concentration						
Р	Probability						
PAHs	Polycyclic aromatic hydrocarbons						
PCB	Polychlorinated biphenyl						
PCDD	Polychlorinated dibenzo-p-dioxin						
PCDF	Polychlorinated dibenzofuran						
QT ratio	Qualifier ion/target ion						

Appendix 5. Abbreviations and acronyms

Abbreviations / acronyms					
RI	Retention index				
RT	Retention time				
SD	Synthetic defined				
Y2H	Yeast two-hybrid				
Zn ²⁺	Zinc (metal ion)				