



Ravensdown Napier Baseline Technical Investigations



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Executive Summary

Preamble

This report presents an ecological and water quality assessment of past and current storm and process water discharges, discussed in the context of the current discharge permit DP040143Wa discharge and receiving water conditions. It does not comment on future new consents which is part of the next phase of work Streamlined Environmental and Boffa Miskell are working on with the Ravensdown technical team. This additional work will be reported in the Aurecon s105 alternatives assessment report and the options chosen will form the Ravensdown stormwater and process water strategy which will underpin the new discharge permit when this is applied for in November 2021.

Introduction

Ravensdown Limited (Ravensdown) operates a fertiliser manufacturing plant at Awatoto, near Napier and holds a number of permits to enable operation of the plant. These include a consent to discharge contaminants into water, with the receiving environment being the Tūtaekurī River and the associated Waitangi Estuary. An initial review of available information on the current state and effects of discharges arising from the Awatoto facility (Phillips et. al, 2020) identified additional information needs required to support a discharge consent application. This report presents existing and new information to address these information gaps relating to process and stormwater contaminants and effects on the receiving environment.

Background

The immediate receiving environment for the discharge is the Ravensdown and Awatoto Drain, with the ultimate receiving environment being the Tūtaekurī River and Waitangi Estuary (which have been identified as outstanding waterbodies under Proposed Plan Change 7¹). The mixing zone encompasses the Ravensdown Drain and 90m of the Awatoto Drain and has a total length of around 170m metres) (**Figure 1**). Upstream catchments input contaminants via the Mission and Waitangi Drains and comprise a mixture of agriculture, commercial, industrial and urban landuses. In addition, a Hawke's Bay Regional Council operated pump controls the Mission and Waitangi Drain upstream flows through a stop bank to Awatoto Drain.

¹ Decisions on first instance hearing pending.



Figure 1: Map showing location of Ravensdown Napier facilities and the receiving environment, surrounding landuse and relevant features.

Ravensdown Napier undertakes weekly and 6 monthly compliance monitoring of the quality of its discharge. In addition, monitoring is also undertaken of the receiving environment (upstream and downstream of the discharge point) for water quality (monthly ambient and 6 monthly rainfall sampling) and ecological and ecotoxicological effects (4 yearly).

Discharge and receiving environment water quality

Very high compliance has been recorded for discharge flow (100%), pH (94%), TSS (100%), and fluoride (100%). Very high compliance has also generally been observed for SRP and DRP limits.

Under ambient sampling conditions, nickel, copper and aluminium have been elevated in the mixing zone and some sites further downstream, when compared with upstream sites. Some metal concentrations have been similarly high (or higher) at upstream sites e.g. cadmium, zinc, fluoride. All nutrient concentrations other than nitrate have been comparable upstream (within the Waitangi Drain) and downstream of the discharge and guidelines are exceeded at all sites. TSS

has been highest upstream of the discharge and lowest further downstream in the $T\bar{u}taekur\bar{i}$ River, indicating that the Ravensdown discharge is not a source.

Under rainfall sampling conditions, cadmium, fluoride and sulphur have been higher in in the mixing zone when compared with sites upstream of the discharge. In addition, mixing zone nutrient concentrations have been elevated compared to upstream, although guidelines have been exceeded both upstream as well as in mixing zone and downstream. TSS concentrations have been comparable across all sites.

Analysis of trends indicates decreasing trends in concentrations of copper, fluoride, SRP, TP and TSS in the discharge that are meaningful (being statistically significant and having greater than 1% change per year). An increasing trend in discharge flow reflects the recent change in practice of adding bore water directly to the settling pond as part of the dilution process.

Under ambient sampling conditions, sulfur and fluoride concentrations have shown increasing trends at some upstream sites but have been decreasing (albeit not significantly) downstream of the discharge, while most nutrients have shown decreasing trends at all sites other than in the mainstem Tūtaekurī River site.

Under rainfall sampling conditions, fluoride showed an increasing trend at sites both upstream and downstream of the discharge, though only upstream sites showed meaningful trends. For nutrients, ammoniacal nitrogen concentrations showed a meaningful increasing trend at upstream sites, while downstream concentrations tended to decrease.

Overall, concentrations of some metals exceed guideline values both upstream and downstream of the Ravensdown discharge under wet weather conditions. In addition, concentrations of some metals are higher at upstream sites than within the mixing zone or downstream under ambient conditions. This indicates that sources other than the Ravensdown discharge are also contributing to downstream metal concentrations. For fluoride, sulphur and some nutrients, average concentrations downstream of the discharge are higher than upstream sites under wet weather conditions, indicating that the discharge may be contributing to short-term effects associated with these events.

Mixing zone dye study

A dye study was undertaken in March 2021 to provide a quantitative estimate of dilutions achieved at different stages of the tidal cycle, under the base flow discharge rate from the settling pond. Within the mixing zone, dilutions at the water surface range between 1.7 and 17.8 fold (median = 3.5, average = 6.8 fold) when discharged prior to low tide and between 2.1 and 14.9 fold (median = 5.3, average = 6.6 fold) when discharged prior to high tide. Dilutions of upto 113 fold were recorded at 500mm below the surface under high tide conditions, but there was generally little evidence of mixing.

Risk assessment of process chemicals

Ravensdown Napier uses nine process chemicals (in formulations) as part of the operation of the plant. In addition, Sandfords also uses two chemicals for their truck wash (with use of one having recently ceased). Process chemicals are not required to be measured in the discharge or in the receiving environment. To assess potential effects of such chemicals, a risk assessment approach is used, in which chemical and ecotoxicological properties are used to assess potential risk. This is a highly conservative approach. It assumes all the chemicals enter the settling pond, with no degradation or evaporation. It also assumes the lowest dilution from dye study. It thus represents the worst-case scenario in terms of potential risk. While it may over-estimate risk, it is considered the most prudent approach in the absence of degradation data (for most process chemicals) and the inability to measure most of the process chemicals in the pond or receiving environment (due to lack of accredited laboratory methods).

Four of the eleven formulations present negligible risk under either discharge scenario. The potential risk when discharging prior to low tide is elevated for the majority of the formulations used at Ravensdown. While biodegradation may reduce effects somewhat, it is considered unlikely that this would result in a significant reduction in such effects, given that the calculated risk quotients are orders of magnitude greater than 1. The potential risk when discharging prior to high tide is markedly reduced, but still elevated for 6 formulations. As all are readily biodegradable and risks are only marginally greater than 1 in some instances, effects are generally considered to be unlikely.

Whole Effluent Toxicity Testing

The ecotoxicity of the discharge is assessed 4 yearly by undertaking tests on 3 typical test species. The concentrations of a range of contaminants are also determined and dilutions required to meet guideline values calculated. Results for 2015, 2019 and 2020 consistently indicate that the discharge would not be considered toxic to organisms in the receiving environment. A dye study was undertaken in March 2021 to determine the dilution achieved in the mixing zone (see Chapter 4). While these dilutions are generally lower than the 100-fold dilution required to meet the toxicity compliance limit, this does not mean toxic effects have occurred. For example, the 2020 WET testing results indicated that dilutions of only 13 fold and 25 fold were necessary to achieve no toxicity.

Marine Ecology

The discharge is into brackish water in the estuary and therefore is considered a marine environment for ecological and water quality assessment. Marine ecology surveys have been undertaken in 2011, 2015, 2019 and in July 2020. Sites upstream of the discharge, within the mixing zone, and within the Tūtaekurī (Blind Arm) and Waitangi Estuary have been surveyed for macrofauna, fish, periphyton and sediment contamination.

Sites within the mixing zone are characterised by reduced diversity and abundance of benthic fauna, most likely reflecting impacts from the discharge. Differences in sediment composition and in freshwater inputs may contribute partially to the observed differences. There is little evidence of effects on marine benthic communities beyond the mixing zone.

While it is difficult to determine the exact effects from the Ravensdown discharge on fish communities in the Tūtaekurī River and wider Waitangi Estuary, the large number of species observed in the river and estuary, including non-migratory species, would suggest that any effects are most likely short-lived, localised and are not impacting on fish communities.

Chlorophyll a concentrations (as an indicator of periphyton) in sediments have been consistently highest immediately downstream of the discharge, with a general decrease downstream. In addition, there is no evidence to indicate effects of the discharge on macrophyte communities.

Elevated concentrations of some contaminants in sediment have been observed immediately downstream of the discharge and at the boundary of the mixing zone (when compared with upstream) but have reduced in more recent studies. Sediment contaminant concentrations were generally below default guideline values in 2020 at most sites.

1. Preamble

This report presents an ecological and water quality assessment of past and current storm and process water discharges, discussed in the context of the current discharge permit DP040143Wa discharge and receiving water conditions. It should be noted that Ravensdown Napier discharges into brackish water and then into the Waitangi estuary and therefore is considered a marine environment for the ecological and water quality assessments.

This report does not comment on future new consents which is part of the next phase of work Streamlined Environmental and Boffa Miskell are working on with the Ravensdown technical team. This additional work will be reported in the Aurecon s105 alternatives assessment report and the options chosen will form the Ravensdown stormwater and process water strategy which will underpin the new discharge permit when this is applied for in November 2021.

2. Introduction

Ravensdown Limited (Ravensdown) operates a fertiliser manufacturing plant at Awatoto, near Napier. Ravensdown holds a number of permits to enable operation of the plant, including a consent to discharge contaminants into water, with the receiving environment being the Tūtaekurī River and the associated Waitangi Estuary. Streamlined Environmental Ltd (SEL), in partnership with Boffa Miskell Ltd (BML), was commissioned to provide technical expertise for the reconsenting process on the matters of water quality and aquatic ecology. An initial review of available information on the current state and effects of discharges arising from the Awatoto facility (Phillips et. al, 2020) identified additional information needs required to support a discharge consent application. Relevant extracts from that report are presented throughout this report to provide context for the additional technical work that is presented. This report presents the results of our investigations, which have been largely focused on characterising the effects of the discharge. Specific chapters cover discharge and receiving environment water quality (Chapter 4), a dye study (Chapter 5), risk assessment of process chemicals (Chapter 6), ecotoxicity (Chapter 7) and marine ecology (Chapter 8).

3. Background information

3.1 Onsite water collection and distribution

There are two components to the discharge (Hanna, 2016);

- Stormwater from approximately 8 hectares within the site and which is likely to contain hydrocarbons, heavy metals and suspended material from fertiliser processing and handling.
- Process water which contains contaminants from a truck wash, cooling water (from air compressors, hydraulic drive and acid plant), rinse water from a boiler water treatment unit and high pressure boiler water.

In addition, truck wash water from the adjacent Sandfords distribution facility also enters the Ravensdown collection system (N. Phillips, pers. obs., Feb 2020).

Stormwater and process water is collected in a covered drain system and diverted to a sump, where it can be pumped to a storage pool or to a settling pond (Death & Ekelund, 2019). Stormwater collected from around the site accumulates in the Archimedes Basin. Here the water is monitored to ensure the pH is between 6.5 and 8.5 (the consent limits) before being pumped to the settling pond. Due to water in the site drains being predominantly acidic, the Archimedes Screw is fitted with two pH probes, which are used to determine the amount of pH adjustment required to ensure consent limits are not breached and also has an alarm system to allow for careful monitoring. pH can then be adjusted before discharging. The storage pool is used as a first flush storm water catchment vessel, allowing water generated on site to be recycled. The settling pond is designed to maximise particulate drop out as water moves around the pond and into the outlet sump, before being discharged into the marine environment. The settling pond pH is also monitored to ensure levels are within consented limits before discharging occurs. The Settling Pond is the last point in the Ravensdown Awatoto drainage system. As such, it is the final control point prior to discharge from site and the collection point for stormwater samples used to monitor the Hawke's Bay Regional Council (HBRC) resource consent requirements for water discharged to the Tūtaekurī River (DP040143W).

The Settling Pond has three potential sources of water from the Ravensdown site:

- Drain water via Archimedes.
- Acid plant cooling tower water.
- Fresh water can be discharged into the settling pond outlet pump sump by a ground valve located at the north end of the Acid cooling tower in the acid plant.

Discharge from the settling pond is controlled by the activation of two pumps, one used during baseflow conditions (up to 20L/s) and the other also utilised during storm condition events (up to 200 L/s).

3.2 Discharge consent conditions

A copy of the discharge consent conditions is found in Appendix A. Condition 4 requires that the discharge complies with the following standards at the outlet of the settling pond and that these parameters be measured at least weekly (Condition 5):

- pH to be between 6.5 and 8.5.
- Fluoride not to exceed 30 mg/L.
- Suspended solids not to exceed 100 mg/L.
- Rate of discharge not to exceed 265 L/sec.
- Total phosphorus over a 12 month period not to exceed 22 mg/L for more than 99% of the time or 17 mg/L for more than 95% of the time.
- Soluble reactive phosphorus not to exceed 20 mg/L for more than 99% of the time or 15 mg/L for more than 95% of the time.

Condition 5 also requires 6 monthly flow-proportional composite sampling (over a period of 1 week) for total metals (copper, zinc, cadmium, chromium, aluminium and sulphur).

In addition to parameters included in the discharge consent, process chemicals have the potential to enter the discharge as they are used at various points throughout the operations. As no studies have previously been undertaken, an assessment of the potential risks of process chemicals to stormwater discharge quality is presented Chapter 5.

3.3 Receiving Environment

The receiving environment for the Ravensdown discharge is a series of drains that lead to the Tūtaekurī River, and ultimately the Waitangi Estuary (which have been identified as outstanding waterbodies under Proposed Plan Change 7²) (Figure 2). The discharge from the Ravensdown settling pond enters the Ravensdown Drain. Ravensdown Drain is approximately 2-3 meters in width and 80 meters in length, is grassed to the drain edge and is unshaded. Downstream the Ravensdown Drain discharges into the Awatoto Drain. The mixing zone encompasses the Ravensdown Drain and 90m of the Awatoto Drain and has a total length of around 170m metres. The Awatoto Drain is fed from upstream of the Ravensdown discharge point by the Waitangi Drain, Ravensdown Drain and the Mission Drain. Upstream of the Awatoto Drain is a pump station, occurring at the confluence of the Waitangi and Mission Drains. The pump station is operated by Hawke's Bay Regional Council and discharges into the Awatoto Drain when water levels are elevated, with discharge into the Awatoto drain equating to 0, 250, 900, or 1800 L/s at any one time. Catchments of Awatoto and Waitangi Drains comprise a mixture of agriculture, commercial, industrial and urban landuses and therefore the water quality, sediment quality and ecology are influenced by the contaminants from those landuses as well as the Ravensdown discharge. The Mission Drain appears to capture runoff from both industrial and agricultural landuses, including orchards and an open compost and green waste factory (BioRich). Water quality in the Mission Drain may be affected by contaminants originating from all of these landuses.

² Decisions on first instance hearing pending.

The Awatoto Drain discharges to the blind arm of the Tūtaekurī River some 150m downstream from the confluence of the Ravensdown drain and the mouth of the Awatoto Drain. The discharge then enters the Waitangi estuary via the Tūtaekurī River. The landuse of the Tūtaekurī River catchment is largely pastoral/agricultural.

Condition 6 (a - g) of the discharge resource consent (Appendix A) requires monitoring every four years to characterise ecological effects, and includes surveying of benthic macrofauna, fish, periphyton and macrophytes as an indicator of nutrient enrichment, determination of sediment health and potential for metal accumulation and Whole Effluent Toxicity (WET) Testing to determine the effects of the combined discharge on biota. A dilution of at least 100:1 for no detectable toxicity in the WET test is set as the compliance measure. Condition 7 requires that a monitoring programme designed to meet the requirements of Condition 6 be submitted for approval by the Council prior to undertaking this monitoring.

In addition, Condition 6h (Appendix A) requires monthly collection of samples collected from sites upstream and downstream of the discharge point and analysis of a range of physico-chemical parameters (see **Table 6** for details). Six-monthly (summer and winter) rainfall-event related samples are also required to be collected (Condition 6i) and analysed for a similar suite of parameters (see **Table 1**).



Figure 2: Map showing location of Ravensdown Napier facilities and the receiving environment, surrounding landuse and relevant features.

4. Discharge and receiving environment water quality

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4.1 Water quality consent monitoring conditions

The HBRC granted Ravensdown consent to discharge stormwater and process water produced by Ravensdown into the Waitangi Estuary (Consent DP040143W) via the Ravensdown and Awatoto Drains.

This consent includes a suite of conditions. Conditions 5 (a) and (c) require monitoring of the Ravensdown discharge and the receiving environment. Conditions 6 (h) and (i) require Ravensdown to monitor specific water quality parameters both in drains that receive the discharge, and the receiving environment. A summary of the consent conditions relevant to the monitoring of the quality of the Ravensdown discharge and the receiving environment is presented below.

5 (b) A representative, flow proportional, composite sample (sampled continuously over a period of 24 hours) is to be collected at the discharge outfall once per week.

5 (c) A representative, flow proportional, composite sample (sampled continuously over a period of one week) is to be collected at the discharge outfall at 6 monthly intervals and tested for trace metals.

6 (h) Every month, the consent holder shall monitor receiving water quality at specific sites to determine whether contaminants of concern are present and in what concentrations.

6 (i) Each year, on two occasions (one during either January or February and one during June, July, or August) the consent holder shall monitor stormwater discharged in the "first flush" of a rainfall event at specific sites.

Sampling in accordance with condition 6h is referred to as sampling under 'ambient conditions', and sampling required to meet condition 6i is referred to as sampling under 'rainfall conditions'.

4.2 Water quality parameters to be monitored

Parameters required to be monitored under each condition are summarised in **Table 1** and **Table 2**.

Table 1: Trace metals (sampled 6 monthly) and other parameters (sampled weekly) monitored in Ravensdown <u>discharge</u> to meet compliance requirements for Conditions 5 (b) and (c).

Trace metals (6 monthly)	Other (weekly)
Aluminium (Al)	Flow/Rate of discharge
Cadmium (Cd)	рН
Chromium (Cr)	Total Suspended Solids (TSS)

Trace metals (6 monthly)	Other (weekly)
Copper (Cu)	Fluoride (F)
Nickel (Ni)	Sulphur (S)
Zinc (Zn)	Total Phosphorus (TP)
	Soluble Reactive Phosphorus (SRP)

Table	2:	Trace	metals/e	elements,	nutrients,	and	other	parameters	monitored	in	the
receiv	ing	enviro	nment to) meet con	npliance re	quire	ments	for Condition	ıs 6 (h) and ((i).	

Trace metals/elements	Nutrients	Other
Aluminium (Al)	Total Nitrogen (TN)	Total Suspended Solids (TSS)
Cadmium (Cd)	Total Ammoniacal Nitrogen (NH ₄ -N)	Chlorophyll-a*
Chromium (Cr)	Nitrite-Nitrogen (NO ₂ -N)	рН
Copper (Cu)	Nitrate-Nitrogen (NO ₃ -N)	Dissolved Oxygen (DO)
Nickel (Ni)	Nitrite/Nitrate-Nitrogen (NO ₂ /NO ₃ -N)	Temperature
Zinc (Zn)	Total Kjeldahl Nitrogen (TKN)	Conductivity
Sulphur (S)	Soluble Reactive Phosphorus (SRP)	Salinity
Fluoride (F)	Total Phosphorus (TP)	

* - excluded from rainfall condition monitoring.

4.3 Water quality monitoring sites

Condition 7 of the resource consent requires that a suitable monitoring plan, designed to meet the requirements of Condition 6 and to the satisfaction of the Council, be submitted to HBRC, prior to the receiving environment monitoring occurring. Strong (2013) set out the locations and methodologies to comply with this condition. This monitoring plan was subsequently reviewed and revised by Aquanet in 2014 (Aquanet 2014) and again in 2019 (Aquanet, 2019) and approved by HBRC. The locations for sampling sites under both ambient (AS1 - AS7) and rainfall (SWS1 -SWS11) conditions are presented in **Figure 3**. It is important to note the position of the monitoring sites in relation to the Ravensdown wastewater discharge point:

- Sites AS1 AS3 and SWS1 SWS6 are located along the Waitangi Drain that runs parallel to the plant, with AS1 and SWS1 upstream of the Ravensdown site. Contaminants within these sites are likely be attributed to inputs from a variety of land uses surrounding the drain. This includes intensive agriculture and a composting facility along the true right bank of the drain and the fertiliser plant itself along the drains true left bank. Additionally, it is likely contaminants enter from the road that runs parallel to the drain.
- Sites AS4 and SWS7 are located in the Mission Drain. The composting facility adjacent to this site may contribute to contaminants recorded at these sites. There is also a council pump station where the Awatoto Drain and Mission Drain meet, which passes through a stop bank and enters the downstream extent of the Awatoto Drain above the confluence

with the Ravensdown Drain. The releasing of water from this upstream point into the drain and estuary is controlled by water volume. Consequently, contaminants in these drains are likely to be influencing contaminant concentrations at sites AS4, SWS7 and SWS6 if the pump is not activated.

- Site SWS8 is located in the Ravensdown Drain, the point where the Ravensdown process/stormwater is discharged. This is likely to be indicative of only the Ravensdown discharge contaminant concentrations in the receiving environment.
- Sites AS5 and SWS9 are situated in the Awatoto Drain, part of which is designated as the reasonable mixing zone for the Ravensdown discharge. This is likely reflective of contaminants found in the Mission Drain, Waitangi Drain, and the Ravensdown discharge as it is downstream of all three.
- The sites representing the receiving environment are AS6, AS7, SWS10 and SWS11. AS6 and SWS10 are slightly downstream of the end of the mixing zone, in the Tūtaekurī Blind Arm. These sites are likely to be indicative of influences from the Tūtaekurī River and the Mission/Awatoto drain discharge (assuming that the discharge is fully mixed at the mixing zone boundary). Lastly, AS7 and SWS11 are sites distant from all discharges and are located on the Tūtaekurī River.



Figure 3: Locations of water quality monitoring sites determined by Strong (2013). Red stars are ambient (AS) and rainfall (SWS) sampling sites. Blue stars are rainfall only sampling sites. The purple marker is the location of the Ravensdown discharge point.

4.4 Previous water quality studies

4.4.1 Discharge quality

Death & Ekelund (2019) provide a useful summary of data collected between 2012 and 2019 for the purpose of assessing compliance of the discharge with relevant consent conditions (**Table 3 and Table 4**). Very high compliance has been recorded for discharge flow (100%), pH (94%), TSS (100%), and fluoride (100%). Very high compliance has also generally been observed for SRP and DRP limits, excluding 2013 – 2014 (SRP, 95% limit; TP, 95% and 99% limit) and 2017-2018 (SRP, 95% limit), where exceedances were greater than allowable (**Table 4**).

Table 3: Summary of weekly discharge data from Ravensdown settling pond outlet between 2012 and 2019. Source: Death & Ekelund (2019).¹ = see Table 4 for details.

	Discharge Flow (L/s)	рН	Fluoride (g/m³)	SS (g/m³)	SRP (g/m³)	TP (g/m³)				
ALL DATA (01 July 2012 – 31 July 2019)										
Average	2.5	7.2	4.4	7.9	7.6	8.3				
50%ile (median)	2.5	7.2	3.2	6.0	6.6	7.0				
95%ile	5.2	7.9	11.6	20.8	15.0	16.7				
99%ile	6.7	8.1	18.3	43.4	20.4	23.0				
N. of Samples	253	364	366	365	366	366				
Condition limit	< 265	6.5 - 8.5	< 30	< 100	< 15 (95% of the time) < 20 (99% of the time)	< 17 (95% of the time) < 22 (99% of the time)				
% Compliance	100	94	100	100	95% / 95% ¹	95% / 98% ¹				

Table 4: Summary of compliance for Total Phosphorus and SRP based on weekly samples from the Ravensdown settling pond outlet between 2012 and 2019. Source: Death & Ekelund (2019).

т	P	Limit: TP shall not exc	eed 17 mg/L for more	e than 95% of the time	Limit: TP shall not exceed 22 mg/L for more than 99% of the time			
Year	Number of samples	No. Exceedances	Allowable exceedances	Compliant	No. Exceedances	Allowable exceedances	Compliant	
2012-2013	52	1	5	V	0	1	V	
2013-2014	52	10	5	×	4	1	×	
2014-2015	52	1	5	V	1	1	1	
2015-2016	52	0	5	V	0	1	V	
2016-2017	52	0	5	V	0	1	V	
2017-2018	52	3	5	V	0	1	V	
2018-2019	52	1	5	V	1	1	A	

SRP		Limit: SRP shall not ex	ceed 15 mg/L for mo	re than 95% of the time	Limit: SRP shall not exceed 20 mg/L for more than 99% of the time			
Year	Number of samples	No. Exceedances	Allowable exceedances	Compliant		No. Exceedances	Allowable exceedances	Compliant
2012-2013	52	1	5	√		0	1	V
2013-2014	52	10	5	×		1	1	V
2014-2015	52	1	5	V		1	1	V
2015-2016	52	0	5	\checkmark		0	1	V
2016-2017	52	1	5	\checkmark		0	1	V
2017-2018	52	4	5	Ń		2	1	×
2018-2019	52	1	5	N N		0	1	1

4.4.2 Receiving environment water quality

Water quality data collected monthly between 2013 and 2019 from sites within the receiving environment to characterise ambient conditions, namely the Ravensdown and Awatoto Drains, the Tūtaekurī Blind Arm and the mainstem of the Tūtaekurī River, are summarised below (Death & Ekelund, 2019):

• Cadmium concentrations were much higher upstream of the discharge. Concentrations of nickel were highest within the mixing zone, decreasing with distance downstream. Concentrations of cadmium and nickel were well below ANZG (2018) trigger values for lowland rivers at the 95% protection level at all sites.

- Total aluminium concentrations exceeded ANZG (2018) trigger values for lowland rivers at the 95% protection level at all sites except in the mainstem of the Tūtaekurī River. Concentrations were higher downstream of the discharge than upstream and increased between sites within the mixing zone and the Blind Arm of the Tūtaekurī River. This suggests that the Ravensdown fertiliser plant may be a source of total aluminium in these drains.
- Total chromium concentrations were similar across all sites in the Awatoto and Mission Drains but decreased considerably in the mainstem of the Tūtaekurī River. Concentrations of chromium were above ANZG (2018) trigger values for lowland rivers at the 95% protection level at all sites. This suggests the discharge is not the main source of chromium.
- Total copper concentrations were slightly below the ANZG (2018) trigger values for lowland rivers at the 95% protection level in the Waitangi and Mission Drains and increased to just exceeding the guideline at sites downstream of the discharge on the Awatoto Drain, suggesting some contribution from the Ravensdown discharge. Sites on the mainstem of the Tūtaekurī River were well below the ANZG (2018) trigger value.
- Total zinc concentrations exceeded ANZG (2018) trigger values for protection of 95% and 80% of species in the Waitangi Drain upstream of the Ravensdown site, whereas only the 95% protection level is exceeded in the mixing zone and downstream in the Blind Arm of the Tūtaekurī River. Concentrations in Mission Drain and the mainstem of the Tūtaekurī River were below detection limits. This suggests that the plant is not contributing significantly to zinc concentrations in the drain.
- Fluoride concentrations were highest in Mission Drain upstream of the discharge, decreasing through the mixing zone to the lowest concentrations in the mainstem of the Tūtaekurī River. There are no ANZG (2018) trigger values for fluoride. A guideline of 5 mg/L for protection of 95% of species has been developed by Hickey et al. (2004) for high salinity (25-35 psu) waters.
- Sulphur concentrations increased from upstream of the discharge along the Awatoto Drain to the mixing zone, decreasing slightly in the blind arm of the Tūtaekurī River, with further decreases in the main stem of the Tūtaekurī River. There are no ANZG (2018) trigger values for sulphur.
- Total ammoniacal nitrogen concentrations were moderately elevated at all sites (i.e. upstream and downstream of the discharge), apart from the mainstem of the Tūtaekurī River. Average total ammoniacal-N concentrations did not exceed the ANZG 95% protection level trigger value at AS7 (the reference site) and the risk of toxic effects from ammoniacal nitrogen here can be considered low. All other sites exceeded the 95% protection level but met the 80% protection level, which may be more applicable to these highly modified drain sites.
- Nitrate values were generally higher upstream of the discharge, decreasing within the mixing zone and further downstream, indicating that the Ravensdown discharge is not a source.
- Nitrite concentrations were elevated within the mixing zone when compared with upstream or downstream sites.
- Total nitrogen exceeded the ANZG (2018) trigger values at all sites other than AS7 in the mainstem of the Tūtaekurī River.

- Phosphorus (total and soluble) concentrations were high and exceeded ANZG (2018) trigger values at all sites but were significantly lower at the furthest downstream site (AS7) in the mainstem of the Tūtaekurī River. Concentrations of phosphorus increased in the Awatoto Drain in the reach of the drain running alongside the fertiliser plant, pointing to sources of phosphorus inputs to the drain within this reach. TP and SRP concentrations in Mission Drain were similar to those found downstream of the discharge in the blind arm of the Tūtaekurī River. This suggests that sources of phosphorus from both the surrounding catchment and the Ravensdown discharge are contributing equally to the Tūtaekurī River.
- TSS was highest upstream of the discharge and lowest further downstream in the Tūtaekurī River, indicating that the Ravensdown discharge is not a source.
- Chlorophyll *a* concentrations decreased downstream indicating the Ravensdown discharge is less likely to be contributing to increased algal growth in the Tūtaekurī River or wider Waitangi Estuary than upstream sites.
- Water pH, temperature and DO did not differ significantly between sites along the Awatoto Drain upstream and downstream of the discharge. In contrast, conductivity and salinity were much lower at AS7 (salinity = 0.1 ppt), indicating that this site is predominantly influenced by upstream Tūtaekurī River water. All other sites recorded salinities indicative of brackish water.

Additional wet-weather water quality sampling (required by Condition 6i) undertaken between 2013 and 2019 provided generally similar conclusions to those of the monthly sampling, although the concentrations of some metals, in particular aluminium, cadmium, chromium, copper and zinc were more elevated at all sites compared (i.e. upstream and downstream of the discharge) with the monthly sampling and exceeded the ANZG trigger values at most sites (Death & Ekelund, 2019). Results of note for wet weather sampling are summarised below:

- Highest median aluminium concentrations were recorded upstream of the discharge.
- Cadmium concentrations within the mixing zone were around 50% higher than upstream and exceeded the ANZG (2018) trigger value. Values decreased downstream of this point. All upstream sites were below the ANZG (2018) trigger value.
- Nickel concentrations increased in the mixing zone when compared to upstream but all sites were below the ANZG (2018) trigger value.
- The ANZG (2018) trigger values for chromium, copper, and zinc was exceeded at all but the furthest downstream site (SWS11).
- Both fluoride and sulphur were elevated in the mixing zone in comparison to upstream or downstream sites, although more recent sampling (2015-2019) reported reduced concentrations.
- Ammoniacal nitrogen, total nitrogen and SIN (Soluble Inorganic Nitrogen) were considerably elevated within the mixing zone and in the Tūtaekurī Blind Arm, when compared with upstream or downstream sites. More recent sampling (2015-2019) reported reduced concentrations.
- Nitrate concentrations were comparable between sites.
- Both TP and SRP were considerably elevated in the mixing zone and Tūtaekurī Blind Arm, when compared to upstream and downstream sites.

• TSS, pH, temperature and DO were comparable across all sites, whereas conductivity and salinity were more variable, both between sites and between years, most likely reflecting the extent of the rainfall prior to collection of the water quality samples.

Death & Ekelund (2019) concluded that the Ravensdown Napier discharge was having a localised effect on contaminant concentrations downstream during wet weather events, but that this effect dissipates with increasing distance from the discharge, due to dilution with river water.

4.5 Trend analysis of discharge and receiving environment water quality

4.5.1 Introduction

To identify any significant changes in the quality of the discharge or receiving environment, we undertook a temporal trend analysis of the data collected by Ravensdown as part of their resource consent monitoring requirements. As sampling sites are located upstream and downstream of the discharge and in separate drains that also enter the receiving environment, we were also able to undertake an analysis of spatial trends, along with a consideration of the influence of other inputs to the receiving environment downstream of the Ravensdown discharge point.

4.5.2 Datasets analysed

The parameters analysed for trend analysis are monitored regularly by Ravensdown for compliance. Three different compliance monitoring datasets were analysed. The datasets included monthly discharge monitoring covering the years 2007 – 2020, ambient monitoring datasets covering 2012 – 2020, and rainfall monitoring datasets covering 2014 – 2019. For details on the methodology used for sample collection by Ravensdown refer to Strong (2013). The water quality parameters were separated into three categories: trace metals/elements, nutrients, and other parameters (**Table 1** and **Table 6**). Following conservative principles, when analysing results which were below the detection limit, the values were set at the detection limit. Therefore, if data is always under the detection limit, the resulting trend will be no change.

4.5.3 Trend analysis

The statistical tool Time Trends (version 3.31) was used for the temporal trend analysis (NIWA, 2020) and uses the Seasonal Kendall test to assess the significance of trends over time. The Seasonal Kendall Slope Estimator (SKSE) was used to represent the magnitude and direction of trends in flow-adjusted data. Values of the SKSE were normalised by dividing through by the raw data median to give the relative SKSE (RSKSE), allowing for direct comparison between sites measured as per cent change per year. The RSKSE may be thought of as an index of relative rate of change. A positive RSKSE value indicates an overall increasing trend, while a negative RSKSE value indicates an overall decreasing trend. Trend analysis was undertaken to assess any changes in the concentration of each parameter in the Ravensdown discharge and at the drain/receiving environment sampling sites. Stormwater sampling data for one of the 2018 sampling dates was missing for all parameters.

4.5.4 Categorisation of trends

The approach and reasoning for the categorisation of each trend were based on Scarsbrook (2006), which considered both the statistical significance of the trend and whether or not it was meaningful. A statistically significant trend does not imply a meaningful trend, which is defined as a trend likely to be relevant from a management perspective. A meaningful trend is defined as one in which the RSKSE is statistically significant (P< 0.05) and has an absolute magnitude of change of > 1% per year (which can be either positive or negative). It is recognised that a 1% per year as the meaningful threshold is arbitrary, however, a 1% change per annum corresponds to a 10% change per decade, a 10% change would be detectable within a human lifespan.

Trends were categorised as follows:

- No significant change The null hypothesis for the Seasonal Kendall test was not rejected (P > 0.05). In the following results tables, non-significant trends are shown with an arrow to indicate the direction of the trend (increasing ↑; decreasing ↓; no change →).
- Significant increase/decrease The null hypothesis for the Seasonal Kendall test was rejected (P < 0.05) and the RSKSE value was less than 1% per year. In the following results tables, significant trends are shown with a bold arrow to indicate the direction of the trend (increasing ↑; decreasing ↓; no change →).
- 'Meaningful' increase/decrease The null hypothesis or the Seasonal Kendall test was rejected (P < 0.05) and the RSKSE value was greater than 1% per year. Increasing meaningful trends are indicated in the following results tables by being highlighted in red. Meaningful decreasing trends are indicated in the following results tables by being highlighted in blue.

The focus of our assessment is on trends that are both significant **and** meaningful.

4.6 Results

4.6.1 Temporal trend analysis of discharge quality

The results of the temporal trend analysis of Ravensdown discharge water quality data are summarised in **Table 5**.

Table 5: Summary of trend analysis results for parameters measured in the Ravensdown discharge. Significant trend arrows are in **bold** (non-significant trends are not bold); significant and meaningful <u>increasing</u> trends are highlighted in **red** and significant and meaningful <u>decreasing</u> trends are highlighted in <u>blue</u>.

Parameter	Median value	Р	Mean annual Sen slope	RSKSE (%)	Trend
Copper	0.01	0.01	-0.001	-10.0	$\mathbf{\Psi}$
Zinc	0.048	0.29	-0.001	-2.1	\downarrow
Cadmium	0.001	0.02	<0.001	0.0	→

Parameter	Median value	Р	Mean annual Sen slope	RSKSE (%)	Trend
Chromium	0.006	0.22	<0.001	0.0	\rightarrow
Aluminium	0.232	0.22	0.01	4.3	↑
Sulphur	84.66	0.06	-3.777	-4.5	\downarrow
Flow	2.697	<0.001	0.149	5.5	↑
рН	7.19	0.02	0.011	0.2	↑
Fluoride	4.04	<0.001	-0.241	-6.0	↓
SRP	7.778	<0.001	-0.54	-6.9	$\mathbf{\Psi}$
ТР	8.99	<0.001	-0.754	-8.4	¥
TSS	6.9	<0.001	-0.323	-4.7	¥

Trace metals

Copper showed a significant and meaningful decrease in concentration (Table 5, Figure 4).

Significant trends were detected for cadmium (no change), although this was not meaningful. Aluminium was the only metal that showed an increasing trend, although this trend was not significant or meaningful. Zinc showed a decreasing trend, although this was neither significant nor meaningful. It is evident that the significant trends for both copper and cadmium are influenced by single outliers. However, excluding these outliers did not change the result markedly.

Other parameters

Five of the seven other parameters measured in the Ravensdown discharge showed significant and meaningful trends (**Table 5**; **Figure 4** and **Figure 5**). Flow showed a significant and meaningful increasing trend. This increasing trend reflects the recent change in practice of adding bore water directly to the settling pond as part of the dilution process (H. Hurring, pers. comm. 12 January 2020). The remaining four parameters (fluoride, SRP, TP, TSS) showed significant and meaningful decreasing trends (**Figure 5**). There was no significant relationship between increasing flow and the decrease in concentration over time for any of these parameters, with Pearson's correlation coefficients of 0.013, 0.086, 0.066 and -0.089 for F, SRP, TP and TSS, respectively.

While pH showed a significant increasing trend, this was not meaningful.

The trend in sulphur concentrations was neither significant or meaningful.



Figure 4: Plots showing trends in trace metal concentrations for the Ravensdown discharge. Only significant or near significant trends are presented.



Figure 5: Plots showing trends in measures of other parameters for the Ravensdown discharge. Only significant trends are presented.

4.6.2 Temporal trend analysis of water quality at Ambient condition sampling sites

A summary of the trend analysis results for water quality data collected and analysed monthly for trace metals, nutrients, and other parameters (October 2013 – February 2020) (as per Condition 6h) is presented in **Table 6**. The results of the analysis of all trends are presented in Appendix B.

Table 6: Summary of trace metals and element trends for ambient condition sampling sites. Significant trend arrows are in **bold** (non-significant trends are not bold); significant and meaningful <u>increasing</u> trends are highlighted in **red** and significant and meaningful <u>decreasing</u> trends are highlighted in **blue**. Near-significant trends (p=0.05) highlighted in **orange**.

Site Name	AS1	AS2	AS3	AS4	AS5	AS6	AS7
Parameter/Site location	Upstream of/Adjacent to Plant			Mission Drain	Awatoto Drain (Mixing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)
Aluminium	¥	↑	\downarrow	\rightarrow	\downarrow	↓	\rightarrow
Cadmium	→	→	→	→	\rightarrow	\rightarrow	\rightarrow
Chromium	\rightarrow	\rightarrow	→	\rightarrow	\rightarrow	\rightarrow	\rightarrow
Copper	→	\rightarrow	\rightarrow	\rightarrow	→	\rightarrow	\rightarrow
Nickel	\rightarrow	→	→	→	\rightarrow	\rightarrow	\rightarrow
Zinc	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
Sulphur	¥	\mathbf{A}	↑	↑	Ļ	↑	\rightarrow
Fluoride	\rightarrow	1	↑	↑	\rightarrow	\rightarrow	\rightarrow

Trace metals and elements

There were significant **and** meaningful trends detected in sulphur, fluoride and aluminium concentrations. Sulphur showed two significant and meaningful decreasing trends (AS1 and AS2), and two significant and meaningful increasing trends (sites AS3 and AS4) (**Figure 6**). Two significant and meaningful increasing trends also occurred at sites AS2 and AS3 for fluoride (**Figure 7**). A significant and meaningful decreasing trend was observed for aluminium at site AS6. while there was a near-significant (p=0.05) meaningful trend at AS1 (**Figure 7**).

Cadmium, chromium, copper, nickel, and zinc showed no change trends across all sampling sites (**Table 6**), with some of these trends being significant, although none were meaningful. Site AS5 also showed decreasing trends in aluminium and sulphur, however, these were non-significant. Trends in fluoride concentrations were non-significant at all sites (other than AS2 and AS3.



Figure 6: Plots showing trends in sulphur at ambient condition sampling sites.



Figure 7: Plots showing trends in fluoride and aluminium at ambient condition sampling sites.

A visual summary of the significant and meaningful trends is presented in **Figure 8**. It is evident that sulfur and fluoride concentrations are showing increasing trends at some upstream sites but are decreasing (albeit not significantly) downstream of the discharge, indicating that it is unlikely to be contributing to the increasing (non-significant) trend at the site in the Tūtaekurī Blind Arm. It is also evident that aluminium concentrations are generally decreasing or remaining unchanged at most sites.



Figure 8 Map showing the spatial extent of significant and meaningful trends for sulphur (S), fluoride (F) and aluminium (Al).

<u>Nutrients</u>

Significant and meaningful trends were observed for most nutrients at site AS1 and for SRP and TP and sites AS2 and AS3. All of these sites are upstream the Ravensdown discharge point (**Table 7**, **Figure 9**, **Figure 10** and **Figure 11**). Ammoniacal-nitrogen also showed a near-significant and meaningful decreasing trend (p=0.05) at AS1.

Site AS7 showed a significant but non-meaningful no change trend for ammoniacal nitrogen and total Kjeldhal nitrogen.

For all other sites, non-significant decreasing trends or no change trends were observed for most nutrients.

Table 7: Summary of trends in nutrients for ambient condition sampling sites. Significant trend arrows are in **bold** (non-significant trends are not bold); significant and meaningful <u>increasing</u> trends are highlighted in **red** and significant and meaningful <u>decreasing</u> trends are highlighted in **red** and significant and meaningful trends (p=0.05) are highlighted in **orange**.

Site Name	AS1	AS2	AS3	AS4	AS5	AS6	AS7
Parameter/Site location	Upstream of/Adjacent to Plant			Mission Drain	Awatoto Drain (Mixing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)
Total N	\mathbf{A}	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	1
Ammoniacal Nitrogen	¥	\downarrow	Ļ	\downarrow	Ļ	↓	→
Nitrite-Nitrogen	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
Nitrate-Nitrogen	\mathbf{A}	\rightarrow	\downarrow	\downarrow	\downarrow	\downarrow	\rightarrow
Nitrite/Nitrate- Nitrogen	¥	\rightarrow	Ļ	Ļ	Ļ	↓	\rightarrow
Total Kjeldahl Nitrogen	\rightarrow	\downarrow	\downarrow	↓	\downarrow	\rightarrow	→
Soluble Reactive Phosphorus	≯	→	¥	→	\downarrow	\rightarrow	\rightarrow
Total Phosphorus	$\mathbf{\Psi}$	¥	V	Ļ	Ļ	\downarrow	\rightarrow



Figure 9: Plots showing trends in nutrients at ambient condition sampling sites.



Figure 10: Plots showing trends in SRP at ambient condition sampling sites.



Figure 11: Plots showing trends in TP at ambient condition sampling sites.

A visual summary of the significant and meaningful trends is presented in **Figure 8**. It is evident that most nutrients are showing decreasing trends at all sites other than at the mainstem Tūtaekurī River site.



Figure 12 Map showing the spatial extent of significant and meaningful trends for nutrients measured from ambient samples.

Other parameters

Significant and meaningful increasing trends in conductivity were observed at sites AS2 and AS3, while significant and meaningfully decreasing trends were observed at sites AS1 and AS6 (**Table 9**, **Figure 13**). For salinity, a significant and meaningful decrease was observed at sites AS1, AS5 and AS6, while a significant and meaningful increase was observed at site AS2 (**Figure 14**).

Of the non-significant or meaningful trends, temperature showed increasing trends for all sites except AS2, pH showed no change trends for all sites, dissolved oxygen showed decreasing trends

across all sites, other than at Site AS7, chlorophyll showed no change trends at all sites, and TSS trends were variable across sites.

Table 8: Summary of trends in other parameters for ambient condition sampling sites. Significant trend arrows are in **bold** (non-significant trends are not bold); significant and meaningful <u>increasing</u> trends are highlighted in **red** and significant and meaningful <u>decreasing</u> trends are highlighted in **blue**. Near-significant trends (p=0.05) highlighted in **orange**.

Parameter	AS1	AS2	AS3	AS4	AS5	AS6	AS7
Parameter/Site location	Upstream of/Adjacent to Plant			Mission Drain	Awatoto Drain (Mixing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)
TSS	\downarrow	\rightarrow	1	1	\rightarrow	\downarrow	\rightarrow
Chlorophyll-a	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
рН	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	1
DO	\downarrow	\downarrow	↓	\rightarrow	\downarrow	\downarrow	\rightarrow
Temperature	Ť	Ť	\rightarrow	Ť	Ť	Ť	1
Conductivity	≯	ŕ	ŕ	Ť	\downarrow	≯	۲
Salinity	→	1	Ť	Ť	¥	¥	→


Figure 13: Plots showing trends in conductivity at ambient condition sampling sites.



Figure 14: Plots showing trends in salinity at ambient condition sampling sites.

A visual summary of the significant and meaningful trends is presented in **Figure 15**. It is evident that conductivity and salinity is showing an increasing trend at sites adjacent to the Ravensdown, but a decreasing trend upstream of the plant and downstream of the discharge (other than on the mainstem of the Tūtaekurī River).



Figure 15 Map showing the spatial extent of significant and meaningful trends for conductivity and salinity measured from ambient samples.

4.6.3 Temporal trend analysis of water quality at Rainfall Condition sampling sites

Water quality data collected 6 monthly for trace metals, organic compounds, and other parameters (June 2014 – June 2019) as per Condition 6i, are summarised in **Table 9**. Trend analysis results for all trends are provided in Appendix B.

Trace metals/elements

The only significant and meaningful trend for trace metals and elements was an increasing trend in fluoride concentrations, occurring at sites SWS2, SWS3, and SWS5 (**Table 9**; **Figure 16**).

Significant (but not meaningful) trends were also observed for zinc (decreasing trend SWS2 and SWS3), aluminium (decreasing SWS9), cadmium (no change trend SWS11) and copper (no change trend SWS6).

All other trends were neither significant or meaningful, with most showing no change.

Table 9: Summary of trace metals/element trends for rainfall condition sampling sites. Significant trend arrows are in **bold** (non-significant trends are not bold); significant and meaningful increasing trends are highlighted in **red**.

Parameter	SWS1	SWS2	SWS3	SWS4	SWS5	SWS6	SWS7	SWS8	SWS9	SWS10	SWS11
Parameter/Site location	Upstream of/Adjacent to Plant						Mission Drain	Ravensdov Drain (Mix	vn/Awatoto ing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)
Aluminium	\downarrow	\downarrow	\downarrow	↑	↓	\downarrow	\downarrow	\downarrow	$\mathbf{+}$	\downarrow	1
Cadmium	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	→
Chromium	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
Copper	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	→	\rightarrow	\rightarrow	\rightarrow
Nickel	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\rightarrow
Zinc	↓	¥	¥	\rightarrow	↓	\downarrow	\downarrow	\downarrow	\rightarrow	\downarrow	\rightarrow
Sulphur	↑	↑	↑	↑	1	↑	1	\downarrow	\downarrow	\downarrow	↑ (
Fluoride	1	1	1	↑	1	↑	\downarrow	1	↑	1	\rightarrow



Figure 16: Plots showing trends in metals at rainfall condition sampling sites.

A visual summary of the significant and meaningful trends is presented in **Figure 17**. It is evident that fluoride concentrations have showed an increasing trend at all sites other than on the mainstem of the Tūtaekurī River and the Mission Drain. However, only sites upstream of the discharge show a significant and meaningful increasing trend.



Figure 17 Map showing the spatial extent of trends for fluoride measured from rainfall samples.

<u>Nutrients</u>

The only nutrient that had a significant and meaningful increasing trend was ammoniacal nitrogen (sites SWS5 and SWS6) (**Table 10**; **Figure 18**).

In terms of non-significant or meaningful trends, TN and TKN showed increasing trends between sites SWS1-SWS7, as well as at Site SWS11 and ammoniacal nitrogen also showed increased trends between sites SWS2-SWS7. In contrast, decreasing trends were observed between sites SWS8 and SWS10. SRP showed a decreasing trend between sites SWS1 andSWS6, and an increasing trend between SWS6 and SWS10. There was no change in SRP at SWS11. Total phosphorus showed 4/11 increasing trends (SWS1, SWS4, SWS5, SWS10) and 6/11 decreasing trends (SWS2, SWS3, SWS6, SWS7, SWS8, SWS9). There was no change in total phosphorus at SWS11.

Table 10: Summary of trends in nutrients for rainfall condition sampling. Significant trend arrows are in bold; meaningful trends are highlighted in red (increasing).

Parameter	SWS1	SWS2	SWS3	SWS4	SWS5	SWS6	SWS7	SWS8	SWS9	SWS10	SWS11
Parameter/Site location	Upstream of/Adjacent to Plant					Mission Drain	Ravensdow Drain (Mix	n/Awatoto ing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)	
Total N	↑	1	↑	↑	1	↑	1	\downarrow	\downarrow	\downarrow	↑
Ammoniacal Nitrogen	\downarrow	1	1	1	^	↑	1	↓	↓	↓	\rightarrow
Nitrite- Nitrogen	1	\rightarrow	\rightarrow	\rightarrow	\rightarrow	\downarrow	\rightarrow	↓	\rightarrow	\rightarrow	\rightarrow
Nitrate- Nitrogen	1	\downarrow	\downarrow	\downarrow	\downarrow	↓	1	↓	↓	↓	↑
Nitrite/Nitrate- Nitrogen	1	1	\downarrow	\downarrow	\downarrow	↓	1	↓	↓	↓	↑
Total Kjeldahl Nitrogen (TKN)	1	1	1	1	↑	1	1	↓	↓	↓	↑
Soluble Reactive Phosphorus (SRP)	Ţ	Ļ	Ļ	Ţ	Ļ	Î	Î	↑	Ť	Ť	\rightarrow
Total Phosphorus	↑	Ļ	↓	↑	↑	Ļ	Ļ	\downarrow	\downarrow	1	\rightarrow



Figure 18: Plots showing trends in fluoride and ammoniacal-nitrogen (NH₃-N) at rainfall condition sampling sites.

A visual summary of the significant and meaningful trends in nutrients in rainfall samples is presented in **Figure 19**. It is evident that most sites upstream of the discharge point show an increasing trend, while those downstream show a decreasing or no change trend.



Figure 19 Map showing the spatial extent of trends for ammoniacal nitrogen measured from rainfall samples.

<u>Other parameters</u>

No significant and/or meaningful trends occurred for any other parameters measured as part of rainfall condition sampling (**Table 11**).

In terms of non-significant or meaningful trends, TSS showed increasing trends at sites SWS3 and SWS4 and decreased at all other sites (except SWS11). Sites within the drains upstream/adjacent to the plant and in Mission Drain predominantly showed an increasing trend in pH (6/7). Dissolved oxygen showed increasing trends between sites SWS1 and SWS6, with a shift to decreasing trends between sites SWS7 and SWS10. Temperature trends decreased for 8/11 sites, while sites SWS7, SWS8, and SWS9 all showed increasing trends. Salinity showed a decreasing trend between sites SWS1 and SWS6, with the remaining sites showing an increasing trend. Conductivity showed an increasing trend between SWS1 and SWS7 and SWS9. The remaining 3 sites showed a decreasing trend.

Table 11: Summary of trends in other parameter for rainfall condition sampling sites.

Parameter	SWS1	SWS2	SWS3	SWS4	SWS5	SWS6	SWS7	SWS8	SWS9	SWS10	SWS11
Parameter/Site location	Upstream of/Adjacent to Plant					Mission Drain	Ravensdow Drain (Mix	vn/Awatoto ing zone)	Tūtaekurī Blind Arm	Tūtaekurī River (control)	
TSS	\downarrow	↓	↑	↑	↓	↓	\downarrow	\downarrow	\downarrow	↓	\rightarrow
рН	↑	↑	↑	\rightarrow	↑	1	1	\rightarrow	\rightarrow	↓	1
DO	↑	↑	↑	↑	↑	1	\downarrow	\downarrow	\downarrow	↓	1
Temperature	↓	↓	↓	↓	↓	↓	1	1	1	\downarrow	\downarrow
Conductivity	1	1	1	1	1	1	1	\downarrow	↑	\downarrow	\downarrow
Salinity	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\downarrow	\uparrow	1	1	1	1

4.7 Summary and Conclusions

A summary of our analysis of water quality state (between 2013 and 2019) and trends is presented below.

Discharge quality

• There has been a very high level of compliance of the quality of the discharge for all consent conditions.

Metals/Metalloids

- Nickel concentrations were elevated in the mixing zone when compared with upstream or downstream but were well below the ANZG³ under both ambient and wet weather conditions.
- Under ambient conditions cadmium concentrations at upstream sites were considerably higher than downstream of the discharge, but were below the ANZG.
- Cadmium concentrations within the mixing zone were elevated compared to upstream and exceeded the ANZG under wet weather conditions only.
- Copper concentrations were slightly elevated within the mixing zone (when compared with upstream) under ambient conditions and exceeded the ANZ guideline for protection of 95% of species, but were within the guideline for protection of 90% of species.
- Under wet weather conditions, copper concentrations at all sites except the mainstem of the Tūtaekurī River were comparable and exceeded the ANZG.
- Chromium concentrations exceeded the ANZG under both ambient and wet weather conditions at all sites except the mainstem of the Tūtaekurī River.
- Zinc concentrations exceeded the ANZG within the mixing zone and Tūtaekurī Blind Arm sites under ambient conditions. However, sites upstream of the discharge exceeded the guideline for protection of 80% of species (rather than 95%).
- Under wet weather conditions, zinc concentrations exceeded the ANZG at all sites except the mainstem of the Tūtaekurī River.
- However, there has been no overall change in nickel, cadmium, copper, chromium or zinc concentrations at any site under ambient conditions throughout the monitoring period. Similarly, there has no overall change in nickel, cadmium, copper or chromium under wet weather conditions, whereas there has been a general decrease in zinc concentrations at most sites.
- Aluminium concentrations were elevated under ambient conditions within the mixing zone, compared with upstream or downstream. However, all sites other than the mainstem of the Tūtaekurī River exceeded the ANZG.
- Under ambient conditions, there has been a non-significant decreasing trend in aluminium concentrations within the mixing zone and a significant decreasing trend immediately downstream of the mixing zone.

³ ANZ (2018) guideline for protection of 95% of species, unless otherwise stated.

- Under wet weather conditions, upstream aluminium concentrations were generally higher than within the mixing or downstream. However, concentrations at all sites exceeded the ANZG.
- There has been a general decrease in aluminium concentrations at most sites under wet weather conditions, although increasing trends have occurred at one upstream site and also on the mainstem of the Tūtaekurī River.
- Fluoride concentrations were highly elevated in the Mission Drain under ambient conditions (compared with all other upstream sites), which was reflected in elevated concentrations at downstream sites.
- Under ambient conditions sulphur concentrations were elevated at all sites (i.e. upstream and downstream of the discharge) other than on the mainstem of the Tūtaekurī River.
- Under wet weather conditions, fluoride and sulphur concentrations were elevated in the mixing zone when compared with upstream and downstream sites.
- There has been an increase in fluoride concentrations upstream of the discharge under ambient conditions, while concentrations downstream have generally decreased or not changed.
- Under ambient conditions, the trends in sulphur concentrations have been variable, with both increases and decreases at upstream and downstream sites. There has been a general decrease within the mixing zone.
- Under wet weather conditions fluoride concentrations have generally increased at all sites other than Mission Drain and the mainstem of Tūtaekurī River, although this trend was only meaningful at upstream sites.
- Sulphur concentrations have generally increased at upstream sites under wet weather conditions, but have decreased at most sites downstream of the discharge.

Nutrients and other parameters

- Ambient ammoniacal nitrogen, total nitrogen and total phosphorus concentrations at all sites other than the mainstem of the Tūtaekurī River exceeded the ANZG.
- Under wet weather conditions, ammoniacal nitrogen, total nitrogen, total phosphorus and soluble reactive phosphorus were elevated in the mixing zone and Tūtaekurī Blind Arm, compared with upstream sites.
- All nutrients showed trends to decreasing concentrations across all survey sites under ambient conditions, with significant trends at some upstream sites.
- Under wet weather conditions, all sites upstream of the discharge showed trends to increasing ammoniacal nitrogen concentrations, whereas sites downstream of the discharge decreased or remained unchanged. Trends in concentration of other nutrients was more variable under wet weather conditions.
- Ambient nitrate and total suspended sediment concentrations were elevated upstream compared with downstream.
- Ambient nitrite concentrations were elevated within the mixing zone compared with other sites.
- Other parameters were comparable amongst sites under ambient and wet weather conditions, other than chlorophyll a, which was elevated upstream compared with downstream of the discharge.

Conclusions

Concentrations of some metals exceed guideline values both upstream and downstream of the Ravensdown discharge under wet weather conditions. In addition, concentrations of some metals are higher at upstream sites than within the mixing zone or downstream under ambient conditions. This indicates that sources other than the Ravensdown discharge are also contributing to downstream metal concentrations.

For fluoride, sulphur and some nutrients, average concentrations downstream of the discharge are higher than upstream sites under wet weather conditions, indicating that the discharge may be contributing to short-term effects associated with these events.

5. Mixing zone dye study

Mike Stewart and Rebecca Eivers

5.1 Introduction

Our initial gap analysis (Phillips et al., 2020) identified the need for further quantification of the dilutions achieved in the receiving environment during discharge from the settling pond. A dye study was undertaken to provide a quantitative estimate of dilutions achieved at different stages of the tidal cycle, under the base flow discharge rate from the settling pond. As the present discharge conditions from the Ravensdown settling pond are not linked to specific hydrological conditions in the receiving environment, i.e. high/low tide, the extent of mixing of the discharge is unclear. The dilutions achieved from the dye study will also be used in other areas of the assessment of environmental effects, specifically, the risk assessment of discharged process chemicals, and the whole effluent toxicity assessment.

5.2 Methods

The dye study was undertaken from 29th March 2021 to 31st March 2021 under HBRC resource consent AUTH-126648-01. The general approach was for the dye to be pre-mixed, added to the settling pond, and allowed to mix before being discharged to the Awatoto Drain.

The settling pond has a capacity of $1500m^3$ and as at 3pm on 29^{th} March 2021 was 80% full, equating to a pond volume of $1200m^3$. The resource consent stipulates a maximum pond concentration of 400ppb (400µg/L). Based on a volume of $1200m^3$ (1,200,000L) the amount of dye required to provide a target concentration of 400ppb was 480g.

Prior to dye application, a sample of pond water (2L) was taken and provided to NIWA Hamilton Water Quality Laboratory to correct for background matrix effects (which can reduce the dye fluorescence) on the pond dye concentrations. Similarly, prior to each discharge scenario being undertaken (see Sections 5.2.1 and 5.2.2), samples of water in the Awatoto Drain were taken to correct for background matrix effects on dye concentrations in the receiving environment.

At 3pm on 29th March, rhodamine dye (Bright Dyes[®] FWT Red Powder, Product Number 105403, Kingscote Chemicals) (480g) was transferred to a barrel (100L) and pond water added to dissolve the dye. Buckets (10L) of the dye concentrate were distributed around the pond. The barrel was rinsed repeatedly, and the rinse water added to the pond until the remaining barrel water was very faint pink. Dye addition to the settling pond was completed at 5.30pm. The dye was left to disperse overnight with the aid of the recirculation pump (running at 1.35L/s) and an easterly wind. At 9:00am on 30th March (15.5 hours after dye addition) the pond appeared uniform red (**Figure 20**) and red water was exiting the hose of the recirculation pump.



Figure 20. Ravensdown discharge pond taken from discharge pump station at 9am on 30th **March 2021.** The bucket contains water collected from the recirculation pump discharge at approximately 400ppb dye concentration.

Two discharge mixing scenarios were investigated. The first was around 1 hour prior to low tide and the second around 1 hour prior to high tide. Under each scenario, the dyed pond water was pumped at a flow of 20L/s using the auxiliary (baseflow) discharge pump. For each scenario, the Awatoto Council pump was turned off 1 hour prior to discharge and remained off for the duration of each study. The low tide discharge scenario was undertaken from 1-2pm on 30th March 2021, using c. 75,000L of pond water from start to finish. It should be noted that following addition of the dye, further dilution water from the Ravensdown site continued to be added the pond (to avoid upstream flooding of the plant), slightly increasing the overall pond volume. The rate of flow or volume was unfortunately unquantifiable but described as "very low" (pers. comms. Ravensdown Operations staff). The overall effect was a reduction in dye concentration in the pond compared with the original dye application. To maintain a consistent dye concentration for the duration of our study, a further 40g of rhodamine dye was added to the pond at 4pm on 30th March 2021, 2 hours after completion of the low tide scenario and 17 hours prior to collection of samples under the high tide scenario.

Samples were collected at 7 sampling points of 15 m intervals down the Awatoto Drain from 0-90m corresponding with the mixing zone as defined in the existing consent. Sampling points commenced at the confluence of the Ravensdown Drain and the Awatoto Drain (0m - A1) and ended at the approximate boundary of the current mixing zone (90m - A7) (**Figure 21**). Samples

were taken from the middle of the channel using a 'Mighty Gripper' sampling pole. During low tide, samples were collected from the surface only. During high tide, samples were collected from the surface and from 500 mm below the surface (subsurface). Samples were kept in the dark and transferred as soon as practical to chilly bins and ice added. Samples were delivered to NIWA Hamilton Water Quality laboratory on the afternoon of 31st March 2021 for analysis of rhodamine dye concentrations.

Samples were filtered through 0.2 μ m membrane filters prior to measurement. Rhodamine standard solutions were prepared by diluting a Rhodamine WT stock solution with "background" water (water collected either prior to addition of Rhodamine WT to the settling pond or from Awatoto Drain prior to discharge) to allow for the matrix effects described earlier. Standards and samples were measured on a Varian Cary Eclipse spectrofluorometer (excitation wavelength 558 nm, emission wavelength 583 nm) and Rhodamine WT concentrations were determined from the standard curve.



Figure 21 Location of Ravensdown settling pond and discharge, Ravensdown Drain, sampling points (A1-A7) along Awatoto Drain, and the Blind Arm of the Tūtaekurī River. The end of the current consented mixing zone is shown by the blue line.

5.2.1 Low tide scenario

Low tide was predicted to be at 1:38pm on 30th March 2021⁴, however a lag of around 30min was known to occur between the predicted tide and the actual low tide at the staff gauge at the confluence of the Ravensdown drain and the Awatoto drain Awatoto Stream (Site 0m: **Figure 21**).

⁴ <u>https://tides.niwa.co.nz/?latitude=-39.556&longitude=176.922&startDate=2021-03-29&numberOfDays=3</u>

Prior to discharge, a receiving environment sample (2L) was collected at 12:35pm, to provide a baseline sample to assess matrix effects as described previously. A sample of the dyed settling pond water was also taken from the pump house at 12:55pm.

The auxiliary (baseflow) discharge pump was started at 1:00pm and the progress of the discharge plume followed. Samples were collected at the surface, with results and discussion presented in Section 5.3.1.

5.2.2 High tide scenario

High tide was predicted to be at 8:17am⁴ on 31st March 2021. Prior to discharge, a receiving environment sample (2L) was collected at 8:00am to provide a baseline sample to assess matrix effects.

A sample of the dyed settling pond water was taken from the pump house at 7:55am. The auxiliary (baseflow) discharge pump was started at 8:00am and the progress of the discharge plume followed visually. As dilutions were expected to be much higher than at low tide and the plume progress more difficult to follow, apples were added at various points down the Ravensdown Drain and at the confluence point in the Awatoto Drain (A1) to track the progress of the discharge plume. This allowed for an alternative and complementary method to visual observations the dyed plume and ensured more accurate tracking of the discharge as it moved down the mixing zone.

Samples were collected as the surface and 500mm below the surface (subsurface), with results and discussion presented in Section 5.3.2.

5.3 Results and discussion

The results from the NIWA laboratory analysis are presented in Appendix C.

5.3.1 Low tide scenario

The discharge was started approximately 45-60 mins prior to low tide. At this time and for the duration of the discharge (total of 62 minutes), the tide was going out or had reached low tide. There was little hindrance to the discharge plume as it progressed through the drain network.

Initially the red dye colour was not apparent in the Ravensdown Drain, however the progress of the discharge could be monitored by the appearance of suspended particulate matter due to physical disturbance of the stream bed and banks by the discharge as it progressed through to Awatoto Drain.

Sample collection was initiated at the confluence of Ravensdown Drain and Awatoto Drain (A1) 15 minutes after the discharge began and samples were collected along the 7 sampling points (approximately 3 minutes between sites), tracking the discharge plume with the aid of floating apples (run 1) for a total run time of 18 minutes (**Figure 22**). By 1:30 pm the red/brown colour was becoming more apparent in the Awatoto Drain (see **Figure 23**). A second round of sampling was undertaken, also tracking the discharge flow with apples (Run 2), giving the same total run time of 18 minutes. Given the same run times for each sampling round, we are confident that the

discharge scenario was run at low tide. For the duration of the discharge, the plume progressed down the middle of the channel in Awatoto Drain from sampling site A1 to A7.



Figure 22. Collection of a surface water sample using the Mighty Gripper pole, being guided by the progress of the 'pink apple' floating with the discharge plume (dark red/brown colour) down the mixing zone.



Figure 23: Awatoto Drain at sampling site A2 at low tide showing red dye. Photo taken at 13:46 on 30th March 2021.

Dye concentrations for the low tide scenario and dilutions at each sample point are presented in **Table 12** and dilutions in **Figure 24**. The dilution is calculated as the dye concentration of the pond (taken at the time of discharge starting) divided by the concentration at each sample point. The pond dye concentration was 223 μ g/L, approximately 56% of the target pond dye concentration of 400 μ g/L. It is conceivable that the pond had not fully mixed prior to discharge, or the pond volume values provided by Ravensdown was too low (by a factor of around 2-fold). Nonetheless, the pond dye concentration was taken at the source of discharge pump, therefore remains relevant for the study. Calculated dilutions in the receiving environment are based on 223 μ g/L, not the target pond concentration of 400 μ g/L.

In Run 1 dilutions ranged from 4.2-fold at A1 to 17.8-fold at A4, with an average dilution of 11.5fold. At A7 (mixing zone boundary) the dilution was 8.4-fold. In Run 2 the dilutions were less variable across the sampling points ranging from 1.7-fold (A2) to 2.8-fold (A7). During run 2 there was a general increase in dilutions from the confluence (A1) to the end of mixing zone (A7). The reasons for this are not clear, however this may be a function of channel widening as it progresses from A1 to A7 causing more dispersion and therefore dilution across the channel.

Sampling point/Run	Time collected	Time after discharge started (min)	Dye concentration (µg/L)	Dilution
Pond	12:55	0	223.0	1.0
		Run	1	
A1	13:15	15	52.6	4.2
A2	13:18	18	24.9	9.0
A3	13:21	21	14.8	15.1
A4	13:24	24	12.5	17.8
A5	13:26	26	13.9	16.0
A6	13:29	29	22.4	10.0
A7	13:32	32	26.7	8.4
		Run	2	
A1	13:44	44	124.0	1.8
A2	13:47	47	135.0	1.7
A3	13:50	50	126.0	1.8
A4	13:53	53	99.9	2.2
A5	13:56	56	98.2	2.3
A6	13:59	59	88.1	2.5
A7	14:02	62	80.9	2.8

Table 12: Rhodamine dye concentrations and dilutions for the low tide discharge scenario.



Figure 24: Dilutions of Run 1 (top) and Run 2 (bottom) at sampling points A1 to A7 in the Awatoto Drain at time after discharge for low tide scenario.

5.3.2 High tide scenario

The discharge was started at approximately 60 mins prior to high tide. For the first hour the tide was incoming with the highest water level reached around 9:00am. After this time, the flow turned and started flowing downstream towards the Blind Arm of the TTūtaekurī River. Once again, we conducted 2 runs, with the turning of the tide coinciding with the start of Run 2. During the first hour of the discharge, while the tide was rising, there was significant hindrance to the discharge plume as it progressed through Ravensdown Drain and into Awatoto Drain (see **Figure 25**). Nevertheless, downstream flow was evident. Unlike the low tide scenario, there was no evidence of particulates being stirred up by the discharge, so the plume was again tracked by floating apples. Water chemistry measurements were also taken continuously at the confluence (site A1) using a YSI Professional Plus handheld multiparameter meter (Yellow Springs Instruments, Ohio, USA) where changes in temperature, conductivity, and salinity indicated the 'arrival' of the discharge plume. Water temperature in the settling pond water was around 2°C cooler than the receiving environment.



Figure 25: Ravensdown Drain just prior to high tide and 28 minutes after discharge started. Photo taken at 8:28am on 31^{st} March 2021.

Sample collection was initiated at the confluence of Ravensdown Drain and Awatoto Drain (A1) an hour after the discharge began and samples were collected along the 7 sampling points, tracking the discharge flow with the aid of floating apples (Run 1), with a total run time of 20

minutes. As for the low tide scenario, the red/brown colour became more apparent in the Awatoto Drain over time. A second sampling was undertaken at the same sampling points, also tracking the discharge flow with apples (Run 2), with a total run time of 13 minutes. The second run (13 minutes) was significantly shorter than the first run (20 minutes), supporting the increase in flow of outgoing tide. As for the low tide scenario, the plume progressed down the middle of the Awatoto Drain channel.

Dye concentrations for the high tide scenario and dilutions at each sample point are presented in **Table 13** (surface samples) and **Table 14** (subsurface samples) and concentrations in **Figure 26**. The pond dye concentration was 159 μ g/L, approximately 40% of the target pond dye concentration of 400 μ g/L. This was a decrease from the low tide pond concentration, despite the addition of a further 40g of dye the night before the discharge.

During Run 1 dilution ranged from 5.6-fold (A3) to 14.9-fold (A7) at the surface, with an average dilution of 10.1-fold. During Run 2 dilutions at the surface ranged from 2.1-fold (A1) to 4.9-fold (A7), with an average of 3.2-fold (**Table 13**).

Conversely, for subsurface samples, during Run 1, there was no evidence of dye present at 6 out of the 7 sampling points, with dye concentrations of <1.0 μ g/L. Sampling point A3 had a dye concentration of 2.5 μ g/L, and corresponding dilution of 64-fold (**Table 14**). During Run 2 there was evidence of some vertical mixing, with subsurface dilutions of between 51-fold and 114-fold between A1 and A3. From A4-A7, there was no evidence of vertical dye mixing with all dye concentrations <1.0 μ g/L (**Table 14**).

The dye concentration results clearly show that – under high tide conditions – the majority of the discharge travels at the surface with minimal or non-existent vertical mixing to subsurface, even after nearly 2 hours of discharge. There was some visual evidence that vertical mixing was starting to occur at the head of Awatoto Drain but this was minimal compared with the discharge volumes at the surface. This also shows that complete mixing was not reached under the high tide scenario in the first 2 hours after discharge.

Sampling point/Run	Time collected	Time after discharge started (min)	Dye concentration (µg/L)	Dilution			
Pond	7:55	0	159	1.0			
		Run 1					
1	9:00	60	26.8	5.9			
2	9:02	62	22.3	7.1			
3	9:07	67	28.2	5.6			
4	9:12	72	14.4	11.0			
5	9:15	75	12.4	12.8			
6	9:17	77	12.1	13.1			
7	9:20	80	10.7	14.9			
Run 2							
1	9:36	96	75.5	2.1			

Table 13: Rhodamine dye concentrations and dilutions for surface samples for high tide discharge scenario.

Sampling point/Run	Time collected	Time after discharge started (min)	Dye concentration (µg/L)	Dilution
2	9:38	98	71.4	2.2
3	9:41	101	68	2.3
4	9:44	104	50.9	3.1
5	9:45	105	44.7	3.6
6	9:47	107	39.9	4.0
7	9:49	109	32.4	4.9

Table 14. Rhodamine dye concentrations and dilutions for subsurface samples for high tide discharge scenario.

Sampling point/Run	Time collected	Time after discharge started (min)	Dye concentration (µg/L)	Dilution				
Pond	7:55	0	159	1				
	Run 1							
1	9:00	60	<1.0					
2	9:02	62	<1.0					
3	9:07	67	2.5	63.6				
4	9:12	72	<1.0					
5	9:15	75	<1.0					
6	9:17	77	<1.0					
7	9:20	80	<1.0					
		Run 2						
1	9:36	96	3.1	51.3				
2	9:38	98	1.9	83.7				
3	9:41	101	1.4	113.6				
4	9:44	104	<1.0					
5	9:45	105	<1.0					
6	9:47	107	<1.0					
7	9:49	109	<1.0					



Figure 26: Dye concentration (μ g/L) at sampling points A1 to A7 in the Awatoto Drain at time after discharge for high tide scenario.

5.4 Conclusions

Under the low tide discharge scenario, the discharge plume was observed to progress down the centre of the Awatoto Drain. Dilutions in surface water along this drain were initially around 10-fold, however over time, dilutions reduced and stabilised to around 2-fold. At the boundary of the currently consented mixing zone (90m, sampling site A7), dilution after 62 minutes of continuous discharge was 2.8-fold. The shallowness of the Awatoto Drain and the observation of particulates being stirred up by the discharge plume provides evidence that the plume was well mixed vertically under the low tide scenario.

Under the high tide discharge scenario, the discharge plume was again observed to progress down the centre of the Awatoto Drain, consistent with the low tide scenario. Dilutions in surface water along Awatoto Drain were initially around 10-fold, virtually the same as for the low tide scenario. Over time, dilutions reduced and stabilised to around 3.2-fold. At the end of the mixing zone (90 m, sampling site A7), dilution at the surface was 4.9-fold after 109 minutes of discharge. There was little evidence for vertical mixing of the plume under the high tide scenario and the dye remained primarily at the surface.

6. Risk Assessment of Process Chemicals

Mike Stewart and Kendall Leitch

6.1 Introduction

Ravensdown use nine process chemicals as part of the operation of the plant (**Table 15**). Uses are varied and include:

- oxygen scavenger;
- corrosion inhibitor;
- deposit and fouling control agent;
- biocide;
- pH modifier/alkalinity builder, and;
- boiler water treatment.

A simplified site plan for the process chemicals is shown in **Figure 27**. Four process chemicals are used in the boiler, while five are used in the cooling system. Furthermore, Sandford Transport wash their trucks off-site, with the resulting wastewater entering the stormwater drain on the Ravensdown site, which ultimately enters the settling pond.

Table 15: Information on process chemicals used at Ravensdown fertiliser manufacture plant at Awatoto, Napier. Source: Ravensdown Awatoto

Formulation	Use	Area used
Cortrol OS7780	Water based dissolved oxygen scavenger / metal passivator	Boiler
Optisperse ADJ5150	Alkalinity builder	Boiler
Solus AP24	Internal boiler water treatment	Boiler
Steammate NA0880	Blend of neutralising amines	Boiler
Flogard MS6222	Water based corrosion inhibitor	Cooling system
Gengard GN8020	Deposit and fouling control agent	Cooling system
Inhibitor AZ8104	Water based corrosion inhibitor	Cooling system
Spectrus BD1500	Water based deposit control agent	Cooling system
Spectrus NX1100	Biocide	Cooling system
Road Film Remover	Fleet wash (Sandfords)⁵	Sandfords truck wash
XT88	Replacement for Road Film Remover (Sandfords)	Sandfords truck wash

Many of the chemicals contained within each formulation are not "traditional" contaminants (such as nutrients, metals, and organic toxicants like polycyclic aromatic hydrocarbons (PAHs)). Important distinctions between "traditional" contaminants and process chemicals are:

 $^{^{5}}$ After the initial results of the risk assessment were communicated, Sandfords have ceased the use of Road Film Remover and replaced it with another formulation, XT88.

- "traditional" contaminants are measured by virtually all analytical laboratories using standard and often validated methods, while most of the chemicals within the process chemical formulations are not;
- "traditional" contaminants are measured routinely in the settling pond discharge (water) and the receiving environment (water, with sediment analyses every 4 years), while (due to lack of analytical capabilities) process chemicals are not.

However, process chemicals may enter the settling pond, from where they may be discharged to the marine receiving environment, potentially leading to adverse ecological effects. A risk assessment procedure that is different to that used for "traditional" contaminants is needed for the process chemicals. A risk assessment of each process chemical formulation was undertaken using the methodology in Section 6.2. Results are discussed in Section 6.3. Formulation and individual chemical data are provided in Appendix D



Figure 27: Simplified site plan for process chemicals used at Ravensdown fertiliser manufacture plant at Awatoto, Napier.

6.2 Methods

6.2.1 Identification of process chemical formulations used at Ravensdown Napier

Ravensdown provided Safety Data Sheets (SDS) for each formulation used at the plant. Some of the formulations used at the plant have chemicals contained within that are proprietary and therefore commercially sensitive. Ravensdown and SEL have signed a non-disclosure agreement (NDA) with Suez Water Technologies. The result of this NDA is that SEL have acquired information to undertake a robust risk assessment, however, we cannot report on the identity of specific chemicals covered by the NDA. For these restricted proprietary chemicals, generic codes are used in this report. For chemicals not covered by an NDA, unique chemical identifiers are reported.

For each formulation, where possible, the following physical and chemical properties were obtained:

- form (liquid or solid);
- water solubility (miscible or immiscible);
- pH (as supplied);

6.2.2 Identification of individual chemical information within each formulation

Information obtained for each individual chemical within a formulation was:

- composition in the formulation (weight %);
- CASRN (Chemical Abstracts Registry Number unique identifier for each chemical);
- chemical formula/structure;
- molecular weight;
- bioaccumulation concentration factor (BCF) (at pH 5.5 and pH 7.4).

6.2.3 Identification of ecotoxicological effects

Ecotoxicological information was sourced from up to two⁶ international ecotoxicology databases, using the unique chemical identifier (CASRN). These were:

- 1. The European Chemicals Agency (ECHA)⁷ information on chemicals database, extracting the lowest predicted no-effects concentration (PNEC) for marine water.
- 2. The NORMAN⁸ Ecotoxicology Database, extracting the lowest PNEC for marine water.⁹

ECHA provide marine PNECs for many chemicals, and as the process for derivation of PNEC is completely transparent these were used as priority PNECs over NORMAN PNECs. However, PNEC data were unavailable for some process chemicals from ECHA. Furthermore, for some chemicals

⁶ The ECHA databased was searched first and if no PNEC was supplied, NORMAN was then searched.

⁷ <u>https://echa.europa.eu/information-on-chemicals</u>

⁸ NORMAN is a network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances. NORMAN has a membership of more than 70 leading laboratories and authorities across Europe and North America.

⁹ <u>https://www.norman-network.com/nds/ecotox/lowestPnecIndex.php</u>

ECHA did not provide a PNEC but stated that "aquatic toxicity unlikely" or "no hazard identified" (see Appendix D). No further database searching was undertaken in these cases.

Lowest NORMAN PNECs were either predicted by Quantitative Structure Activity Relationship (QSAR) or obtained experimentally and voted on by NORMAN ecotoxicology experts. Lowest PNECs are used primarily for prioritisation purposes. NORMAN states that most of the lowest PNECs have been derived for freshwater. As there are likely to be differences in effects of freshwater and marine species in terms of responses to EOCs, conversion of freshwater PNECs to marine PNECs is required. The lowest PNEC for marine water is calculated by dividing the lowest PNEC for freshwater by 10.

Finally, some chemicals are acids (low pH) or bases (high pH). As it is a consent condition that the settling pond cannot be discharged when pH is outside the range 6.5 - 8.5, there is pH control of these chemicals. Therefore, they were excluded from the risk assessment.

6.2.4 Risk assessment

Statement on conservative methodology

A worst-case scenario was used which assumes conservation of all process chemicals. This assumes that all the process chemicals used enter into the settling pond, with no degradation or evaporation (of any volatile chemicals), unless there are specific data to support this. It is noted that this may over-estimate the ecological risk, however, is considered most prudent in the absence of degradation data (for most process chemicals) and the inability to measure most of the process chemicals in the pond or receiving environment (due to lack of accredited laboratory methods).

The intention of this risk assessment is to be incorporated into a weight of evidence approach for the ecological effects assessment. Another important aspect is that it highlights process chemicals used that are of high potential ecological risk, so that management procedures may be undertaken to replace this (or these) formulations with more benign alternatives.

<u>Methodology</u>

The risk assessment was undertaken using a tiered approach.

- 1. A highly conservative worst-case settling pond concentration of each chemical within each formulation was calculated through mass balance.
- 2. An assessment was made of the worst-case scenario settling pond concentration against the lowest ecotoxicological guideline (PNEC) for any individual chemical within each formulation by calculating a risk quotient. The risk quotient (RQ1) was calculated by dividing the settling pond concentration by the ecotoxicological guideline concentration, with a value >1 indicating a potential ecotoxicological effect. The RQ also indicates the dilution required to reduce the concentration of the chemical to below ecotoxicological guidelines.
- 3. Where RQ1 was >1, the dilution outside the mixing zone was calculated from a rhodamine dye study undertaken in 2006 (Bioresearches, 2006), and an updated risk quotient (RQ2) calculated.

4. Where RQ2 was >1, the potential for long-term effects involving persistence and/or bioaccumulation within the receiving environment was also assessed by reference to (a) biodegradation data and (b) a bioaccumulation concentration factor (BCF).

Worst-case settling pond concentration scenario (RQ1)

A mass balance calculation was undertaken to provide the worst-case scenario formulation concentration in the settling pond. The formula used was:¹⁰

settling pond formulation worst-case concentration $\left(\frac{mg}{L}\right) = \frac{Formulation \, usage\left(\frac{mg}{day}\right)}{settling \, pond \, discharge \, volume\left(\frac{L}{day}\right)}$

The worst-case scenario assumes that the concentration in the settling pond is then discharged to the marine receiving environment without further dilution. Usage rates were provided by Ixom for June 2019 to May 2020. Average pond discharge (L/day) was calculated from June 2019 to May 2020 based on total weekly discharge data provided by Ravensdown.

Assessment of worst-case settling pond concentration against lowest ecotoxicological guideline

The ecotoxicological guideline (e.g. PNEC) was adjusted for each individual chemical in a formulation using the formula:

Adjusted ecotoxicological guideline $\left(\frac{mg}{I}\right)$

 $= \frac{Lowest \ ecotoxicological \ guideline \ for \ individual \ chemical \ \left(\frac{mg}{L}\right)}{proportion \ of \ formulation \ (\%)}$

The risk quotient (RQ1) (dilution of each chemical required to meet the lowest ecotoxicological guideline) was calculated by:

> RQ1 = settling point formulation "worst-case" concentration (mg/L)/Adjusted¹¹ ecotoxicological guideline (mg/L)

Where RQ1 <1 (i.e. the concentration being discharged from the settling pond is below the lowest ecological guideline), the chemical (and therefore formulation) is flagged as "no ecological risk". No further analysis is undertaken. This needs to be valid for <u>all chemicals</u> assessed within each formulation.

Where RQ1 >1 (i.e. the concentration being discharged from the settling pond is above the lowest ecological guideline), the chemical (and therefore formulation) is flagged as "potential ecological risk". This needs to be valid for at least one chemical assessed within each formulation. For each chemical with RQ1 >1, calculation of the dilution required within the mixing zone was undertaken.

¹⁰ The usage rate was calculated as kg/day, so a correction factor (1,000,000) was used to convert to mg/day.

¹¹ The PNEC for each chemical is adjusted for the proportion in the formulation. For example, if the chemical is present at 10% of the formulation, the PNEC is increased 10-fold (PNEC/0.1).

Dilution required within mixing zone (RQ2)

Dilution of the settling pond discharge in the receiving environment was calculated using dilutions achieved in the mixing zone under a low tide and a high tide discharge scenario (see Section 5). Each process chemical with RQ>1 had a receiving environment dilution applied at the boundary of the mixing zone to assess whether receiving environment concentrations may lead to adverse effects, which is indicated by RQ2 > 1. We note that, for the high tide discharge scenario, this calculation was undertaken for dilutions at the surface as the discharge plume did not mix vertically. This is discussed in more detail in Section 5.

Environmental fate (RQ2 > 1)

Formulation biodegradation data were obtained, where available, from the ECHA database.

The bioaccumulation concentration factor (BCF) was calculated for each chemical. US EPA^{12} define a chemical with BCF <1000 as having a low bioaccumulation potential. $ECHA^{13}$ define a chemical as fulfilling the bioaccumulation criterion when BCF >2000. Following the most conservative approach, a BCF >1000 was used for assessment.

Tables of risk assessment calculations for each formulation are presented in Appendix D.

6.3 Results and discussion

6.3.1 Cortrol OS7780

Cortrol OS7780 is a water based dissolved oxygen scavenger/metal passivator used in the boiler (**Figure 27**). Cortrol OS7780 is applied at an average rate of 3.07 kg/day. The formulation has a pH of 7.5.

There are six components of Cortrol OS7780, not including water (Appendix D). Five components are restricted under an NDA and are given generic codes. The six components are:

- Hydroquinone (2.5% by weight: CASRN 123-31-9).
- Cort1 (0.024% by weight: CASRN restricted).
- Cort2 (0.008% by weight: CASRN restricted).
- Cort3 (0.01% by weight: CASRN restricted).
- Cort4 (0.0001% by weight: CASRN restricted).
- Cort5 (0.004% by weight: CASRN restricted).

All six components have the required chemical information (CASRN) to assess risk.

A potential ecological risk was identified for hydroquinone (RQ1 = 3340) and Cort2 (RQ1 = 1.5). The high RQ1 for hydroquinone is based primarily on a very low marine PNEC of 0.000057 mg/L. However, the boiler process converts hydroquinone to 1,4-benzoquinone in quantitative yield

¹² US EPA Sustainable Futures / P2 Framework Manual 2012 EPA-748-B12-001 Chapter 5. Estimating Physical / Chemical and Environmental Fate Properties with EPI Suite™.

¹³ ECHA Report. Guidance on Information Requirements and Chemical Safety Assessment Part C: PBT/vPvB assessment Version 3.0 June 2017.

(i.e. 100% conversion). 1,4-benzoquinone has a reported marine PNEC of 0.0136 mg/L (NORMAN), leading to a calculated RQ1 of 14.

As RQ1 for at least one chemical in the formulation (hydroquinone/1,4-benzoquinone RQ1 = 14 and Cort2 RQ1 = 1.5) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.2 Optisperse ADJ5150

Optisperse ADJ5150 is an alkalinity builder used in the boiler (Figure 27). It is applied at an average rate of 0.85 kg/day. The formulation has a pH of 14, so is highly alkaline.

There are two components¹⁴ of Optisperse ADJ5150, not including water (Appendix D). One component is restricted under an NDA and has been given a generic code. The two components are:

- Sodium hydroxide (25% by weight, CASRN 1310-73-2).
- ADJ1 (0.5% by weight, CASRN restricted).

Neither component presented a potential ecological risk. Risk from sodium hydroxide is covered by the consent condition of pH control and ADJ1 is a common salt in seawater. Therefore, no further assessment was undertaken.

6.3.3 Solus AP24

Solus AP24 is used in internal boiler water treatment (**Figure 27**). It is applied at an average rate of 1.42 kg/day. The formulation has a pH of 12.3, so is highly alkaline.

There are four components 14 of Solus AP24, not including water (Appendix D). All four components are restricted under an NDA and have been given a generic code. The four components are:

- Sol1 (0.84% by weight, CASRN restricted).
- Sol2 (0.25% by weight, CASRN restricted).
- Sol3 (16.0% by weight, CASRN restricted).
- Sol4 (0.49% by weight, CASRN restricted).

Sol2 had an ECHA classification that "aquatic toxicity was unlikely" and no NORMAN PNEC available. Sol3 had no PNEC data available, so an assessment could not be undertaken.

Sol1 and Sol4 had calculated RQ1 of 0.01 and 0.02, respectively, so presented a negligible ecological risk. Therefore, no further assessment was undertaken.

 $^{^{\}rm 14}$ Ingredients making up a total of <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

6.3.4 Steammate NA0880

Steammate NA0880 is a blend of neutralising amines used in internal boiler water treatment (**Figure 27**). It is applied at an average rate of 0.40 kg/day. The formulation has a pH of 12.7, so is highly alkaline.

There are three components of Steammate NA0880, not including water (Appendix D). One component is restricted under an NDA and has been given a generic code. The three components are:

- Monoethanolamine (39.6% by weight, CASRN 141-43-5).
- 3-Dimethylaminopropylamine (DMAPA) (19.9% by weight, CASRN 109-55-7).
- SM1 (0.2% by weight, CASRN restricted).

All three components have the required chemical information (CASRN) to assess risk. Two presented a potential ecological risk, with RQ1 = 44 and 28 for monoethanolamine, and DMAPA, respectively, while SM1 had an RQ1 = 1.0. The elevated RQ1 were based primarily on marine PNEC of 0.009 mg/L and 0.007 mg/L for monoethanolamine and DMAPA, respectively. Although SM1 had the lowest PNEC, it is present at only 0.2% (cf. 39.6% and 19.9% for monoethanolamine, DMAPA, respectively) so presents with a borderline potential ecological risk (RQ1 = 1.0).

As RQ1 for two chemicals in the formulation was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.5 Flogard MS6222

Flogard MS6222 is a water-based corrosion inhibitor used in the cooling system (**Figure 27**). It is applied at an average rate of 0.80 kg/day. The formulation has a pH of <1.0, so is highly acidic.

There are is only one component of Flogard MS6222, not including water (Appendix D). It is not restricted under an NDA and is:

• Phosphoric acid (75.0% by weight, CASRN 7664-38-2).

The ECHA state no hazard identified for phosphoric acid in the marine environment. Furthermore, the consent condition of pH control prevents effects from extreme pH. Therefore, no further assessment was undertaken.

6.3.6 Genguard GN8020

Genguard GN8020 is used to control deposit and fouling in the cooling system (**Figure 27**). It is applied at an average rate of 5.75 kg/day. The formulation has a pH of 2.6.

There are five components of Genguard GN8020 present at a minimum proportion of 0.1%¹⁵, not including water (Appendix D). All five components are restricted under an NDA and are given generic codes. The five components are:

- Gen1 (0.56% by weight, CASRN restricted).
- Gen2 (18.75% by weight, CASRN restricted).
- Gen3 (0.32% by weight, CASRN restricted).
- Gen4 (19.21% by weight, CASRN restricted).
- Gen5 (0.67% by weight, CASRN restricted).

All five components have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for Gen1 only, with RQ1 = 8.0, based primarily on a marine PNEC of 0.01 mg/L. Gen5 had an RQ of 0.1, while Gen3 was classified by ECHA as "aquatic toxicity unlikely". No toxicity data could be obtained for Gen2 and Gen4, so an assessment of ecological risk could not be undertaken for these two components. Gen2 is a polymer of Gen1, while Gen4 is a polymer of another component present at <0.05% of the formulation.

As RQ1 for at least one chemical in the formulation (Gen1 RQ1 = 8.0) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.7 Inhibitor AZ8104

Inhibitor AZ8104 is a water-based corrosion inhibitor used in the cooling system (**Figure 27**). It is applied at an average rate of 1.06 kg/day. The formulation has a pH of 12.7, so is highly alkaline.

There are five components of Inhibitor AZ8104, not including water (Appendix D). Two components are restricted under an NDA and are given generic codes. The five components are:

- Chlorotolyltriazole sodium salt (13.1% by weight, CASRN 202420-04-0).
- Sodium tolyltriazole (1.4% by weight, CASRN 64665-57-2).
- Sodium hydroxide (1.14% by weight, CASRN 1310-73-2).
- AZ1 (3.25% by weight, CASRN not assigned).
- AZ2 (5.8% by weight, CASRN restricted).

Four components have the required chemical information (CASRN) to assess risk. AZ1 has not been assigned a CASRN, and an online search on the chemical name failed to provide a CASRN, so no further information could be obtained.

A PNEC (0.008 mg/L) was only available for sodium tolytriazole, which provided a potential ecological risk, with RQ1 = 4.6. Sodium hydroxide is a base for which ecological effects will be mitigated by pH control, while AZ2 is a common salt in seawater.

 $^{^{\}rm 15}$ Ingredients making up a total of <0.1% of formulation were also restricted under an NDA. Due to extremely low proportions these were not assessed further.
As RQ1 for at least one chemical in the formulation (sodium tolytriazole RQ1 = 4.6) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.8 Spectrus BD1500

Spectrus BD1500 is a water-based formulation used for control of deposit in the cooling system (**Figure 27**). It is applied at an average rate of 0.19 kg/day. The formulation has a pH of 12.5, so is highly alkaline.

There are two components¹⁶ of Spectrus BD1500, not including water (Appendix D). One component is restricted under an NDA and has been given a generic code. The two components are:

- Sodium hydroxide (1.14% by weight, CASRN 1310-73-2).
- BD1 (17.88% by weight, CASRN restricted).

Sodium hydroxide is a base, so ecological effects are mitigated by the consent condition of pH control.

BD1 presented a potential ecological risk, with RQ1 = 67, based on an ECHA PNEC of 0.00125 mg/L. Therefore, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.9 Spectrus NX1100

Spectrus NX1100 is a biocide used in the cooling system (**Figure 27**). It is applied at an average rate of 0.2 kg/day. The formulation has a pH of 3.0, so is moderately acidic.

There are seven components of Spectrus NX1100, not including water (Appendix D). Two components are restricted under an NDA and are given generic codes. The seven components are:

- Bronopol (5.54% by weight, CASRN 52-51-7).
- Magnesium nitrate (3.68% by weight, CASRN 13446-18-9).
- Isothiazolinones, mixed (Kathron 886) (2.58% by weight, CASRN 55965-84-9).
- Magnesium chloride (1.66% by weight, CASRN 7786-30-3).
- NX1 (2.94% by weight, CASRN restricted).
- NX2 (0.98% by weight, CASRN restricted).
- NX3 (0.19% by weight, CASRN restricted).

All 7 components have the required chemical information (CASRN) to assess risk.

A potential ecological risk was identified for bronopol and Kathron 886 only, with RQ1 = 28, and RQ1 = 4.3, for bronopol and Kathron 886, respectively. This is based primarily on ECHA marine

 $^{^{\}rm 16}$ Components making up <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

PNECs of 0.001 mg/L and 0.003 mg/L for bronopol and Kathron 886, respectively. NX1 had an ECHA marine PNEC of 0.044 mg/L, with an RQ1 of 0.3.

Magnesium nitrate was classified as non-toxic by ECHA, based on no adverse toxic effects at >100 mg/L, although a PNEC was not provided. Magnesium chloride, NX1, and NX3 had RQ1 of 0.03, 0.3, and 0.01, respectively. NX2 is an acid so ecological effects are mitigated by the consent condition of pH control.

As RQ1 for at least one chemical in the formulation (bronopol and Kathron 886 with RQ1 = 28 and 4.3, respectively) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.10 Road Film Remover (Sandfords)

Until recently, Road Film Remover (RFR) was used by Sandfords to wash their trucks off-site with the resulting wastewater entering the stormwater drain on the Ravensdown site and ultimately entering the settling pond. The formulation has a pH of 9.5-10, so is highly alkaline.

There are five components of RFR, not including water (Appendix D). There is no NDA between the manufacturer (Auto Shine Car Care Products) and SEL. The five components are:

- 4-Nonylphenol, branched, ethoxylated (5-10% by weight, CASRN 127087-87-0).
- Sodium xylenesulfonate (10-15% by weight, CASRN 1300-72-7).
- Ethylenediamine tetraacetic Acid (EDTA) (2-5% by weight, CASRN 60-00-4).
- Sodium phosphate, tribasic (2-5% by weight, CASRN 7601-54-9).
- Sodium hydroxide (2-5% by weight, CASRN 1310-73-2).

Three components have the potential to cause adverse ecological effects. 4-Nonylphenol, branched, ethoxylated (part of the class of alkylphenol ethoxylates (APEs)) has no PNEC available from ECHA or NORMAN. However, it is well known that APEs readily degrade to more persistent shorter-chain APEs and alkylphenols (APs) in the environment (see the review of Ying et al, 2002). Therefore, with no PNECs available for 4-nonylphenol, branched, ethoxylated, potential ecological risk was assessed on its primary degradation product, 4-nonylphenol, branched (NP).

NP presents a high potential ecological risk, with an RQ1 of 680, based primarily on an ECHA marine PNEC of 0.001 mg/L.

Sodium xylenesulfonate and EDTA also present a lower ecological risk with RQ1 of 102 and 1.5, respectively.

As RQ1 for three chemicals in the formulation (NP, sodium xylenesulfonate, and ethylenediamine tetraacetic acid with RQ1 = 680, 102, and 1.5, respectively) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.11 XT88 (alternative to Road Film Remover)

Due to a potential high ecological risk identified for Road Film Remover as part of our assessment, Sandfords ceased use of this formulation and replaced it with another, XT88. The formulation has a pH of 9.0-9.1 (as a 1% solution), so is alkaline.

There are two components of XT88, not including water (Appendix D). There is no NDA between the manufacturer (Waikaraka Holdings Ltd) and SEL. The two components are:

- Sodium dodecylbenzenesulfonate (10-30% by weight, CASRN 25155-30-0).
- Sodium metasilicate (1-10% by weight, CASRN 6834-92-0).

Both components have the required chemical information (CASRN) to assess risk.

A potential ecological risk was identified for sodium dodecylbenzenesulfonate, with RQ1=2.2. This is based primarily on an ECHA marine PNEC of 1.0 mg/L.

As RQ1 for at least one chemical in the formulation (sodium dodecylbenzenesulfonate with RQ1 = 2.2) was >1, an assessment of potential effects after dilution in the receiving environment (RQ2) was undertaken (Section 6.4).

6.3.12 RQ1 summary

Process chemicals present in the Ravensdown settling pond that have a risk quotient RQ1 >1, which indicates the potential to cause adverse ecological effects in the receiving environment, are summarised in **Table 16.** To apply marine ecological guidelines, dilution of the chemicals in the receiving environment needs to be accounted for. Receiving environment risk quotients (RQ2) were calculated using dilutions derived from a dye study (Section 5) and presented in Section 6.4.

Formulation	Component	RQ1
Cortrol OS7780	1,4-Benzoquinone	14
Cortrol OS7780	Cort2	1.5
Genguard GN8020	Gen1	8.0
Inhibitor AZ8104	Sodium tolyltriazole	4.6
Spectrus BD1500	BD1	67
Spectrus NX1100	Bronopol	28
Spectrus NX1100	Kathron 886	4.3
Steammate NA0880	Monoethanolamine	44
Steammate NA0880	3-Dimethylaminopropylamine	28
Road Film Remover	Nonylphenol (technical)	680
Road Film Remover	Sodium Xylenesulfonate	102
Road Film Remover	EDTA	1.5
XT88	Sodium dodecylbenzenesulfonate	2.2

Table 16: Process chemicals present in Ravensdown settling pond with RQ1 > 1.

6.4 Calculation of receiving environment risk quotients (RQ2)

Based on the resource consent, the end of the zone of reasonable mixing is defined as including the Ravensdown Drain and 90m down the Awatoto Drain (see **Figure 2**). We undertook a mixing zone dye study (Section 5) to determine the extent of the discharge plume and to provide quantitative dilutions within the zone of reasonable mixing under low tide and high-tide scenarios. Under both scenarios, the discharge plume was observed to progress down the centre of the Awatoto Drain. For the low-tide scenario, the Awatoto Drain was very shallow and quantitative dilutions were calculated at the surface only. Dilutions were initially around 10-fold, however over time, dilutions reduced and stabilised to around 2-fold. At the end of the currently consented mixing zone, dilution after 62 minutes of continuous discharge was 2.8-fold. Under the high tide discharge scenario, dilutions were initially around 10-fold, and, over time reduced and stabilised to around 3.2-fold. At the boundary of the mixing zone (90 m, sampling site A7), dilution at the surface was 4.9-fold after 109 minutes of discharge.

Therefore, dilutions required within the mixing zone to mitigate risk (RQ2) were calculated for:

- a low tide dilution scenario of 2.8-fold (vertically mixed), and;
- a high tide dilution scenario of 4.9-fold (surface only).

RQ2 for low tide and high tide dilution scenarios are summarised in Table 17.

Formulation	Component	RQ1	RQ2 (low tide discharge scenario) - <u>vertically mixed</u>	RQ2 (high tide discharge scenario) - <u>surface only</u>	BCF
Cortrol 087780	1,4-Benzoquinone	14	5.0	2.9	1.00
Control 037780	Cort2	1.5	0.5	0.3	6.96
Optisperse ADJ5150	ADJ1		Common salt in	seawater	NA
Solus AP24	Sol4	0.02			
	Monoethanolamine	44	16	8.9	1.00
Steammate NA0880	DMAPA	28	10	5.8	1.00
	SM1	1.0	0.4	0.2	1.00
Flogard MS6222	Phosphoric acid	No hazard identified			
Genguard GN8020	Gen1	8.0	2.9	1.6	1.00
Inhibitor AZ8104	Sodium tolyltriazole	4.6	1.6	0.9	No data
Spectrus BD1500	BD1	67	24	14	No data
Sportrue NIV1100	Bronopol	28	9.8	5.6	1.34
Spectrus INXII00	Kathron 886	4.3	1.5	0.9	4.19
	Nonylphenol (technical)	680	243	139	1.00
Road Film Remover	Sodium xylenesulfonate	102	36	21	1.00
	EDTA	1.5	0.6	0.3	1.00
XT88	Sodium dodecylbenzenesulfonate	2.2	0.8	0.4	No data

Table 17: Summary of ecological risk for process chemical formulations.

Colour codes: <mark>RQ< 1 = green</mark>; <mark>RQ>1 orange</mark>

For three formulations – Optisperse ADJ5150, Solus AP24, and Flogard MS6222 – the risk is negligible in the settling pond, even before allowing for dilution in the receiving environment, i.e. RQ1< 1.

For XT88, the risk is negligible under either the low tide or high tide scenario, i.e. RQ2<1.

For the low tide discharge scenario, potential ecological risks (RQ2) were calculated for all toxic components with RQ1>1, with RQ2 ranging from 1.5 (Kathron 886 contained in Spectrus NX1100) to 243 (nonylphenol (technical) contained in Road Film Remover). While biodegradation of chemical constituents of a number of these formulations is possible, it is considered unlikely that this would result in a significant reduction in potential effects, given that the RQ2 values are orders of magnitude greater than 1. As there was clear evidence for vertical mixing for the low tide scenario, these components will potentially lead to adverse effects on <u>both</u> water dwelling and surface sediment dwelling organisms.

For the high tide discharge scenario, there was no evidence for vertical mixing of the discharge plume, and it was present at the surface only. Therefore, under the high tide discharge scenario, the plume would potentially lead to adverse effects only on water dwelling organisms.

For one formulation – Inhibitor AZ8104 – the risk is negligible on water dwelling organisms in the receiving environment (RQ2 = 0.9).

For the remaining six formulations – Cortrol OS7780, Steammate NA0880, Genguard GN8020, Spectrus BD1500, Spectrus NX1100, and Road Film Remover – there is a potential for more than minor adverse effects on water dwelling organisms in the receiving environment (i.e. RQ2>1).

For Cortrol OS7780 an RQ2 of 2.9 was calculated for 1,4-benzoquinone. No aquatic biodegradation data could be obtained for 1,4-benzoquinone. However, it has been stated that in water, 1,4-benzoquinone is not expected to volatilize, adsorb to particulate matter or sediment, or bioaccumulate in aquatic organisms. Biodegradation in water may be important based upon the rapid degradation of 1,4-benzoquinone in soil.¹⁷ Therefore, the conservative approach used in this risk assessment is likely to be over-estimating the risk from 1,4-benzoquinone in the formulation Cortrol OS7780, and more than minor effects are unlikely.

For Steammate NA0880, an RQ2 of 8.9 and 5.8 was calculated for monoethanolamine and DMAPA, respectively. Monoethanolamine and DMAPA have been classified by ECHA as readily biodegradable in water. A key study showed >90% degradation of monoethanolamine after 21 days.¹⁸ Biodegradation of DMAPA was experimentally determined to be 54.8% after 28 days under marine conditions.¹⁹ Therefore, the conservative approach used in this risk assessment is likely to be over-estimating the risk from monoethanolamine and DMAPA in the formulation Steammate NA0880, and more than minor effects are unlikely.

¹⁷ <u>https://webwiser.nlm.nih.gov/substance?substanceId=521&identifier=1,4-</u>

Benzoquinone&identifierType=name&menuItemId=75&catId=112

¹⁸ <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/15808/5/3/2/?documentUUID=33551d85-a5f9-40f6-9227-92987bae3050</u>

¹⁹ <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/14823/5/3/2</u>

For Genguard GN8020, an RQ2 of 1.6 was calculated for Gen1. Gen1 has been classified by ECHA as readily biodegradable in water and reported elsewhere as 97% degraded after 28 days.²⁰ Therefore, the conservative approach used in this risk assessment is likely to be over-estimating the risk from Gen1 in the formulation Genguard GN8020, and more than minor effects are unlikely.

For Spectrus BD1500, an RQ2 of 14 was calculated for BD1. No information on biodegradation could be obtained for the chemical attributed to the elevated risk (BD1). The marine PNEC for BD1 of 0.00125 mg/L has a large uncertainty (assessment factor of 10,000) due to a paucity of relevant ecotoxicological data. Therefore, although there is large uncertainty around the PNEC, no further refinement could be made on the risk from BD1 in the formulation Spectrus BD1500 and more than minor effects are possible.

For Spectrus NX1100, an RQ2 of 5.6 was calculated for bronopol. Bronopol has been classified by ECHA as readily biodegradable in water, with a key experiment reporting 60% degradation after 11 days and 70-80% degradation after 28 days.²¹ Therefore, the conservative approach used in this risk assessment is likely to be over-estimating the risk from bronopol in the formulation Spectrus NX1100, and more than minor effects are unlikely.

Due to a potential high ecological risk identified for Road Film Remover, Sandfords have replaced it with XT88, which presents negligible ecological risk to the receiving environment.

6.5 Potential for bioaccumulation

Some process chemicals have the potential to bioaccumulate. As stated in Section 6.2.4, any chemical with a bioaccumulation concentration factor (BCF) >1000 is likely to bioaccumulate. Of the process chemicals that enter the settling pond and are discharged to the receiving environment, the BCF ranges from 1.00 to 6.96 with one notable exception, nonylphenol, which has a BCF of 896²² (**Table 17**). However, nonylphenol is only present in the Road Film Remover formulation, which is no longer in use. Therefore, the chemicals in the formulations are unlikely to bioaccumulate.

6.6 Summary

The risk assessment methodology used is conservative and may over-estimate risk from process chemicals, however, it is considered to be the most prudent approach in the absence of degradation data (for most process chemicals) and the inability to measure most of the process chemicals in the pond or receiving environment (due to lack of accredited laboratory methods).

Nevertheless, the potential risk when discharging prior to low tide is elevated for the majority of the formulations used at Ravensdown. The potential risk when discharging prior to high tide is markedly reduced and constrained to effects on water dwelling organisms as the discharge plume is not vertically mixed within the mixing zone.

 $^{^{\}rm 20}$ References withheld as Gen1 is covered under an NDA between Suez and SEL.

²¹ <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/11419/5/3/2/?documentUUID=4cc4c467-964e-4db2-bab4-3db79f01ea78</u>

²² <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/15896/5/4/1</u>

Four formulations – Optisperse ADJ5150, Solus AP24, Flogard MS6222, and XT88 – present negligible risk under either discharge scenario. We note that XT88 is a replacement for Road Film Remover, which presents as a significant ecological risk.

Under the high tide discharge scenario:

- For one formulation Inhibitor AZ8104 the risk is negligible on water dwelling organisms in the receiving environment (RQ2 = 0.9).
- For the remaining six formulations Cortrol OS7780, Steammate NA0880, Genguard GN8020, Spectrus BD1500, Spectrus NX1100, and Road Film Remover there is a potential for more than minor adverse effects on water dwelling organisms in the receiving environment (i.e. RQ2>1).
- Use of Road Film Remover has ceased, so no longer presents as an ecological risk.
- For Cortrol OS7780, Steammate NA0880, Genguard GN8020, Spectrus NX1100, the most toxic components are readily biodegradable, so more than minor effects are unlikely.
- For Spectrus BD1500, there is large uncertainty around the PNEC of the most toxic component (BD1) used for the assessment. However, no further refinement could be made on the risk from BD1 in the formulation Spectrus BD1500 and more than minor effects are possible.

None of the chemicals in the formulations (with the exception of nonylphenol in the discontinued Road Film Remover) are likely to bioaccumulate.

7. Whole Effluent Toxicity Testing (WET Testing)

7.1 Background

Condition 6g of the discharge consent requires Ravensdown to undertake WET testing on the discharge every fourth year following commencement of the discharge consent. Collection of discharge samples for WET testing from the Ravensdown site is undertaken by creating a composite sample from 24 samples collected over a 12-hour period during moderate rainfall (1.7 mm/hr average over the previous 24 hours) using an autosampler. Samples are collected after first flush in order to represent average stormwater quality. The composite sample is divided into two samples that are dispatched on the same day of collection (chilled), one being sent to NIWA for WET testing and one being sent to Hill Laboratories for contaminant analyses. The WET testing is carried out on three typical test species – a marine alga, an estuarine amphipod and an estuarine snail. Contaminant analyses include pH, total phosphorus, soluble reactive phosphorus, fluoride, total sulphur, suspended sediment and metals (copper, zinc, cadmium, chromium and aluminium).

Compliance is based on achieving no significant toxicity to any test species at a dilution of no less than 100:1.

7.2 Previous WET test and discharge quality results

The results of previous WET tests undertaken in 2015 and 2019 (NIWA, 2015, 2019) are presented in **Table 18**. Results indicated that, on both occasions, the discharge would not cause significant adverse effects on the species tested (marine alga: *Minutocellus polymorphus*, estuarine amphipod: *Chaetocorophium lacasi*, and an estuarine snail: *Potamopyrgus estuarinus*) after a 100-fold dilution. Hence, the discharge would not be considered toxic to organisms in the receiving environment.

Table 18: WET test results for a) 2015 and b) 2019. Source: NIWA (2015, 2019).

Sample ID: Collected by:	Awatoto Plant disch Triplefin – Shade S	Awatoto Plant dischargeSample Type:StorTriplefin – Shade SmithSample Method:12 h			Storm water 12 h composite	
NIWA Lab ID	Temperature °C	re pH Salinity ppt		Salinity DO ppt mg O ₂ L ⁻¹		Conductivity µS cm ⁻¹
2577/PM1	15.0	7.22	0.53	7.3		1052
Organism	EC ₅₀ ª	EC ₁₀	NOEC ^b	LOEC ^b %	TEC ^b %	Toxicity at 1:100 dilution
Algae	>32	>32	32	>32	>32	No
Snail	>79.6	>79.6	79.6	>79.6	>79.6	No
Amphipod	>79.6	>79.6	79.6	>79.6	>79.6	No

^a The lower the EC₅₀ the greater the toxicity, indicating that a higher dilution was required to reduce toxicity to the test organisms.

b NOEC = No observed effect concentration; LOEC = Lowest observed effect concentration; TEC = threshold effect concentration (Geometric mean of NOEC and LOEC).

Sample ID:	Awatoto Plant disch	arge	Sample Type:			Storm water
Collected by:	Triplefin – Shade Si	mith	Sample Method:		12 h composite	
NIWA Lab ID	Temperature °C	рН	Salinity ppt	DO mg O ₂ L ⁻¹		Conductivity µS cm ⁻¹
2642/SB1	6.5	7.71	0.42	9	.4	810
Organism	EC50 ^a %	EC10 %	NOEC ^b %	LOEC ^b %	TEC ^b %	Toxicity at 1:100 dilution
Algae	>32	>32	32	>32	>32	No
Snail - Survival	>50	>50	50	>50	>50	No
Snail - Mobility	>50	>50	50	>50	>50	No
Amphipod - Survival	>50	>50	50	>50	>50	No
Amphipod - Mobility	>50	>50	50	>50	>50	No

^a The lower the EC₅₀ the greater the toxicity, indicating that a higher dilution was required to reduce toxicity to the test organisms.

NOEC = No observed effect concentration; LOEC = Lowest observed effect concentration; TEC = threshold effect concentration (Geometric mean of NOEC and LOEC).

Results of water quality analysis of the discharge undertaken by Hill Laboratories are presented in **Table 19** for 2015 and 2019.

Concentrations of copper and zinc, as well as fluoride and ammonia exceeded the relevant guidelines in 2015, while cadmium, chromium, copper and zinc, along with ammonia, exceeded relevant guidelines in 2019. However, on both occasions the calculated dilutions required to achieve the guidelines would be less than the 'no toxicity' criterion of no significant effect at a 1:100 dilution defined in the consent condition. In addition, the fluoride concentration on both occasions was well below the maximum allowed by the resource consent (30 mg/L).

Table 19 Chemical analysis results from 12h composite sample of the discharge from the Ravensdown Awatoto fertiliser plant for 2015 and 2019. Source: NIWA (2015, 2019).

	Ravensdown discharge 15-16/3/15	ANZECC (2000) trigger value	Dilution required ^e
	mg L ⁻¹	mg L ⁻¹	
Total Aluminium	1.02	no value	-
Total Cadmium	0.00047	0.0007ª	<1x
Total Chromium (∀I)	0.00162	0.0044	<1x
Total Copper	0.0033	0.0013	2.5x
Total Nickel	0.0089	0.070	<1x
Total Sulphur	126 ^b	no value	-
Total Zinc	0.045	0.015	3.0x
Fluoride	6.3	5.0°	1.3x
Ammonia–N	6.5	0.910	7.1x

^a A 99% protection level is recommended for cadmium to protect for possible bioaccumulation in shellfish and effects on consumers.

^b Analysis of total sulphur usually used to provide an approximate measure of hydrogen sulphide present in discharge – with the toxic unionised hydrogen sulphide calculated based on pH, temperature and salinity. This very high total sulphur is considered likely to be elemental sulphur from the fertiliser processing and so was not used to estimate hydrogen sulphide.
^c Hickey et al (2004) marine guideline value

* Dilution required to comply with ANZECC (2000) trigger values.

	Ravensdown discharge 5-6/6/19	ANZECC (2000) trigger value	Dilution required ^e
	mg L ⁻¹	mg L ⁻¹	
Total Aluminium	0.47	no value	-
Total Cadmium	<0.0011	0.0007ª	>1.6x
Total Chromium (VI)	<0.010	0.0044	>2.3x
Total Copper	<0.011	0.0013	>8.5x
Total Nickel	0.037	0.070	<1x
Total Sulphur	91 ^b	no value	-
Total Zinc	0.050	0.015	3.3x
Fluoride	4.0	5.0°	<1x
Ammonia-N	23	0.910	25x

^a A 99% protection level is recommended for cadmium to protect for possible bioaccumulation in shellfish and effects on consumers.

^b Analysis of total sulphur usually used to provide an approximate measure of hydrogen sulphide present in discharge – with the toxic unionised hydrogen sulphide calculated based on pH, temperature and salinity. This very high total sulphur is considered likely to be elemental sulphur from the fertiliser processing and so was not used to estimate hydrogen sulphide.

Hickey et al (2004) marine guideline value
 Dilution required to comply with ANZECC (2000) trigger values.

7.3 2020 WET test results

Toxicity testing was undertaken on two samples: a settling pond discharge sample (collected 17/08/20) to determine resource consent compliance, and a sample (also collected 17/8/20) from upstream of the discharge (NIWA, 2020). The upstream sample was collected and tested to provide a context for any toxicity associated with the discharge sample, as contaminants sourced from upstream of the site may also be contributing to effects observed in the Awatoto Drain and Tūtaekurī River.

Three marine species were tested and comprised an estuarine snail (*Potamopyrgus estuarinus* - 96-hour survival and morbidity), an amphipod (*Chaetocorophium cf. lucasi* - 96-hour survival and morbidity) and a marine alga (*Minutocellus polymorphus* - 48-hour growth response). **Table 20** presents a summary of the results of the WET tests. The upstream sampled showed no toxicity to the survival or mobility of estuarine snails or amphipods; however, there was a significant reduction in algal growth at 32% dilution. Using the EC_{50} as a comparative measure between the three test species, the settling pond discharge was most toxic to the alga at 6.5% concentration. Therefore, the upstream site was less toxic to algae than the settling pond site. However, based on the estuarine snail, amphipod and alga test results for the supplied settling pond discharge sample (17/08/20), the wastewater complies with the HBRC consent compliance criterion for no toxicity when diluted 100 times with uncontaminated water.

Organism	EC ₅₀ • %	NOEC %	EC50/10	No toxicity dilution ^b	Unacceptable toxicity ^d
Settling Pond Discharge 2664/SX1					
Mollusc (snail) survival	>80	>80	>8.0	<13x	No
Mollusc (snail) morbidity ^c	>80	>80	>8.0	<13x	No
Crustacean (amphipod) survival	>80	27	>8.0	<13x	No
Crustacean (amphipod) morbidity •	>80	27	>8.0	<13x	No
Alga	6.5	4		25x	No
Upstream of Discharge 2664/SX2					
Mollusc (snail) survival	>84	>84	>8.4	<12x	
Mollusc (snail) morbidity ^c	>84	>84	>8.4	<12x	
Crustacean (amphipod) survival	>84	>84	>8.4	<12x	
Crustacean (amphipod) morbidity •	>84	>84	>8.4	<12x	
Alga	>32	<32		>3x	

Table 20 Summary of key toxicity metrics for the three test organisms exposed to August 2020 Ravensdown Awatoto discharge samples. Bold indicates values used for compliance assessment. Source: NIWA (2020).

^a EC_N: The effective median concentration of a substance having an x% effect on the test organisms. The lower the EC_{so} the greater the toxicity, indicating that a higher dilution was required to cause a 50% effect on the test organisms. For the snail and amphipod survival test the EC value is the lethal concentration (LC) value. ^b Based on chronic NOEC values and using an acute to chronic ratio (ACR) of 10 applied to the EC_{so} for the acute amphipod and snail tests. ^c The lack of mobility of the test organisms. ^d Toxicity at 1% sample.

In addition to the WET testing, a sub-sample of the settling pond discharge sample was also analysed for metals, sulphide and ammoniacal-N and compared to guideline values from Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZG). Safety Factors were calculated for each contaminant of interest. The Safety Factor defines the lowest dilution required for the concentration of a particular component of the sample to be reduced to ANZG value. It is a derived ratio of the guideline value to the analyte concentration when diluted 100-fold. A Safety Factor >1 indicates a concentration below the ANZG guideline. **Table 21** presents the results of the chemical analysis. The concentrations of zinc and ammoniacal-N exceeded the ANZG (2018) guidelines. However, after diluting the samples 100 times, the resulting concentration would be less than the guideline value. The fluoride concentration was well below the maximum concentration allowed by the resource consent.

Table 21 Chemical analysis of August 2020 settling pond discharge. Source: NIWA (2020)

Chemical	Sample (mg L ⁻¹)	100-fold dilution (mg L ⁻¹)	ANZG (2018) 95% Guideline Value (mg L ⁻¹)	Safety Factor ^b
Dissolved aluminium	0.022	0.00022	No value	-
Dissolved cadmium	< 0.00005	< 0.000005	0.0007c	>1400x
Dissolved chromium	0.0012	0.000012	0.0044	367x
Dissolved copper	0.0008	0.00008	0.0013	163x
Dissolved nickel	0.0074	0.000074	0.070	946x
Dissolved zinc	0.041	0.00041	0.015	37x
Total sulphide	< 0.002	< 0.00002	No value	-
Hydrogen sulphideª	<0.0008	<0.000008	0.001	>1250x
Fluoride	3.5	0.035	5.0 ^d	143x
Total Ammoniacal-N	25	0.25	0.910	3.64x

^a Calculated as 4.06% of total sulphide at pH 8.0, 20°C, 32.5 ppt (ANZECC 2000). ^b Safety Factor ANZG guideline value / settling pond discharge concentration @ 100-fold dilution. ^c A 99% protection level is recommended for cadmium to protect for possible bioaccumulation in shellfish and effects on consumers. ^d Hickey et al. (2004) marine guideline value.

7.4 Dilutions achieved in the receiving environment

No monitoring of the Ravensdown Drain or Awatoto Drain has been undertaken to verify whether the dilutions required for achieving no toxicity (i.e. at least 1:100) are achieved in the receiving environment or whether this is likely to be affected by tidal cycle.

Condition 3 of the Resource Consent defines the zone of reasonable mixing of the discharge, "to which the Class AE (HB) receiving water quality standards does not apply" as being "the Ravensdown Drain and 90m down the Awatoto Drain (GPS Co-ordinates N6175341, E2846875)". Within this zone it is therefore expected that more than minor effects may result from the discharge but that, by the boundary of this zone, the discharge would be fully mixed to a point where effects would be negligible. A dye study was undertaken in March 2021 to determine the dilution achieved in the mixing zone (see Chapter 5). Within the mixing zone, dilutions at the surface range between 1.7 and 17.8 fold (median = 3.5, average = 6.8 fold) when discharged prior to low tide and between 2.1 and 14.9 fold (median = 5.3, average = 6.6 fold) when discharged prior to high tide. Dilutions of upto 113 fold were recorded at 500mm below the surface under high tide conditions, but there was generally little evidence of vertical mixing. While these dilutions are generally lower than the 100 fold dilution required to meet the toxicity compliance limit, this does not mean toxic effects have occurred. For example, the 2020 WET testing results indicated that dilutions of only 13 fold and 25 fold were necessary to achieve no toxicity. These dilutions are comparable with those recorded from the dye study.

7.5 Conclusions

Whole Effluent Toxicity Testing results for the discharge have consistently complied with the consent requirement of no toxicity with at least 1:100 dilution. While a dye study undertaken in March 2021 indicates such dilutions are not always being achieved, the results of the Whole Effluent Toxicity Testing indicate that much lower dilutions are required to achieve no toxicity of the discharge.

8. Marine Ecology

Sharon de Luca, Ngaire Phillips, Kendall Leitch and Katrina McDermott

8.1 Previous investigations

Condition 6 of Ravensdown Napier's discharge consent requires monitoring of macrofauna and fish, periphyton (biomass and taxonomy), sediment and water quality to be undertaken every four years. This monitoring provides an assessment of the potential effects of the Ravensdown discharge on the in-stream ecology of sites within the receiving environment.

Ecological surveys have been undertaken previously in 2011, 2015 and 2019 (Death & Eckland, 2019). A summary of the key findings is presented below and includes comparison between years.

Figure 28 and **Figure 29** show the location of ecological receiving environment sites previously investigated. These are:

- Ravensdown Drain (RAV1 immediately below discharge, RAV2 at the confluence of Ravensdown and Awatoto Drains).
- Awatoto Drain (AWA 1 upstream of discharge but below the Council pumping station at the flood control stop bank, AWA2 within/at the boundary of the mixing zone, AWA3 downstream of mixing zone at the confluence with Tūtaekurī (Blind Arm).
- Tūtaekurī (Blind Arm) (TUT downstream of confluence of Awatoto Drain and Tūtaekurī River). This is the **Distant Impact Site**.
- Waitangi Estuary (WAI close to the mouth of the Waitangi Clive River). This is a **Reference Site**.



Figure 28: Sites previously monitored in relation to the Ravensdown discharge (Source: Death & Ekelund, 2019)



Figure 29: Sampling locations at sites monitored in relation to the Ravensdown discharge. Insets for AWA3, TUT and WAI sites are indicative only of actual locations sampled (Source: Death & Ekelund, 2019)

Benthic Macrofauna

Boffa Miskell (2019) reported on macrofaunal sampling undertaken in March 2019 and compared these results with two previous surveys undertaken in 2011 and 2015. Effects on the macroinvertebrate community were assessed using a range of biological summary indices.

Boffa Miskell (2019) reported that there was a statistically significant reduction in abundance over time at the Impact Site AWA3 (**Figure 30**). In contrast, number of taxa, diversity and richness increased between 2011 and 2015 and decreased to lower than the 2011 measure in 2019 at this site. Evenness also increased at this site between 2011 and 2015 and remained stable between 2015 and 2019.

Significant increases in the number of taxa, H' diversity, J' evenness and d richness occurred at the Distant Impact site TUT (**Figure 30**). Abundance appeared to remain relatively stable between 2011 and 2019, increasing slightly in 2015 but returning to a similar value to 2011 in 2019.

Large increases occurred across several biological indices at the reference site WAI. Statistically significant increases were observed in the number of taxa, abundance, H' diversity and d richness. Evenness also increased at this site between 2011 and 2015 and remained stable between 2015 and 2019.



Figure 30: Temporal comparison of macroinvertebrate summary indices at discharge sites. Source: Boffa Miskell (2019).

Figure 31 shows the differences in the species assemblages at each site on each sampling occasion. The 2011 data are clearly split, with the reference site WAI, the mixing zone sites (AWA2 and RAV) and three of the 5 distant impact sites samples (TUT) for 2011 being separated from all other sites and samples. The 2011 impact site (AWA3) and two of the five distant impact site samples (TUT) grouped with all other sites and years. Further, Boffa Miskell (2019) report (but do not present) the results of PERMANOVA analysis on this data set. They state that it shows that significant changes in the species assemblages have occurred at each site between years. Similarly, SIMPER analysis (again data not presented) showed that the same dominant species remain across years, despite changes occurring in species abundances and the relative

contribution of each species to the overall assemblage between years within each site. For example, they state that at the impact site (AWA3), pollution tolerant species (consisting of oligochaetes (worms), the snail *Potamopyrgus antipodum* and *Chironomid* sp. (True flies)) remain dominant across years in varying densities. This is also observed at the distant impact site (TUT), with *Potamopygus antipodum*, *Paracorophium excavatum* (amphipod) and oligochaetes dominate in all surveys. The authors also note that *Potamopyrgus antipodum* and *Paracorophium excavatum* are consistently represented across the three surveys at the reference site (WAI).



Figure 31: nMDS plot of benthic macroinvertebrate assemblage at samples sites on 3 sampling occasions. Source: Boffa Miskell (2019).

Boffa Miskell (2019) concluded by noting the variation in macroinvertebrate community structure both over time and between sites. While the impact site, AWA 3, had a significantly lower abundance compared to the mixing zone AWA2 and reference (WAI) sites, there was no evidence of adverse effects on other measures, when compared with reference sites in 2019. However, they also noted that while there had been increases in the value of a number of measures at the reference site over time (WAI), these increases were not observed at the impact sites. They suggested this could potentially be due to the influence of the discharge, nevertheless the species assemblages at these sites were typical of upper estuarine environments that naturally receive higher concentrations of fine sediment and freshwater runoff. They concluded that it was therefore likely that the natural habitat differences between sites within the estuary was the main driving factor in differences in species assemblages observed between sites. These results as a whole do not appear to indicate degradation in ecosystem health between sites and

over time (throughout the sample period between 2011 and 2019), resulting from impacts associated with stormwater and process water discharges. Spatial and temporal changes that have occurred appear to be as a result of natural variation over time and natural habitat differences within the estuary.

Sediment Grain Size

Two previous studies (Death et al., 2015; Death & Ekelund, 2019) have investigated sediment composition for sites RAV2, AWA2, AWA3, TUT2 and WAI (**Figure 32**). Sediment grain size monitoring indicates sediments are dominated by silt and clay in the Ravensdown Drain (RAV) and within the Awatoto/Waitangi Drain (AWA 2 and AWA3). Silt and clay formed a lower proportion at the site within the blind arm of the Tūtaekurī River (c. 54%) (TUT). The grain size composition at the Waitangi Estuary reference site (WAI) is very different to all the other sites, with silt and clay forming approximately a much smaller proportion, with very fine to medium sand grain sizes dominating.

Of the sites monitored for sediment grain size and quality, RAV2 largely only receives Ravensdown discharges (with some contribution also from Sandfords), whereas all other sites (including AWA1 located upstream of the Ravensdown Drain and AWA2 which is located close to the downstream existing mixing zone boundary) are confounded by sediment and contaminants discharged from other landuses in the various catchments.



Figure 32: Sediment composition in cores collected from Ravensdown Awatoto monitoring sites a) 2015, b) 2019. Source: Death et al. (2015), Death & Ekelund (2019).

Trace metals in sediments

Death & Ekelund (2019) compared data from 1992 to 2019 (**Figure 33**). Concentrations of all metals have generally been elevated in the Ravensdown Drain (RAV2) compared with all other sites, across all years. Concentrations of contaminants generally decreased with increasing distance downstream, with the concentrations at TUT and WAI being similar to the regional background levels. In 2019, trace metal concentrations in sediments were generally detected at concentrations below the ANZG Default Guideline Value (DGV) (Australian and New Zealand Governments, 2018) at most sites monitored (RAV2, AWA2, AWA3, TUT), except for zinc and cadmium at RAV2 where the concentrations were just above the DGV. Nickel concentrations were elevated at all sites in 2019, and especially at the reference site WAI, which exceeded the GV-High



guideline value. Chromium and zinc were also elevated at this site in 2019, exceeding the relevant DGVs.

Figure 33: Average trace metal concentrations, normalised, in sediments collected from Ravensdown Awatoto monitoring sites between 1992 and 2019. ANZG (2018) guidelines presented (dashed = GV-High, dotted = DGV). Source: Death & Ekelund (2019).

Fluoride concentrations have historically been highest at RAV2, decreasing with increased distance downstream (**Figure 34**). However, concentrations in 2019 were comparable amongst sites. There are no sediment quality guidelines for fluoride. Studies of the effects of fluoride on marine invertebrates indicated that generally, marine invertebrates were less sensitive to

fluoride than freshwater invertebrates (Camargo, 2002), likely as a consequence of elevated calcium in estuarine and seawaters. However, there are differences in sensitivity to fluoride between estuarine/marine species. Hemens and Warwick (1972) found effects on estuarine prawns after exposure to 100mg F-/L for 96 hours did not cause toxic effects. In addition, Pankhurst et al. (1980) found that exposure to 100 mg F-/L caused negligible mortality to anemone (*Anthopleura aureoradiata*) after 144 hours, the bivalve *Mytilus edulis* (after 160 hours) and the red krill *Munida gregaria* (after 259 hours). The brown mussel, *Perna perna*, showed a 30% mortality after to exposure to 7.2 mg F-/L after 120 hours (Hemens and Warwick, 1972). Fleiss (2011) notes that increased temperature and decreased water hardness increases acute toxicity of fluoride, with juveniles and small individuals being more susceptible than adults. It should be noted that the concentration of fluoride in the Ravensdown discharge in 2019 was consistently below the threshold concentration required in the conditions of consent (**Table 3**) and Whole Effluent Toxicity Testing (Chapter 6) does not indicate significant toxicity for the discharge.

Phosphorus concentrations in sediment showed a similar pattern to metals, with elevated concentrations at RAV2 and a decrease with distance downstream (**Figure 34**). There are no sediment quality guidelines for phosphorus. Phosphorus is a common ingredient in commercial fertilisers. High concentrations of phosphorus may also result from poor agricultural practices, runoff from urban areas and lawns, leaking septic systems or discharges from sewage treatment plants. Too much phosphorus in aquatic systems can cause increased growth of algae and large aquatic plants, which can result in decreased levels of dissolved oxygen as the plants degrade (via eutrophication).



Figure 34: Average concentrations of a) fluoride, b) sulphur and c) phosphorus in sediments collected from Ravensdown Awatoto monitoring sites, 1992 - 2019. Source: Death & Ekelund (2019).

<u>Fish</u>

Despite habitat alteration and loss reducing the functional capacity of the Waitangi Estuary, nevertheless it is considered to play an important role in the life cycles of many fish species (Madarasz-Smith et al., 2016). Estuarine areas are particularly important for native fish which are diadromous (that is, they require migration between the sea and freshwater in order to breed) and the Waitangi Estuary has been identified as the largest inanga spawning site in the Hawke's Bay (Rook, 1993). Walls (2005) also noted that the estuary is a traditional and important harvesting site for eels and whitebait (mostly juvenile inanga, the adults of which spawn in places in the estuary). It is a breeding, feeding and nursery area for mullet, flounders and kahawai.

Fish species identified as being present in the Waitangi Estuary by Death & Ekelund (2019) are listed in Appendix E. While not all of these species may be present in the Awatoto drain or blind arm of the Tūtaekurī River, some at least, may spend part of their life cycle in these habitats.

Death & Ekelund (2019) observed that, during their 2019 survey, the only fish species present were eel, which were seen in the Ravensdown Drain immediately downstream of the discharge and in the Awatoto Drain at the AWA3 site.

Death & Ekelund (2019) concluded that, while it is difficult to determine the exact effects from the Ravensdown discharge on fish communities in the Tūtaekurī River and wider Waitangi Estuary, the large number of species observed in the river and estuary, including non-migratory species, would suggest that any effects are most likely short-lived, localised and are not impacting on fish communities here.

Periphyton and Macrophytes

As an indicator of nutrient enrichment, periphyton biomass (Chlorophyll *a*) is required to be assessed under Conditions 6c and 6f. Elevated nutrient loads can stimulate planktonic primary production and result in nuisance macrophyte blooms where turbidity is low (generally in lower reaches of estuaries). In turn, when algal blooms decompose, oxygen levels in waterways can be reduced and in worst cases turn hypoxic, which can have adverse effects on benthic macrofauna. Monitoring of Chlorophyll *a* and nuisance macroalgae provide an indication of eutrophication. Chlorophyll *a* concentration in sediments has been consistently highest at RAV2, and with a general decrease downstream (**Figure 35**).

No species of macrophytes were observed at any of the sites in 2019 (Death & Ekelund, 2019). Given the complete absence, Death & Ekelund (2019) concluded that the discharge did not appear to be having any effect on macrophyte communities downstream of the discharge point. Further, they noted that the results from previous years also showed low biomass of macrophytes when they were observed, and no macrophytes at the Impact (AWA3) and Reference (WAI) sites, concluding that there were no effects that could be attributed to the Ravensdown discharge.



Figure 35: Average Chlorophyll a concentrations measured in sediments collected from Ravensdown Awatoto sites, March 2011, 2015 and 2019. Source: Death & Ekelund (2019).

8.2 July 2020 Ecological Surveys

Based on our analysis of information gaps (Phillips et al, 2020), further sampling of benthic macrofauna and sediment was conducted in 2020 to address the lack of replication of benthic sampling at specific sites and large natural variance between the reference site and other sampling sites chosen in the previous monitoring assessments. The additional sampling undertaken provides a more robust assessment of any effects the Ravensdown discharge may be having on the in-stream ecology of the receiving environment.

This assessment is based on marine ecological surveys conducted on 21-23 July 2020 by Streamlined Environmental/Boffa Miskell. Work was undertaken within 2-3 hours before/after the low tide.

8.2.1 Methodology

Survey Design

Monitoring the effects from the Ravensdown discharge on the receiving environment is challenging due to the myriad of other discharges and runoff from the surrounding land use. In addition, at the time of the survey the upstream Council operated pump was activated. Sites depicted in **Figure 36** were chosen to cover areas with and without potential effects from Ravensdown discharge, and to also determine any impacts beyond the zone of reasonable mixing. These sites are comparable in location to those previously surveyed, other than the reference

site. A new reference site was selected to address sediment grain size differences identified with the previously used reference site. It was also chosen to be representative of a site undisturbed by the Ravensdown discharge, as well as being an area further away from the estuary with more freshwater influence.

A total of nine sites were identified and surveyed (**Figure 36**). Two sites were within the Ravensdown Drain (RAV1, RAV2), directly downstream of the discharge. Three sites were located within the Awatoto Drain, one upstream of the confluence with Ravensdown Drain (near the council operated pump) (AWA1), one within the mixing zone (AWA2), and one beyond the boundary of the mixing zone (AWA3). Three sites were located downstream within the Tūtaekurī Blind Arm (TUT1, TUT2 and TUT3). A single reference site was located within a tributary of the Ngaruroro River (NGA1).



Figure 36: Marine ecological survey sampling sites (blue circles). Red triangles indicate location of the council operated pump. Orange triangle represents Ravensdown discharge outfall.

Benthic Infauna Community Composition

At each site five replicate benthic infauna samples were collected. A sediment corer, measuring 13 cm x 10 cm (area = 1,327 cm³), was randomly placed on the sediment surface. The core was then driven into the sediment, and the removed sediment was bagged. The contents were then sieved through a 0.5 mm sieve using seawater and all material was retained and preserved in 60-70% ethanol and sent to a taxonomist.

Epifauna and Macroalgae Community Composition

At each site five replicate quadrats were surveyed for epifauna and macroalgae. A 0.5 m x 0.5 m quadrat was randomly placed on the sediment surface. The quadrats were photographed and all

epifaunal or macroalgae species within the quadrat were recorded. Any worm/crab holes that were present were also noted.

Sediment Anoxic Layer

At each site five replicate redox discontinuity layer (RDL) samples were taken to assess the depth of the sediment anoxic layer. A 60mm diameter cylinder, capped with a rubber bung, was driven into the sediment to a depth of 8-10cm. The core was then gently removed from the cylinder and cut in half lengthways. The depth of the start of the anoxic sediment layer (where present) was measured and recorded.

Sediment Grain size

A surface sediment sample (top 2 cm) was collected at each site for sediment grain size analysis. Samples were sent to the University of Waikato for analysis using a laser particle analyser (Malvern Mastersizer) for the fraction <2 mm, while a sieve was used for the >2 mm fraction. Typically, 1-2 cm³ of the sample is analysed, with results reported as a percentage of the analysed sample.

Sediment Contaminants

A surface sediment sample (top 2 cm) was collected at each site for sediment chemistry analysis. Samples were sent to Hill Laboratories for analysis. Samples were analysed for:

- Total Phosphorus
- Total Sulphur
- Fluoride
- Total Arsenic
- Total Cadmium
- Total Chromium
- Total Copper
- Total Lead
- Total Nickel
- Total Zinc

Water Physico-chemistry

Basic water quality parameters were measured within the adjacent channel at the time of the sampling using a handheld YSI ProDSS Multimeter. The parameters measured were:

- Temperature
- pH
- Dissolved Oxygen (% and mg/L)
- Conductivity (µS/cm and mS/cm)

8.2.2 Survey Results

Existing Habitat

Site RAV1 (**Figure 37**) is located immediately downstream of the Ravensdown outfall. The outfall had been discharging immediately prior (15 minutes) to sampling. The tributary channel had abundant woody debris and gravels within the channel thalweg (lowest point in the stream channel). The channel bed, at the sampling location, contained high organic material and sandy sediment. The riparian margin was a mixture of overgrown native and exotic grasses and shrub species.



Figure 37: Site photos taken at Site RAV1 facing upstream to Ravensdown discharge point.

Site RAV2 (Figure 38) is located slightly downstream of the confluence of the Ravensdown and Awatoto Drains. The available habitat for sampling at this site was limited, with only a narrow strip of exposed channel present. The Ravensdown outfall was discharging during the sampling of this site. The tributary channel had abundant woody debris within both the channel and on the banks. The channel banks, at the sampling location, contained reasonably high content of organic material. The riparian margin was a mixture of overgrown pasture grasses and exotic shrubs such as blackberry.



Figure 38: Site photos taken at Site RAV2 facing downstream to confluence with Awatoto Drain.

Site AWA1_(Figure 39)_is located within Awatoto Drain immediately downstream of a council pump, which drains the Waitangi and Mission Drains. As a result, this site appears to be heavily influenced by freshwater. AWA1 is upstream of the confluence of Ravensdown and Awatoto Drains, and therefore, upstream of the mixing zone. Sampling was undertaken around the margin only, where sediment was very fine and very soft. Broken concrete and roading metal were present along the banks. Overgrown pasture grasses were present along both stream banks.



Figure 39: Site photos taken at Site AWA1 facing downstream and showing the council operated pump outlet.

Site AWA2_(Figure 40) is located in the Awatoto Drain, downstream of the confluence of the Ravensdown and Awatoto Drains and is within the designated mixing zone. Sampling at site AWA2 was undertaken on a small area of exposed channel bed. The sediment was very soft, with abundant woody debris present. Channel banks were covered with overgrown pasture grass.



Figure 40: Site photos taken at Site AWA2 facing upstream.

Site AWA3_(Figure 41) is located upstream of the confluence with the larger tributary of the Tūtaekurī Blind Arm and is downstream of the boundary of the mixing zone. The sediment surface was covered in a thin film of short green filamentous algae. There was abundant woody debris present across the exposed channel. Stream banks contained overgrown pasture species, rush species (unconfirmed *Bolboschoenus fluviatilis*) and raupō (*Typha orientalis*). Bird life on the exposed channel bed was abundant with banded dotterel, oyster catcher, white faced heron, mallard ducks, and pied stilt all being observed.



Figure 41: Site photos taken at Site AWA3 facing downstream to confluence of Awatoto Drain and Tūtaekurī Blind Arm.

Site TUT1 (**Figure 42**) is located within the larger tributary of the Tūtaekurī River, known as the Tūtaekurī Blind Arm, immediately downstream of the Awatoto Drain and Tūtaekurī Blind Arm confluence. Sediment was very soft and fine, with some woody debris and organic matter present. Some rare areas of filamentous green algae were also observed. Stream banks were overgrown with pasture grass and rush species (unconfirmed *Bolboschoenus fluviatilis*).



Figure 42: Site photos taken at Site TUT1 facing downstream.

Site TUT2 (**Figure 43**) is located approximately mid-way along the Tūtaekurī Blind Arm. Sampling occurred under the branches of a willow where a small area of exposed channel was present. Woody debris was present on the sediment surface and small *Potamopyrgus sp.* snails were observed. Stream banks were covered in rush species (unconfirmed *Bolboschoenus fluviatilis*).



Figure 43: Site photos taken at Site TUT2 facing downstream.

Site TUT3 (**Figure 44**) is located at the confluence of the Tūtaekurī Blind Arm and the Tūtaekurī River. A small, exposed margin was present with very soft mud and abundant crab holes. Woody debris or organic matter was rare. Stream banks were overgrown with pasture species, with mature exotic trees present on the opposite bank.



Figure 44: Site photos taken at Site TUT3 facing downstream to the confluence with Tūtaekurī River.

Site NGA1 (**Figure 45**) is the control site and is located on the southern side of the Ngaruroro River. The survey site is located downstream of a series of drainage canals, and areas containing broken concrete and metal. The site is upstream of a watercourse that has a Council operated pump that drains water from agricultural land. Small areas of woody debris were present and crab holes were present in the sediment surface. Rare small gravels were observed across the site. Channel banks were overgrown with pasture grass species and an overhanging willow was present.



Figure 45: Site photos taken at Site NGA1 facing upstream.

Benthic Infauna Community Composition

Benthic infauna communities were sampled across three consecutive days, during low tide, in July 2020. Five replicate infauna samples were collected at each site, with the mean values presented below.

Species richness overall was moderately low. Richness was highest at site TUT3 (9 taxa) closely followed by the control site NGA1 (8.6 taxa) (**Figure 46**). The lowest species richness was observed at site RAV1 (2.8 taxa), located immediately downstream of the Ravensdown discharge point.



Figure 46: Average number of taxa (n=5) per site sampled in July 2020. Error bars represent +/- standard error.

The Shannon-Wiener Diversity Index is a measure of diversity that uses the evenness of the taxa richness and their relative abundances. Overall, sites generally had poor diversity with sites TUT2

and NGA1 having moderate diversity. The highest diversity was observed at site TUT2 (1.27) and the lowest diversity was observed at site RAV1 (0.35) (**Figure 47**).



Figure 47: Average Shannon-Wiener Diversity Index Score (n=5) per site sampled in July 2020. Error bars represent +/- standard error.

The main taxa groups within the benthic communities were generally similar across the sites (**Figure 48**). Overall, the dominant taxa across most sites were oligochaete worms and gastropod snails (predominantly *Potamopyrgus estuarinus*), with the Corophiidae amphipods being the dominant taxa at sites TUT2 and TUT3.

Sites RAV1 and RAV2 had a high abundance of oligochaete worms, the estuarine snail *P. estuarinus* and smaller number of the freshwater snail *Potamopyrgus antipodarum*. These taxa are typically considered to be tolerant of a wide range of habitat and water quality conditions. The species assemblage present also shows a strong freshwater influence at both sites.

Sites AWA1, AWA2 and AWA3 were also dominated by oligochaete worms, the estuarine snail *P. estuarinus* and smaller numbers of the freshwater snail *P. antipodarum*. Diptera contained two *Chironomus* spp.

Sites TUT1, TUT2 and TUT3 demonstrated increasing taxa diversity, with less of a freshwater influence across the benthic assemblage. Site TUT1 was located directly downstream on the Awatoto Drain and Tūtaekurī River Blind Arm confluence and has a taxa assemblage more similar to those sites that are highly freshwater influenced. Site TUT2 and TUT3 have assemblages that have high proportions of the taxa group 'other', primarily driven by the high abundance of the burrowing amphipod Corophiidae. The gastropod *P. estuarinus* is still abundant, while no *P. antipodarum* were recorded. The polychaete worm *Scolecolepides benhami* is also increasingly abundant at TUT2 and TUT3. This worm is generally considered to be tolerant to organic enrichment.

The control site NGA1 had one of the highest number of taxa present, but the lowest abundance of individuals. The most abundant taxa were the gastropod *P. estuarinus* and the burrowing amphipod Corophiidae. The Nereidae rag worm *Nicon aestuariensis*, the tunnelling mud crab *Helice crassa* and the cockle *Austrovenus stutchburyi* were recorded only at site NGA1.

There was a large variation in individual abundance across the sampling sites with site AWA1 having an average of 404 individuals, while site NGA1 had an average of 73 individuals (**Figure 48**).



Figure 48: Average abundance of main taxonomic groups sampled in July 2020 (n=5). Note: Category 'Other' includes Mysidacea, Ostracoda, Corophiidae, Melitidae, *Helice crassa*, Elmidae, Hydrophilidae, Collembola and Nematoda.

A non-metric multi-dimension scaling (n-MDS) plot was created using Primer 7 (**Figure 49**). The n-MDS plot shows the differences and similarities in benthic invertebrate assemblages in 2dimensional space, with sites that are closer together having higher similarity, and sites that are further apart having less similarities. The nMDS indicates that the sites on the Tūtaekurī River (TUT2, TUT3 and NGA1) support somewhat different communities than other sites surveyed, although there is variability within this group and within each site (indicated by the wide spread of replicates). RAV1 is also different from most sites, although some replicates were similar to RAV2. Sites within and beyond the mixing zone (AWA1, AWA2 and AWA3) grouped reasonably close together.



Figure 49: n-MDS plots of benthic invertebrate community data, showing individual replicates from each survey site.

Permanova analysis enables the statistical significance of the differences and similarities presented in the nMDS to be determined. Results of a Permanova analysis indicated statistically significant difference across all sites (p=0.0001). Analysis of variability within sites indicated generally high average similarity across replicates (**Table 22**), with sites TUT3 and RAV1 showing the greatest variability (lowest similarity). Pairwise analysis between sites showed that sites AWA2 and AWA3 were very similar and not statistically different (p=0.09, % dissimilarity = 19.42) (**Table 23**). All other sites were statistically different to each other (p<0.05), with greatest difference between site TUT3 and RAV1 (74.74%).

Table 22 Average similarity with each site, based on macrobenthos composition.

Site	Average similarity within sites
AWA1	74.27
RAV1	66.46
RAV2	73.01
AWA2	84.19
AWA3	80.20
TUT1	79.72
TUT2	85.29
TUT3	64.46
NGA	73.29

Site	AWA1	RAV1	RAV2	AWA2	AWA3	TUT1	TUT2	TUT3	NGA
AWA1									
RAV1	44.80								
RAV2	47.10	41.89							
AWA2	33.33	38.92	36.98						
AWA3	33.21	35.35	35.01	19.42					
TUT1	40.72	42.66	39.51	32.07	27.55				
TUT2	54.21	61.64	50.77	42.37	41.35	39.09			
TUT3	67.63	74.74	62.64	62.02	60.24	53.53	34.76		
NGA1	67.68	68.18	60.26	59.22	55.10	51.21	38.79	48.33	

Table 23: Average % dissimilarity between pairs of sites based on macrobenthos composition.

A SIMPER analysis was performed using Primer 7. This analysis identifies the taxa that contribute most to the similarities (similarity) or differences (dissimilarity) between sites. **Figure 50** presents the results of this analysis. This graph shows the % contribution of each taxa at a site that collectively comprise more than 90% of the total abundance. Clear differences can be seen between sites, with a much greater number of taxa contributing at sites AWA1 and in the downstream and reference sites (TUT1-TUT3 and NGA).



Figure 50: % contribution of taxa contributing >90% of the macrobenthos composition at each site.

Epifauna and Macroalgae Community composition

Very few species were identified living on the sediment surface (**Appendix F**). Crab and polychaete burrow holes were observed across all sites. The estuarine snail *Potamopyrgus* sp. was observed in low abundance at site TUT2. Macroalgae in the form of fine green filaments were observed on the sediment surface at site AWA3. Photographs of the quadrats are included in **Appendix F**.

Sediment Anoxic Layer

The average depth detected of the anoxic layer across all sites except TUT3 was less than 1 cm, indicating anoxic surface sediment (**Appendix G**). Anoxic surface sediment is common within low energy environments and often results in a low abundance and distribution of marine species, due to sensitivity to an oxygen depleted environment. No definitive anoxic layer was observed at site TUT3. Prior to sampling a major storm event occurred in the area which required large volumes of water to be discharged from both the Ravensdown outfall and the Awatoto council pump. This event may have resulted in mixing of the sediment within the channels by the large flows of water, leading to oxygenation of the surface sediments. Additionally, dissolved oxygen within the sediment at TUT3 may have been influenced by higher river flows in the Tūtaekurī River and bioturbation, as large numbers of holes caused by burrowing fauna were observed on site.

Sediment Grain Size

Sediment across all sites was predominantly silt and clay (**Figure 51**, **Appendix H**). Site AWA2 had the largest proportion of silt and clay (80.9%) and site RAV1 had the lowest (41.3%). Site RAV1 had the highest proportion of coarser grain sizes, and the highest proportions of medium sand (11.0%), coarse sand (8.8%) and very coarse sand (4.5%).



Figure 51: Percent proportion of sediment grain size from each of the survey sites.

Sediment Contaminants

Sediment contaminant values were generally below default guideline values (DGV) (ANZG 2018; **Table 24**, Appendix I), where guidelines exist. Site NGA1 and RAV1 both had levels of cadmium, nickel and zinc that were above trigger values. Site AWA1 recorded zinc concentrations above the ANZG trigger values. Phosphorus, sulphur and fluoride do not have ANZG (2018) default guideline values.

Water Physiochemistry

There are no ANZG (2018) or ANZECC (2000) default water quality guidelines for values within estuarine environments. Instead, physiochemical parameters were compared with ANZG (2018) DGVs for cool, wet, lowland rivers.

Dissolved oxygen (%) at sites RAV1, RAV2, AWA2 and AWA3 were below the DGV (20th percentile). Sites AWA1, TUT1, TUT2 and NGA1 were within the DGV values (**Table 25**).

Conductivity (μ S/cm) had high variability across the sites owing to freshwater inflows. The highest conductivity was recorded at site AWA3, and the lowest at site NGA1.

pH was generally within the DGVs across all sites, with AWA1, TUT2 and NGA1 slightly above the DGV (80th percentile).
Table 24: Sediment contaminant values for each of the survey sites. Red indicates the value is above the ANZG (2018) Default Trigger Values.

	Units (Dry weight)	AWA1	RAV1	RAV2	AWA2	AWA3	TUT1	TUT2	TUT3	NGA1	ANZG (2018)
Parameter		Upstream of mixing zone	Witl	hin mixing :	zone	Do	wnstream	of mixing z	one	Reference site	
Total Recoverable Phosphorus	mg/kg	9,900	8,100	1,480	5,100	1,680	640	590	530	8,100	NA
Total Sulphur	g/100g	0.65	0.25	0.12	0.28	0.24	0.04	0.06	0.03	0.62	NA
Fluoride	mg/kg	980	3,200	380	880	450	310	320	330	6,500	NA
Total Recoverable Arsenic	mg/kg	16.1	9.8	3.9	7.2	3.9	3	3.9	4.1	8.5	20
Total Recoverable Cadmium	mg/kg	1.36	2.1	0.174	0.75	0.25	0.056	0.07	0.031	3.3	1.5
Total Recoverable Chromium	mg/kg	25	32	17.6	23	19.1	13.7	15	13	36	80
Total Recoverable Copper	mg/kg	25	24	9.5	17.4	11.4	6	7.7	7.7	71	65
Total Recoverable Lead	mg/kg	21	15.2	11.1	15.6	12	7.8	10	14.2	25	50
Total Recoverable Nickel	mg/kg	21	32	15	19.6	15.6	11.8	13	10.5	28	21
Total Recoverable Zinc	mg/kg	340	260	81	186	96	51	54	54	210	200

Table 25: Water physiochemistry measured parameters from sampling undertaken in July 2020. Red text indicates exceedance of guideline values

	AWA1	RAV1	RAV2	AWA2	AWA3	TUT1	TUT2	TUT3	NGA1	ANZG (2018)
Parameter	Upstrea m of mixing zone	Within mixing zone			Downstream of mixing zone				Reference site	
Time of Day	1430	1400	1307	1300	1210	1115	1359	1200	1200	-
Temperature (°C)	12.9	11.6	10.9	12.9	13.7	13.1	13.7	13.3	10.7	-
Dissolved Oxygen (%)	94.1	62.2	63.0	70.8	75.4	84.2	80.4	69.8	97.3	105 ²³ 80 ²⁴
Dissolved Oxygen (mg/L)	9.83	6.75	6.92	7.40	7.76	8.76	8.28	7.22	10.76	-
Specific conductivity (µS/cm)	3170	1389	1894	2476	2894	2901	2314	2466	792	145
рН	8.00	7.34	7.57	7.76	7.77	7.76	7.87	7.8	8.1	7.8 ² 7.23 ³

 23 80th percentile. 24 20th percentile.

8.2.3 Summary

Infauna community composition

- Highest species richness at TUT3 and NGA1 and lowest at RAV1.
- Poorest species diversity was observed at TUT2.
- Species diversity was poor overall, lowest at RAV1, moderate at TUT2 and NGA1 and highest at TUT2.
- The main taxa groups were similar across all sites, although different individual taxa dominated at the TUT sites and the reference site (NGA1).
- RAV1, RAV2, AWA1, AWA2, and AWA3 all had high numbers of species tolerant of a wide range of habitats and typical of habitats with larger freshwater influences.
- TUT1, TUT2, and TUT3 all showed lower freshwater influenced species and increasing diversity. TUT2 and TUT3 had a higher number of burrowing amphipods.
- NGA1 had the highest number of species present, but lowest individuals.
- There is moderate variability within sites and high variability between sites.

<u>Sediment</u>

Grain size

- All sites were predominantly comprised of silt and clay.
- Sites downstream of the mixing zone gradually got sandier, as was seen upstream of the mixing zone.
- RAV2 and AWA1 had similar amounts of sand and silt and clay.
- AWA2 had the highest proportion of silt and clay of all sites.
- RAV1 had the least amount of silt and clay and largest proportion of coarser grain sizes.

Sediment contaminants

- Cadmium, nickel, and zinc were all above ANZG (2018) Default Trigger Values at RAV1 and NGA1. Zinc was also over ANZG (2018) Default Trigger Values at site AWA1.
- Total recoverable phosphorus, total sulphur and fluoride largely followed the same pattern as trace metals.
- NGA1 has much higher phosphorus and fluoride values than most sites, and the same amount of phosphorus as RAV1.

Water Physiochemistry

- Dissolved oxygen (%) was well below guideline (20th percentile) at sites RAV1 and RAV2.
- Conductivity $(\mu S/cm)$ was variable across the sites owing to freshwater inflows.
- pH was generally within DGVs across all sites.

9. References

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Appendix A: Current Resource Consent Conditions (DP040143W) as required by Hawkes Bay Regional Council. Appendix B Results of trend analyses for ambient water quality samples collected between 31 October 2013 and 13 February 2020.

Site	Parameter	Median value	Р	Mean annual	RSKSE
	TSS	0	0.08	o 72	9 156
	Total Al	9	0.06	-0.73	-0.130
	Total Cd	0.25	0.05	-0.02	-6.400
	Total Ca	0	0.01	0	0.000
		0	0.11	0	0.000
	Total Ni	0	0.01	0	0.000
		0	0.26	0	0.000
		65	0.01	-6.59	-10.145
	Iotal Zn	0.02	0.74	0	0.000
	Fluoride	0.28	0.35	0	-0./14
	Total N	2	0.00	-0.19	-9.450
	Total Ammoniacal Nitrogen	0.50	0.05	-0.06	-11.200
AS1	Nitrite-N	0.03	0.15	0	-5.882
	Nitrate-N	0.76	0.01	-0.08	-10.789
	Nitrite/Nitrate-N	0.82	0.01	-0.08	-10.122
	TKN	1.22	0.10	-0.07	-5.656
	SRP	0.14	0.00	-0.02	-12.676
	TP	0.24	0.00	-0.03	-12.500
	Chlorophyll-a	0.01	0.27	0	0.000
	рН	0.01	0.21	0	-20.000
	DO	7.4	0.48	-0.05	-0.635
	Temperature	20.3	0.60	0.10	0.512
	Conductivity	3440	0.00	-346.33	-10.068
	Salinity	1.90	0.00	-0.22	-11.526
	TSS	14	0.92	0	0.000
	Total Al	0.36	0.11	0.02	5.833
	Total Cd	0	0.00	0	0.000
	Total Cr	0	0.18	0	0.000
	Total Cu	0	0.28	0	0.000
	Total Ni	0	0.04	0	0.000
	Total S	90	0.03	-6.59	-7.327
	Total Zn	0.02	0.57	0	0.000
	Fluoride	0.44	0.00	0.03	6.591
AS2	Total N	3.20	0.57	-0.04	-1.156
	Total Ammoniacal Nitrogen	0.79	0.10	-0.06	-7.215
	Nitrite-N	0.06	0.69	0	-1.695
	Nitrate-N	1.64	0.88	0	0.122
	Nitrite/Nitrate-N	1.70	0.89	0	0.000
	TKN	1.28	0.27	-0.05	-3.828
	SRP	0.99	0.00	-0.14	-14.242
	ТР	1.16	0.00	-0.12	-10.086
	Chlorophyll-a	0.01	0.58	0	0.000

Site	Parameter	Median value	Р	Mean annual Sen slope	RSKSE
	рН	8.00	0.60	0	0.000
	DO	7.20	0.35	-0.06	-0.847
	Temperature	19.50	0.71	0.10	0.503
	Conductivity	4550	0.02	254.49	5.593
	Salinity	2.40	0.05	0.11	4.375
	TSS	21	0.34	1.23	5.838
	Total Al	0.42	0.29	-0.01	-2.381
	Total Cd	0	0.02	0	0.000
	Total Cr	0	0	0	0.000
	Total Cu	0	0.05	0	0.000
	Total Ni	0	0.02	0	0.000
	Total S	103	0.01	4.55	4.420
	Total Zn	0.02	0.30	0	6.250
	Fluoride	0.52	0.00	0.03	5.385
	Total N	3.20	0.17	-0.12	-3.719
	Total Ammoniacal Nitrogen	0.88	0.13	-0.06	-6.932
AS3	Nitrite-N	0.06	0.21	0	-3.448
	Nitrate-N	1.27	0.75	-0.01	-0.551
	Nitrite/Nitrate-N	1.39	0.56	-0.02	-1.655
	TKN	1.46	0.27	-0.05	-3.356
	SRP	1.03	0.00	-0.10	-9.320
	ТР	1.26	0.00	-0.08	-6.667
	Chlorophyll-a	0.01	0.99	0	0.000
	рН	8.00	0.66	0	0.000
	DO	7.20	0.25	-0.06	-0.847
	Temperature	19.70	0.34	0.35	1.766
	Conductivity	5320	0.00	310.00	5.827
	Salinity	2.70	0.11	0.09	3.259
	TSS	14	0.62	0.22	1.557
	Total Al	0.22	0.61	0	-1.818
	Total Cd	0	0.02	0	0.000
	Total Cr	0	0.07	0	0.000
	Total Cu	0	0.93	0	0.000
	Total Ni	0	0.02	0	0.000
	Total S	110	0.01	5.64	5.126
	Total Zn	0.01	0.13	0	0.000
AS4	Fluoride	1.90	0.49	0.04	2.105
	Total N	2.60	0.25	-0.09	-3.500
	Total Ammoniacal Nitrogen	0.53	0.21	-0.03	-5.472
	Nitrite-N	0.07	0.74	0.00	-1.493
	Nitrate-N	0.66	0.17	-0.05	-7.576
	Nitrite/Nitrate-N	0.74	0.17	-0.07	-8.919
	TKN	1.54	0.35	-0.04	-2.597
	SRP	0.30	0.69	-0.01	-1.667
	ТР	0.07	0.79	-0.01	-11.765

Site	Parameter	Median value	Р	Mean annual Sen slope	RSKSE
	Chlorophyll-a	0.01	0.69	0	0.000
	рН	7.90	0.66	0	0.000
	DO	7.10	0.56	-0.03	-0.423
	Temperature	19.70	0.38	0.23	1.142
	Conductivity	4320	0.14	162.19	3.754
	Salinity	2.30	0.77	0	0.000
	TSS	20	0.81	0	0.000
	Total Al	0.50	0.40	-0.02	-3.200
	Total Cd	0	0.08	0	0.000
	Total Cr	0	0.08	0	0.000
	Total Cu	0	0.02	0	0.000
	Total Ni	0	0.28	0	0.000
	Total S	102	0.70	-1.80	-1.764
	Total Zn	0.01	0.43	0	0.000
	Fluoride	1.67	0.90	0	0.000
	Total N	3.20	0.72	-0.03	-0.938
	Total Ammoniacal Nitrogen	0.94	0.24	-0.06	-5.851
AS5	Nitrite-N	0.10	0.32	0	-4.124
	Nitrate-N	0.55	0.49	-0.02	-3.818
	Nitrite/Nitrate-N	0.61	0.38	-0.03	-4.262
	TKN	1.93	0.44	-0.05	-2.798
	SRP	1.02	0.18	-0.06	-5.490
	ТР	1.43	0.57	-0.03	-1.958
	Chlorophyll-a	0.01	0.52	0	0.000
	рН	7.90	0.85	0	0.000
	DO	7.10	0.61	-0.08	-1.099
	Temperature	20.40	0.69	0.08	0.402
	Conductivity	3560.00	0.11	-106.41	-2.989
	Salinity	2.10	0.01	-0.09	-4.095
	TSS	22	0.07	-1.49	-6.782
	Total Al	0.70	0.03	-0.05	-6.571
	Total Cd	0	0.45	0	0.000
	Total Cr	0	0.09	0	0.000
	Total Cu	0	0.68	0	0.000
	Total Ni	0	0.35	0	0.000
	Total S	79	0.49	1.06	1.338
156	Total Zn	0.01	0.86	0	0.000
A30	Fluoride	1.14	0.89	0	0.000
	Total N	1.92	0.79	-0.01	-0.677
	Total Ammoniacal Nitrogen	0.47	0.50	-0.02	-4.043
	Nitrite-N	0.06	0.55	0	-1.667
	Nitrate-N	0.41	0.62	-0.01	-2.683
	Nitrite/Nitrate-N	0.49	0.59	-0.01	-2.041
	TKN	1.21	0.56	-0.03	-2.231
	SRP	0.72	0.33	-0.03	-4.167

Site	Parameter	Median value	Р	Mean annual Sen slope	RSKSE
	ТР	0.95	0.60	-0.02	-2.421
	Chlorophyll-a	0.01	0.93	0	0.000
	рН	7.90	1.57	0	0.025
	DO	7.20	0.59	-0.03	-0.375
	Temperature	20.40	0.60	0.12	0.593
	Conductivity	3130	0.01	-200.84	-6.417
	Salinity	1.74	0.00	-0.17	-9.713
	TSS	1.50	0.99	0	0.000
	Total Al	0.04	0.41	0	4.545
	Total Cd	0	0.61	0	0.000
	Total Cr	0	0.75	0	0.000
	Total Cu	0	0.76	0	0.000
	Total Ni	0	0.56	0	0.000
	Total S	6	0.82	0	0.000
	Total Zn	0	0.09	0	0.000
	Fluoride	0.17	0.98	0	0.000
	Total N	0.18	0.25	0.01	3.889
	Total Ammoniacal Nitrogen	0.01	0.04	0	0.000
AS7	Nitrite-N	0	0.05	0	0.000
	Nitrate-N	0.06	0.33	0	0.000
	Nitrite/Nitrate-N	0.07	0.48	0	0.000
	TKN	0.06	0.05	0	0.000
	SRP	0.02	0.83	0	0.000
	ТР	0.02	0.98	0	0.000
	Chlorophyll-a	0	0.82	0	0.000
	рН	8.20	3.22	0.06	0.720
	DO	8.50	0.50	0	0.000
	Temperature	19.80	0.54	0.09	0.439
	Conductivity	305	0.05	4.55	1.491
	Salinity	0.15	0.00	0	0.000

Appendix C: Results of dye study (NIWA)

Appendix D: Process chemical risk assessment spreadsheets

Cortrol OS7780

	Cortrol OS7780										
Formulation	Use			Water base	ed dissolved oxygen scavenger / meta	l passivator					
Liquid	Supplier				GE Betz (a part of Suez)						
Water miscible	Area				Boiler						
pH 7.5	Use (kg/day)			3.07 (ba	sed on IXOM re-calculated useage for	2019-20)					
			Chemical Information								
	Ingredient(s)-NDA	Hydroquinone	1,4-Benzoquinone	Cort1	Cort2	Cort3	Cort4	Cort5			
	Composition (%)	2.5000	2.5000	0.0240	0.0080	0.0100	0.0001	0.0040			
	CAS #	123-31-9	106-51-4	Restricted	Restricted	Restricted	Restricted	Restricted			
	Chemical formula/ structure	CH CH Restricted Restr		Restricted	Restricted	Restricted					
	Molecular weight	110.1	108.1	134.2	151.2	117.2	44.1	40.0			
	Physical and Chemical Properties										
	LogP	0.64	0.26	No data	1.77	0.74	-0.16	Inorganic			
	Log D (pH 5.5, pH 7.4) ¹	0.53	0.13	No data	1.41	,-2.49,-1.73	0.29	Inorganic			
	ВСF (рН 5.5, рН 7.4) ¹	1.48	1.00	No data	6.96/6.95	1.00	1.00	Inorganic			
				Ecological In	formation						
	ECHA PNEC (Marine)	0.000057	No data	0.01	0.000403	0.006230	No data	Base - controlled by pH consent condition			
	ECHA Assessment Factor	100	No data	10,000	100	10,000	NA	NA			
	NORMAN PNEC (marine)		0.0136				0.0044				
	NORMAN Assessment Factor (marine)		10,000				10,000				
	Comment		Oxidation of hydroquinone during process to 1,4- benzoquinone								

Optisperse ADJ5150

Optisperse ADJ5150										
Formulation	Use	Alkalinity builder								
Liquid	Supplier	GE Betz (a part of Suez)								
Water miscible	Area			Boiler						
pH 14.0	Use (kg/day)	0.85	5 (based on IXOM r	e-calculated useage for 2019-20)						
		Chemical Information								
	Ingredient(s)-NDA	Sodium Hydroxide	ADJ1	Components (3) making up <0.1% of formulation (ADJ2)						
	Composition (%) CAS #		0.5000	0.0703 (total)						
			Restricted	Restricted						
	Chemical formula/ structure	NaOH								
	Molecular weight	40.0	58.4	NA						
		Physical and	d Chemical Pr	operties						
	LogP ¹	Inorganic	Inorganic							
	Log D (pH 5.5, pH 7.4) ¹	Inorganic	Inorganic							
	BCF (pH 5.5, pH 7.4) ¹	Inorganic	Inorganic							
		Ecolog	cical Informat	ion						
	ECHA PNEC (Marine)	Base - controlled by pH consent condition	Common salt in seawater							
	ECHA Assessment Factor	NA	NA							

Solus AP24

Solus AP24										
Formulation	Use		In	ternal boiler water	treatment					
Liquid	Supplier			GE Betz (a part of	Suez)					
Water miscible	Area			Boiler						
pH 12.3	Use (kg/day)		1.42 (based or	n IXOM re-calculate	ed useage for 20	019-20)				
		Chemical Information								
	Ingredient(s)-NDA	Sol1	Sol2	Sol3	Sol4	Components (9) making up 0.26% of formulation (Sol5)				
	Composition (%)	0.8400	0.2456	16.0000	0.489	0.2613 (total), 0.024 (average)				
	CAS #	Restricted	Restricted	d Restricted		Restricted				
	Chemical formula/ structure	Restricted	Restricted	Restricted	Restricted	Restricted				
	Molecular weight	205.9 105.0		Polymer	142.0	NA				
			Physical and Chem	ical Propertie	S					
	LogP	Inorganic	Inorganic		Inorganic					
	Log D (pH 5.5, pH 7.4)	Inorganic	Inorganic		Inorganic					
	BCF (pH 5.5, pH 7.4)	Inorganic	Inorganic		Inorganic					
			Ecological Inf	ormation						
	ECHA PNEC (Marine)	4.89	No data: ECHA state aquatic toxicity unlikely	No data	1.11					
	ECHA Assessment Factor	3	NA	NA	1000					
	NORMAN PNEC (marine)		No data	No data						
	NORMAN Assessment Factor (marine)	NA	NA						

Steammate NA0880

Steammate NA0880								
Formulation	Use		Blend of neutralising an	nines				
Liquid	Supplier	GE Betz (a part of Suez)						
Water miscible	Area		Boiler					
рН 12.7	Use (kg/day)	0.	.40 (based on IXOM re-calculated us	seage for 2019-20)				
		C	hemical Information					
	Ingredient(s)-NDA	SM1	Monoethanolamine	Dmapa				
	Composition (%)	0.2000	39.6000	19.9000				
	CAS #	Restricted 141-43-5		109-55-7				
	Chemical formula/ structure	Restricted	HO NH ₂	H ₃ C _N NH ₂ CH ₃				
	Molecular weight	105.1	61.1	102.2				
		Physica	al and Chemical Propertie	es				
	LogP	-1.50	-1.31	-0.29				
	Log D (pH 5.5, pH 7.4)	-4.13,-2.71	-4.19,-3.41	-4.31,-3.47				
	BCF (pH 5.5, pH 7.4)	1.00	1.00	1.00				
		Ec	cological Information					
	ECHA PNEC (Marine)	0.002	0.009	0.007				
	ECHA Assessment Fact	500	100	500				

Flogard MS6222

Flogard MS6222									
Formulation	Use	Water based corrosion inhibitor							
Liquid	Supplier	GE Betz (a part of Suez)							
Water miscible	Area	Cooling system							
pH <1.0	Use (kg/day)	0.80 (based on re-calculated usage from IXOM)							
	Chen	nical Information							
	Ingredient(s)	Phosphoric acid							
	Composition (%)	75.0000							
	CAS #	7664-38-2							
	Chemical formula/ structure	H3PO4							
	Molecular weight	98.0							
	Physical ar	nd Chemical Properties							
	LogP	Inorganic							
	Log D (pH 5.5, pH 7.4)	Inorganic							
	BCF (pH 5.5, pH 7.4)	Inorganic							
	Ecolo	gical Information							
	ECHA PNEC (Marine)	ECHA state no hazard identified							
	ECHA Assessment Factor	NA							

Gengard GN8020

Gengard GN8020								
Formulation	Use			Deposit a	and fouling con	trol agent		
Liquid	Supplier			GE I	Betz (a part of S	Suez)		
Water miscible	Area				Cooling system	1		
рН 2.6	Use (kg/day)	5.75	(based on IXOM	re-calculated usea	ge for 2019-20)	or 8.44 (based c	on worst-case of 2017-18)	
			Che	mical Inform	ation			
	Ingredient(s)-NDA	Gen1	Gen2	Gen3	Gen4	Gen5	Components (8) making up 0.1% of formulation (Gen6)	
	Composition (%)	0.5625	18.7500	0.3208	19.2101	0.6737	0.1061 (total), 0.0133 (average)	
	CAS #	Restricted	Restricted	Restricted	Restricted	Restricted	Restricted	
	Chemical formula/ structure	Restricted	Restricted	Restricted	Restricted	Restricted	Restricted	
	Molecular weight	116.1	Polymer	106.0	Polymer	142.0		
			Physical a	and Chemical	Properties			
	LogP	-0.01	No data	Inorganic	No data	Inorganic		
	Log D (pH 5.5, pH 7.4)	,-3.42,-4.73	No data	Inorganic	No data	Inorganic		
	BCF (pH 5.5, pH 7.4)	1.00	No data	Inorganic	No data	Inorganic		
			Ecol	ogical Inform	ation			
	ECHA PNEC (Marine)	0.01	No data	No data: aquatic toxicity unlikely	No data	1.11		
	ECHA Assessment Factor	1000	NA	NA	NA	1000		
	NORMAN PNEC (marine)		No data	No data	No data			
	NORMAN Assessment Factor (marine)		NA	NA	NA			

Spectrus BD1500

Spectrus BD1500								
Formulation	Use	Water based deposit control agent						
Liquid	Supplier	GE Betz (a part of Suez)						
Water miscible	Area	Cooling system						
рН 12.5	Use (kg/day)	0.19 (based on IXOM re-calculated useage for 2019-20)						
	Chemical Information							
	Ingredient(s)-NDA	Sodium hydroxide	BD1	Components (8) making up <0.1% of formulation (Spec2)				
	Composition (%)		17.8790	0.0075 (total), 0.001 (average)				
	CAS #	1310-73-2	Restricted	Restricted				
	Chemical formula/ structure	NaOH	Restricted	Restricted				
	Molecular weight	40.00	Polymer					
	Physical and Chemical Properties							
	LogP	Inorganic	No data					
	Log D (pH 5.5, pH 7.4)	Inorganic	No data					
	BCF (pH 5.5, pH 7.4)	Inorganic	No data					
	Ecological Information							
	ECHA PNEC (Marine)	Base - controlled by pH consent condition	0.00125					
	ECHA Assessment Factor	NA	10,000					

Inhibitor AZ8104

Inhibitor AZ8104										
Formulation	Use	Water based corrosion inhibitor								
Liquid	Supplier	GE Betz (a part of Suez)								
Water miscible	Area	Cooling system								
pH 12.7	Use (kg/day)		1.06 (based on IX)	OM re-calculated useage	for 2019-20)					
	Chemical Information									
	Ingredient(s)-NDA	Chlorotolyltriazole	AZ1	Sodium Tolyltriazole	Sodium Hydroxide	AZ2				
	Composition (%)	13.1000	3.2500	1.4000	1.1400	5.8000				
	CAS #	202420-04-0	Not assigned	64665-57-2	1310-73-2	Restricted				
	Chemical formula/ structure	CI N=N Na⁺	Not available	Na ⁺	NaOH	Restricted				
	Molecular weight	215.6	Not available	181.2	40.0	58.4				
	Physical and Chemical Properties									
	LogP ¹	Not available	Not available	1.78 Inorganic		Inorganic				
	Log D (pH 5.5, pH 7.4) ¹	Not available	Not available	1.78	Inorganic	Inorganic				
	BCF (pH 5.5, pH 7.4) ¹	Not available	Not available	Not available	Inorganic	Inorganic				
		Eco	logical Informati	ion						
	ECHA PNEC (Marine)	No data	No CASRN	0.008	Base - controlled by pH consent condition	Common salt in seawater				
	ECHA Assessment Factor	NA	NA	50	NA					
	NORMAN PNEC (marine)	No data	NA			NA				
	NORMAN Assessment Factor (marine)	NA	NA			NA				

Spectrus NX1100

Spectrus NX1100									
Formulation	Use	Biocide							
Liquid	Supplier	GE Betz (a part of Suez)							
Water miscible	Area			Со	oling system				
рН 3.0	Use (kg/day)			0.20 (based on IXOM r	re-calculated usea	ge for 2019-20)			
	Chemical Information								
	Ingredient(s)-NDA	Bronopol	Magnesium nitrate	Kathron 886	Magnesium chloride	NX1	NX2	NX3	
	Composition (%)	5.5440	3.6800	2.5760	1.6560	2.9400	0.9800	0.1903	
	CAS #	52-51-7	10377-60-3	55965-84-9	7786-30-3	Restricted	Restricted	Restricted	
	Chemical formula/ structure	HO NO ₂ HO	MgNO ₃		MgCl ₂	Restricted	Restricted	Restricted	
	Molecular weight	200.0	148.3	264.0	95.2	294.1			
	Physical and Chemical Properties								
	LogP ¹	1.72	Inorganic		Inorganic		Inorganic	Inorganic	
	Log D (pH 5.5, pH 7.4) ¹	0.47	Inorganic		Inorganic		Inorganic	Inorganic	
	BCF (pH 5.5, pH 7.4) ¹	1.34	Inorganic		Inorganic		Inorganic	Inorganic	
	Ecological Information								
	ECHA PNEC (Marine)	0.001	No adverse toxicity at 100 mg/L:	0.003	0.32	0.044	Acid - controlled by pH consent condition	0.068	
	ECHA Assessment Factor	100	NA	10	1000	10000	NA	10000	

Road Film Remover

Road Film Remover										
Formulation	Use	Fleet wash (Sandfords)								
Liquid	Supplier	Auto Shine Car Care Products								
Water miscible	Area			Sandfords trucl	c wash					
pH 9.5-10	Use (kg/day)			2.74						
	Chemical Information									
	Ingredient(s)	A-(4-Nonylphenyl)-w- hydroxy-poly(oxy-1,2- ethanyedlyl) branched	4-Nonylphenol, branched	Sodium Xylenesulfonate	Ethylenediamine Tetraacetic Acid	Sodium Phosphate, Tribasic	Sodium Hydroxide			
	Synonym	4-Nonylphenol, branched, ethoxylated	Nonylphenol (technical)							
	Composition (%)	5.0-10.0	5.0-10.0	10.0-15.0	2.0-5.0	2.0-5.0	1.0-2.0			
	CAS #	127087-87-0	84852-15-3	1300-72-7	60-00-4	7601-54-9	1310-73-2			
	Chemical formula/ structure	C25H44O6	C ₉ H ₁₉ OH	H ₃ C CH ₃		NaH ₂ PO ₄	NaOH			
	Molecular weight	440.6	221.4	208.2	292.2	138.0	40.0			
		1	Physical and Chemic	cal Properties						
	LogP ¹		5.82	No data	-0.43	Inorganic	Inorganic			
	Log D (pH 5.5, pH 7.4) ¹		5.43	No data	-5.98, -6.40	Inorganic	Inorganic			
	BCF (pH 5.5, pH 7.4) ¹		>7800	No data	1.00	Inorganic	Inorganic			
	Ecological Information									
	ECHA PNEC (Marine)	Data not provided	0.001	No data	0.22	ECHA state no hazard identified	Base - controlled by pH consent condition			
	ECHA Assessment Factor	NA	5	NA	100	NA				
	NORMAN PNEC (marine)	No data		0.01						
	NORMAN Assessment Factor (marine)	NA		10000						
	Comment	NP ethoxylates break down to NP	NP ethoxylates break down to NP							
XT88

		XT88					
Formulation	Use		Fleet wash (Sandford	ls)			
Opaque thin gel	Supplier		Waikaraka Holdings L	td			
Water miscible	Area		Sandfords truck was	h			
pH 9.0-9.1 (1% dilution)	Use (kg/day)		2.92				
		Chemical Inf	ormation				
	Ingredient(s)-NDA	Sodium dodecylbenzenesulfonate	Sodium metasilicate	Other non hazardous ingredients			
	Composition (%)	10 - 30	1 - 10	To 100			
	CAS #	25155-30-0	6834-92-0	Not applicable			
	Chemical formula/ structure	CH ₃ (CH ₂) ₁₀ CH ₂	Na_2SiO_3	Not applicable			
	Molecular weight	348.48	122.06	Not applicable			
		Physical and Chem	nical Properties				
	LogP	No data	Inorganic	Not applicable			
	Log D (pH 5.5, pH 7.4)	No data	Inorganic	Not applicable			
	BCF (pH 5.5, pH 7.4)	No data	Inorganic	Not applicable			
		Ecological Information					
	ECHA PNEC (Marine)	1.0	1.0	Not applicable			
	ECHA Assessment Factor	10	Not stated	Not applicable			

Mass balance

	Average use June 2019 to	Average discharge for								
	May	June 2019 to	Average pond	Average pond						
	2020	May 2020	concentration	concentration			Toxic component	Adjusted ecological		
Formulation	(kg/day)	(L/day)	(kg/L)	(mg/L)	PNEC (mg/L)	NDA code	% of formulation	guideline (mg/L)	RQ1	BCF
Cortrol OS7780	3.07	403,136	7.6E-06	7.62	0.000057	Hydroquinone	2.5%	0.002	3340	1.48
Cortrol OS7780	3.07	403,136	7.6E-06	7.62	0.0136	1,4-Benzoquinone	2.5%	0.5	14	1.00
Cortrol OS7780	3.07	403,136	7.6E-06	7.62	0.01	Cort1	0.024%	42	0.2	No data
Cortrol OS7780	3.07	403,136	7.6E-06	7.62	0.000403	Cort2	0.008%	5.0	1.5	6.96
Cortrol OS7780	3.07	403,136	7.6E-06	7.62	0.00623	Cort3	0.010%	62	0.1	1.00
Flogard MS6222	0.80	403,136	2.0E-06	1.98	No hazard identified	Phosphoric acid	75.0%	No hazard identified	No hazard identified	Inorganic
Genguard GN8020	5.75	403,136	1.4E-05	14.26	0.01	Gen1	0.5625%	1.8	8.0	1.00
Genguard GN8020	5.75	403,136	1.4E-05	14.26	1.11	Gen5	0.6737%	165	0.1	Inorganic
Inhibitor AZ8104	1.06	403,136	2.6E-06	2.63	0.008	Sodium tolyltriazole	1.4%	0.6	4.6	No data
Solus AP24	1.42	403,136	3.5E-06	3.52	4.89	Sol1	0.84%	582	0.01	Inorganic
Solus AP24	1.42	403,136	3.5E-06	3.52	1.11	Sol4	0.489%	227	0.02	Inorganic
Spectrus BD1500	0.19	403,136	4.7E-07	0.47	0.001	BD1	17.879%	0.007	67	No data
Spectrus NX1100	0.20	403,136	5.0E-07	0.50	0.001	Bronopol	5.544%	0.02	28	1.34
Spectrus NX1100	0.20	403,136	5.0E-07	0.50	0.003	Kathron 886	2.576%	0.12	4.3	4.19
Spectrus NX1100	0.20	403,136	5.0E-07	0.50	0.32	Magnesium chloride	1.656%	19.3	0.03	Inorganic
Spectrus NX1100	0.20	403,136	5.0E-07	0.50	0.044	NX1	2.940%	1.5	0.3	Inorganic
Spectrus NX1100	0.20	403,136	5.0E-07	0.50	0.068	NX3	0.193%	35	0.01	Inorganic
Steammate NA0880	0.4	403,136	9.9E-07	0.99	0.009	Monoethanolamine	39.6%	0.02	44	1.00
Steammate NA0880	0.4	403,136	9.9E-07	0.99	0.007	3-Dimethylaminopropylamine	19.9%	0.04	28	1.00
Steammate NA0880	0.4	403,136	9.9E-07	0.99	0.002	SM1	0.2%	1.0	1.0	1.00
Road Film Remover	2.74	403,136	6.8E-06	6.80	0.001	Nonylphenol (technical)	10.0%	0.01	680	1.00
Road Film Remover	2.74	403,136	6.8E-06	6.80	0.01	Sodium xylenesulfonate	15.0%	0.07	102	1.00
Road Film Remover	2.74	403,136	6.8E-06	6.80	0.22	EDTA	5.0%	4.4	1.5	1.00
XT88	2.92	403,136	7.2E-06	7.24	1.0	Sodium dodecylbenzenesulfonate	30.0%	3.3	2.2	No data
XT88	2.92	403.136	7.2E-06	7.24	1.0	Sodium metasilicate	10.0%	10.0	0.7	Inorganic
		,							RO<1	
									RQ>1	

Formulation	Component	RQ1	RQ2 (low tide discharge scenario) - vertically mixed	RQ2 (high tide discharge scenario) - surface only		BCF
Cortrol OS7780	1,4-Benzoquinone	14	5.0		2.9	1.00
Cortrol OS7780	Cort2	1.5	0.5		0.3	6.96
Optisperse ADJ5150	ADJ1		Common sa	alt in seawater		
Solus AP24	Sol4	0.02				
Steammate NA0880	Monoethanolamine	44	16		8.9	1.00
Steammate NA0880	DMAPA	28	10		5 . 8	1.00
Steammate NA0880	SM1	1.0	0.4		0.2	1.00
Flogard MS6222	Phosphoric acid		No hazai	d identified		
Genguard GN8020	Gen1	8.0	2.9		1.6	1.00
Inhibitor AZ8104	Sodiumtolyltriazole	4.6	1.6		0.9	No data
Spectrus BD1500	BD1	67	24.1		14	No data
Spectrus NX1100	Bronopol	28	9.8		5.6	1.34
Spectrus NX1100	Kathron 886	4.3	1.5		0.9	4.19
Road Film Remover	Nonylphenol (technical)	680	243		139	1.00
Road Film Remover	Sodium xylenesulfonate	102	36		21	1.00
Road Film Remover	EDTA	1.5	0.6		0.3	1.00
XT88	Sodium dodecylbenzenesulfonate	2.2	0.8		0.4	No data

Appendix E Fish species identified in the Waitangi Estuary, Tūtaekurī, Ngaruroro and Clive catchments from the New Zealand Freshwater Fish Database. Conservation status based on Goodman et al. (2013). Source: Death & Ekelund (2019)

	Migratory & Non-migratory spec	ies observed within the Waitangi Es	tuary
NZFFD code	Scientific name	Common name	Conservation Status
aldfor	Aldrichetta forsteri	Yelloweye mullet	Not threatened
angaus	Anguilla australis	Shortfin eel	Not threatened
angdie	Anguilla dieffenbachii	Longfin eel	At risk, declining
chefos	Cheimarrichthys fosteri	Torrentfish	At risk, declining
galmac	Galaxias maculatus	Inanga	At risk, declining
gamaff	Gambusia affinis	Gambusia	Introduced
golocot	Gobiomorphus cotidianus	Common bully	Not threatened
gobgob	Gobiomorphus gobioides	Giant bully	Not threatened
gobhut	Gobiomorphus huttoni	Redfin bully	At risk, declining
graham	Grahamina sp.	Estuarine triplefin	
hymen	Hyridella menziesi	Freshwater mussel	
marine	Marine	Marine species	
parane	Paranephrops spp.	Koura	
parcur	Paratya curvirostris	Freshwater shrimp	
retret	Retropinna	Common smelt	Not threatened
rhombo	Rhombosolea spp.	Unidentified flounder	
rhoret	Rhombosolea retiaria	Black flounder	Not threatened

	Migratory and estuarine species of	bserved within the Tutaekuri Catch	ment
NZFFD code	Scientific name	Common name	Conservation Status
angaus	Anguilla australis	Shortfin eel	Not threatened
angdie	Anguilla dieffenbachii	Longfin eel	At risk, declining
chefos	Cheimarrichthys fosteri	Torrentfish	At risk, declining
galbre	Galaxias brevipinnis	Koaro	At risk, declining
galmac	Galaxias maculatus	Inanga	At risk, declining
geoaus	Geotria australis	Lamprey	Threatened Nationally vulnerable
gobbas	Gobiomorphus basalis	Crans bully	Not threatened
golocot	Gobiomorphus cotidianus	Common bully	Not threatened
gobgob	Gobiomorphus gobioides	Giant bully	Not threatened
gobhub	Gobiomorphus hubbsi	Bluegill bully	At risk, declining
gobhut	Gobiomorphus huttoni	Redfin bully	At risk, declining
oncmyk	Oncorhynchus mykiss	Rainbow trout	Sports fish
retret	Retropinna	Common smelt	Not threatened
rhoret	Rhombosolea retiaria	Black flounder	Not threatened
salmo	Salmo	Unidentified salmonid	Sports fish
saltru	Salmo trutta	Brown trout	Sports fish

	Migratory and estuarine species	observed within the Ngaruroro Catch	ment
NZFFD code	Scientific name	Common name	Conservation status
angaus	Anguilla australis	Shortfin eel	Not threatened
angdie	Anguilla dieffenbachii	Longfin eel	At risk, declining
chefos	Cheimarrichthys fosteri	Torrentfish	At risk, declining
galbre	Galaxias brevipinnis	Koaro	At risk, declining
galmac	Galaxias maculatus	Inanga	At risk, declining
gobbas	Gobiomorphus basalis	Crans bully	Not threatened
golocot	Gobiomorphus cotidianus	Common bully	Not threatened
gobgob	Gobiomorphus gobioides	Giant bully	Not threatened
gobhub	Gobiomorphus hubbsi	Bluegill bully	At risk, declining
gobhut	Gobiomorphus huttoni	Redfin bully	At risk, declining
mugil	Mugil	Unidentified mullet	
oncmyk	Oncorhynchus mykiss	Rainbow trout	Sports fish
parcur	Paratya curvirostris	Freshwater shrimp	
retret	Retropinna	Common smelt	Not threatened
rhoret	Rhombosolea retiaria	Black flounder	Not threatened
salmo	Salmo	Unidentified salmonid	Sports fish
saltru	Salmo trutta	Brown trout	Sports fish

Migratory and estuarine species observed within the Clive Catchment							
NZFFD code	Scientific name	Common name	Conservation Status				
angaus	Anguilla australis	Shortfin eel	Not threatened				
angdie	Anguilla dieffenbachii	Longfin eel	At risk, declining				
chefos	Cheimarrichthys fosteri	Torrentfish	At risk, declining				
galmac	Galaxias maculatus	Inanga	At risk, declining				
geoaus	Geotria australis	Lamprey	Threatened Nationally vulnerable				
gobbas	Gobiomorphus basalis	Crans bully	Not threatened				
golocot	Gobiomorphus cotidianus	Common bully	Not threatened				
gobgob	Gobiomorphus gobioides	Giant bully	Not threatened				
oncmyk	Oncorhynchus mykiss	Rainkow trout	Sports fish				
retret	Retropinna	Common smelt	Not threatened				
rhoret	Rhombosolea retiaria	Black flounder	Not threatened				

Appendix F Quadrats for each site sampled in July 2020. Note: 5 replicates were taken at sites where able to do so.





Appendix G Profiles of sediment core samples collected at Ravensdown Awatoto monitoring sites collected July 2020.



Appendix H Particle size distribution of sediment samples from Ravensdown Awatoto

Site	Silt and Clay	Very Fine Sand	Fine Sand	Medium Sand	Coarse Sand	Very Coarse Sand
RAV1	41.26	15.66	18.81	10.97	8.79	4.46
RAV2	68.25	12.35	8.48	4.94	4.68	1.3
AWA1	68.76	15.17	9.09	5.45	1.53	0
AWA2	80.90	10.73	5.14	2.76	0.47	0
AWA3	76.88	14.06	6.05	2.56	0.45	0
TUT1	74.16	16.41	7.52	1.91	0	0
TUT2	66.56	19.66	10.54	3.06	0.18	0
TUT3	61.48	19.54	12.41	5.34	1.23	0
NGA1	59.03	14.21	20.95	5.81	0	0

monitoring sites collected July 2020.

Appendix I Sediment quality results



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Certif	icate of	Analys	sis				Page 1 of 2
Client: Contact:	Boffa Miskell L S De Luca C/- Boffa Misk PO Box 13373 Tauranga 314	Limited Iell Limited 3 1		Lat Dat Dat Qu Orc Clic Sul	o No: te Received: te Reported: ote No: der No: ent Reference: bmitted By:	2407079 24-Jul-2020 06-Aug-2020 105878 BM19983 BM19983 S De Luca	SPv1
Sample Ty	ype: Sediment						
	Si	ample Name:	AWA1 23-Jul-2020 2:00 pm	AWA2 22-Jul-2020 1:00 pm	AWA3 22-Jul-2020 12:19 pm	RAV1 23-Jul-2020 1:00 pm	RAV2 23-Jul-2020 1:10 pm
		Lab Number:	2407079.1	2407079.2	2407079.3	2407079.4	2407079.5
Individual T	ests						
Total Recove	erable Phosphorus	mg/kg dry wt	9,900	5,100	1,680	8,100	8,100
Total Sulphu	r*‡	g/100g dry wt	0.65	0.28	0.24	0.62	0.25
Fluoride*		mg/kg dry wt	980	880	450	6,500	3,200
Heavy metal	, trace level As,Cd,C	Cr,Cu,Ni,Pb,Zn					
Total Recov	erable Arsenic	mg/kg dry wt	16.1	7.2	3.9	8.5	9.8
Total Recov	erable Cadmium	mg/kg dry wt	1.36	0.75	0.25	3.3	2.1
Total Recov	erable Chromium	mg/kg dry wt	25	23	19.1	36	32
Total Recov	erable Copper	mg/kg dry wt	25	17.4	11.4	71	24
Total Recov	erable Lead	mg/kg dry wt	21	15.6	12.0	25	15.2
Total Recov	erable Nickel	mg/kg dry wt	21	19.6	15.6	28	32
Total Recov	erable Zinc	mg/kg dry wt	340	186	96	210	260
	Si	ample Name:	TUT1 22-Jul-2020 11:50 am	TUT2 21-Jul-2020 2:00 pm	TUT3 21-Jul-2020 12:00 pm	NGA1 23-Jul-2020 12:00 pm	
		Lab Number:	2407079.6	2407079.7	2407079.8	2407079.9	
Individual T	ests						
Total Recove	erable Phosphorus	mg/kg dry wt	1,480	640	590	530	-
Total Sulphu	r*‡	g/100g dry wt	0.120	0.040	0.060	0.030	-
Fluoride*		mg/kg dry wt	380	310	320	330	-
Heavy metal	, trace level As,Cd,C	Cr,Cu,Ni,Pb,Zn		1		1	
Total Recov	erable Arsenic	mg/kg dry wt	3.9	3.0	3.9	4.1	-

Total Recoverable Cadmium	mg/kg dry wt	0.174	0.056	0.070	0.031	-
Total Recoverable Chromium	mg/kg dry wt	17.6	13.7	15.0	13.0	-
Total Recoverable Copper	mg/kg dry wt	9.5	6.0	7.7	7.7	-
Total Recoverable Lead	mg/kg dry wt	11.1	7.8	10.0	14.2	-
Total Recoverable Nickel	mg/kg dry wt	15.0	11.8	13.0	10.5	-
Total Recoverable Zinc	mg/kg dry wt	81	51	54	54	-
Analyst's Comments						

[‡] Analysis subcontracted to an external provider. Refer to the Summary of Methods section for more details.

Summary of Methods

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively 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 Laboratories, 28 Duke Street, Frankton, Hamilton 3204.



Sample Type. Sediment			
Test	Method Description	Default Detection Limit	Sample No

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.

Sample Type: Sediment			
Test	Method Description	Default Detection Limit	Sample No
Environmental Solids Sample Drying*	Air dried at 35°C Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-9
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%.	-	1-9
Non-Routine sample preparation. Air drying and 180 um sieving.*	Air dried and sieved, <180 um fraction. Used for sample preparation.	-	1-9
Heavy metal, trace level As,Cd,Cr,Cu,Ni,Pb,Zn	Dried sample, <2mm fraction. Nitric/Hydrochloric acid digestion, ICP-MS, trace level.	0.010 - 0.4 mg/kg dry wt	1-9
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	1-9
Total Fluoride in solids alkaline fusion*	Alkaline fusion of sample. Methods of Soil Analysis 2nd Edition, Pt2, 26-4.3.3.	-	1-9
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	1-9
Total Sulphur (Sub SGS)*	LECO S144 Sulphur Determinator, high temperature furnace, infra-red detector. Subcontracted to SGS, Waihi. ASTM 4239.	0.010 g/100g dry wt	1-9
Total Fluoride in Solids*	Ion selective electrode. Methods of Soil Analysis 2nd Edition, Pt2, 26-4.3.3. (modified).	20 mg/kg dry wt	1-9

The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

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

Dates of testing are available on request. Please contact the laboratory for more information.

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.

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Ara Heron BSc (Tech)

Client Services Manager - Environmental

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