Marsden Point Refinery:

A Resource Consent Application to Renew 20 Resource Consents from the Northland Regional Council



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ChanceryGreen on behalf of The New Zealand Refining Company Limited, trading as **'Refining NZ'**

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Extended Executive Summary

Introduction

Streamlined Environmental Ltd (SEL) has been commissioned by The New Zealand Refining Company Ltd (trading as Refining NZ, and referred to herein as "Refining NZ") to undertake a water quality assessment to support the application for renewal of existing resource consents for the Marsden Point Refinery site at Ruakaka ("the Refinery"). The current resource consents are described in the Assessment of Environmental Effects (AEE) to which this report is attached.

There are two types of drainage system employed by the Refinery: the Continuously Oil Contaminated System ("the COC") and the Accidentally Oil Contaminated System ("the AOC").

The COC intercepts process water, stormwater and tank drainage water that is likely to be contaminated from processing and treatment activities at the site. The oil that is collected in the interceptors is directed back to the slops processing unit for recycling. The separated water is then pumped to the water treatment unit (the biotreater unit) for further treatment. When rainfall intensity exceeds 6 mm/h the treated water from the interceptors is discharged into the AOC.

The AOC is effectively the stormwater system for the site and generally has lower concentrations of contaminants from the Refinery. The reticulated stormwater network drains to the open channel drains within the site that all flow to the stormwater retention ponds and eventually discharge to the stormwater storage basin ("the SWB"). Stormwater from the SWB is pumped through a pipe along the No. 2 (western) Oil Jetty to an outfall. The stormwater discharge is tested for a range of water quality parameters in accordance with the consent conditions.

The impacts on the lower Whangarei Harbour marine receiving environment associated with contaminants discharged to surface water (as opposed to groundwater) from the Refinery SWB were assessed. The assessment addressed impacts on water and sediment in the marine receiving environment.

For this assessment, it was necessary to separate contaminants into those that are considered to be "traditional" (for example, petroleum hydrocarbons, metals, ammoniacal-nitrogen) and those that are considered to be "non-traditional", which encompasses many chemicals contained within formulations (hereafter called "process chemicals") used in the refinery process. "Traditional" contaminants are those that are routinely measured in the SWB and receiving environment. The majority of process chemicals have not been measured in the SWB or in the receiving environment. Therefore, a risk assessment approach was used to assess potential ecological effects of process chemicals in the receiving environment.

Hydrocarbon contamination of groundwater is managed by a hydraulic containment system that has operated at the site since 1983. The current extraction system comprises recovery wells and operates continuously. Recovered product is pumped to the COC and slops system for separation and treatment.

The impacts on the lower Whangarei Harbour marine receiving environment are associated with contaminants discharged to groundwater after discharge to surface water and subsequent flow of that surface water to the marine receiving environment.

Contaminants assessed

Parameters consistently measured¹ and herein assessed are:

- 16 polycyclic aromatic hydrocarbons (PAHs) acenaphthene; acenaphthylene; anthracene; benzo(a)anthracene; benzo(a)pyrene; benzo(b)fluoranthene; benzo(ghi)perylene; benzo(k)fluoranthene; chrysene; dibenzo(ah)anthracene; fluorene; fluoranthene; indeno(1,2,3,c,d)pyrene; naphthalene; phenanthrene; pyrene.
- 14 Phenols phenol; 2-methylphenol; 4-methylphenol; 2-chlorophenol; 2-nitrophenol; 4chloro-3-methylphenol; 2,4-dimethylphenol; 2,4-dichlorophenol; 2,6-dichlorophenol; 2methyl-4,6-dinitrophenol; 2,4,5-trichlorophenol; 2,4,6-trichlorophenol; 2,3,4,6tetrachlorophenol; pentachlorophenol.
- Total metals/<u>metalloids</u> <u>arsenic</u>; cadmium; chromium; copper; lead; mercury; nickel; zinc.
- Ammoniacal-nitrogen (NH_4 -N).
- Biochemical oxygen demand (5-day).
- Dissolved oxygen (DO).
- Faecal coliforms.
- pH.
- Salinity.
- Sulphide.
- Temperature.
- Total petroleum hydrocarbon (TPH).
- Total suspended solids (TSS).

With the exception of BOD_5 , all of these parameters are measured at NRC receiving environment water quality sites.

Nitrate-nitrogen (NO₃-N) was assessed in groundwater only.

Assessment criteria

Stormwater basin

Contaminant concentrations measured in the SWB during 2018 were assessed against consent limits to assess recent compliance of the refinery.

SWB data for the period 2014–2019 were used to assess discharge water quality status and temporal trends.

SWB sediment quality data from three sampling events – 2012, 2014 and 2016 – were used to assess sediment quality status and temporal trends.

¹ Some parameters have been measured sporadically. These have not been assessed due to lack of consistent data.

Receiving environment

The proposed Regional Plan for Northland (pNRP) is currently undergoing revision. The timeframe for the pNRP to become operative is not known at the time of writing as appeals continue to progress. Therefore, and until the pNRP is implemented, assessment of effects will be made against coastal water quality standards (CWQS), coastal sediment quality guidelines (CSQG) and groundwater quality guidelines (GWQG), where present, in both the currently operative Regional Plan (oNRP) and the pNRP (most recent appeals version dated June 2020).

Surface water quality guidelines (SWQG) used in this assessment are a combination of coastal water quality standards from both the oNRP and the pNRP, the Australian and New Zealand (ANZ) Guidelines for Fresh and Marine Water Quality 95% marine default guideline values (DGV), and water quality indices from Auckland Council. Generally, the <u>most restrictive ecological standards/guidelines</u> were used for the assessment, except for NH_4 -N, for which both oNRP and pNRP CWQS were assessed.

Sediment quality guideline values (SGVs) used in this assessment are the Canadian Council of Ministers of the Environment (CCME) Sediment Quality Guidelines for the Protection of Aquatic Life (metals) and the ANZ DGV for TPH and PAHs². CCME sediment guidelines for metals have been proposed by NRC in the pNRP.

Stormwater basin water and sediment quality

All parameters measured in the SWB in 2018 were within consent limits. Parameters assessed were: temperature; pH; BOD₅; TSS; COD; TPH; total phenols; NH₄-N; and sulphides.

SWB water quality data were assessed against SWQG to evaluate the risk quotient (RQ)³. This serves two main purposes:

- 1) The RQ provides an early warning of contaminants present in the SWB that may potentially cause adverse effects in the receiving environment; specifically, RQ > 1 for a particular contaminant signifies that the SWB concentration of that contaminant is <u>above</u> the applicable ecological guideline.
- 2) SWB RQs are used as inputs (maximum, mean, median values) into hydrological models to assess associated receiving environment concentrations under different scenarios (e.g., different combinations of winds and tides), from which potential adverse effects on water quality can be inferred.

The RQ does not include nearfield or far-field dilution, which may reduce contaminant concentrations in the receiving environment; instead, the RQ is akin to a "traffic light" approach to identifying contaminants in the SWB of potential concern. Contaminants in SWB with the greatest <u>potential</u> to cause adverse effects in the receiving environment are NH_4 -N, copper, zinc and faecal coliforms.

² ANZ DGV replaced the ANZECC Interim Sediment Quality Guidelines (ISQG) in 2018.

³ The dilution required to reduce the SWB contaminant concentrations to below applicable receiving environment SWQGs.

Sediment SWB contaminant concentrations were stable between 2012 and 2016, with the possible exception of total PAH. Contaminants in SWB sediment with the greatest potential for adverse effects in the receiving environment – i.e. those contaminants that exceed SQG by the largest margin – are mercury, zinc, copper, and TPH.

Although the SWB sediment contaminant concentrations are high in comparison with SQG, SQG are designed to be applied to the receiving environment. SWB sediment concentrations were input into a 3D-hydrodynamic model to estimate the receiving environment sediment concentrations, against which SQG can be compared for a more robust assessment.

Whole-effluent toxicity testing was undertaken on SWB water in September 2017 by NIWA and in May 2019 and September 2019 by Cawthron. All three tests were under normal Refinery operating conditions. There were two species in common, marine alga and blue mussel, across the three sampling events. By comparison of data for these two species, the September 2019 SWB discharge appears to have been more toxic than the May 2019 and September 2017 discharges. The maximum dilution required to reduce the toxicity of the SWB discharge water to a no-toxicity threshold is 256x, which is the worst-case scenario for the most sensitive marine species. There is evidence that pipi (*Paphies australis*) populations have been declining at Mair Bank since 2010. However, although based on only two toxicity tests, the SWB water is non-toxic to pipi at almost no dilution.

Between 2014 and 2019, SWB concentrations of some parameters changed significantly (P<0.05) and meaningfully (defined as >1% annual change):

- pH increased by 0.15 annually;
- NH_4 -N decreased by 0.44 mg/L-N annually;
- chromium increased by 0.001 mg/L annually.⁴

There are no significant temporal trends in SWB sediment quality data.

Northport operates a significant discharge in proximity to the Refinery. TSS concentration is higher in the Northport discharge (median 34 mg/L) compared with the Refining NZ discharge (median 13 mg/L) by a factor of around 3. The minimum, median and mean pH in Northport (6.40, 7.00, and 7.06, respectively) is lower compared with Refining NZ (7.40, 8.10, 8.00, respectively) by around 1 pH unit. Copper and lead concentrations are similar between Northport (median 0.0021, 0.0006 mg/L, respectively) and Refining NZ (median 0.0027, 0.0006mg/L, respectively). Zinc concentrations are higher at Refining NZ (median 0.0420 mg/L) than Northport (median 0.0178 mg/L) by a factor of around 2. Total PAHs were below the detection limit in both discharges.

Receiving environment water quality

NRC carry out monitoring of water, sediment and shellfish at sites within Whangarei Harbour. Relevant to this assessment, NRC monitor nine (9) water quality sites in Whangarei Harbour, including 4 sites in the inner harbour (100263, 100270, 100264, and 100537), 2 sites at the edge of the mixing zone (100265 and 100266), and 3 sites in the outer harbour (100268, 100190, and

 $^{^4}$ Chromium has 50% censored data (below detection limit). When censored data are replaced with a value 0.5x the detection limit, the annual increase is 0.0004 mg/L (+23% annually) (p = 0.01).

100269). Water quality data for the period 2014 to 2019 were used to assess the current receiving environment. In summary:

- All sites were consistently well oxygenated.
- At all sites, pH was well within the range of 7 to 8.5 required by the pNRP.
- There was very little difference in surface water temperature (generally less than 1 °C) across all sites.
- All sites had median annual NH_4 -N concentrations below the pNRP SWQG, but most sites consistently exceeded the oNRP SWQG of 0.005 mg/L. Sites on the edge of the mixing zone had low NH_4 -N concentrations (generally <0.010 mg/L) compared with sites in the inner harbour and the outer harbour.
- Metal/metalloid concentrations were generally below detection limits. Arsenic (a metalloid) was the only metal/metalloid consistently above detection limits.
- All phenols were below detection limits and less than 2% of the applicable ANZ marine DGV.
- Annual maximum total petroleum hydrocarbon (TPH) concentrations were generally very low and below detection limits, except in 2016, when maximum TPH concentration ranged between 0.4 and 1.7 mg/L. Over the period 2014 to 2018, there was no apparent difference between mixing zone sites and sites in the inner harbour and the outer harbour, suggesting that Refining NZ's SWB is not causing any elevation of TPH concentrations in the marine receiving environment. There are no applicable marine water quality guidelines for TPH.
- Sulphide was below the detection limit at all sites. There are no ANZ marine DGVs for sulphide.
- Annual-average TSS concentration for each of the years 2014 to 2018 was around 20 mg/L at all sites, which is not excessively high.

Temporal trends for selected parameters at NRC water quality sites were assessed with the NIWA software, Time Trends. The parameters selected for analysis were NH_4 -N, DO, pH and temperature. For each of these parameters there were consistent data and the concentrations were predominantly above detection limits.

- NH_4 -N, DO and pH trends were not significant at any site.
- For temperature, only the mixing zone and outer harbour sites showed significant (p = 0.04) or borderline significant (p = 0.05 0.06) trends, with all sites showing an increase in temperature between 2014 and 2019.

Receiving environment sediment quality

Seven (7) NRC sediment quality sites in Whangarei Harbour have been monitored reasonably consistently. These consist of 3 sites in the inner harbour (109265, 100127, 110593), 2 sites at the mixing zone boundary (100605 and 110624) and 2 sites in the outer harbour (100268 and 100190)⁵. The Refining NZ SWB was also monitored (site 100532). Sites 100127, 100605 and 100268 have been monitored since 2002, with data used for sediment quality status and temporal trend assessment.

 $^{^{\}scriptscriptstyle 5}$ The outer harbour sites – 100268 and 100190 – are also water quality sites.

The other 4 sites (and the Refining NZ SWB site) have been monitored since 2012 and data used only for sediment quality status.

The same suite of PAHs, phenols, TPH and metals/metalloids as measured at the water quality sites and the Refining NZ SWB was measured in receiving environment sediments. Additional total organic carbon (TOC) and grainsize (sediment texture, or particle size) analyses were undertaken at the sediment sites.

Refining NZ have also undertaken a one-off sediment quality analysis of eight (8) soft-sediment sites around the mixing zone in May 2019. This analysis is described in detail by De Luca (2020).

Sediment texture

Between 2012 and 2016, sediment texture at some NRC sediment sites was highly variable. NRC sampling protocol states that a single surficial sediment sample is collected at each site and samples are analysed for grain size by either Watercare or University of Waikato. Therefore, the high variability may be in part due to the lack of replicate samples and a single laboratory used for analysis.

Inner harbour sites were predominantly sandy over this time with very low coarse gravel and mud (<10%). The exception was a high mud content at site 110593 (64%), but this was observed only in 2012 and was 3% in 2014 and 2016.

Mixing zone sites were also predominantly sandy over this time period with a consistently low mud content but variable coarse sand and gravel. In 2012, mixing zone sites had a coarse sand and gravel of between 12% and 14%, which reduced to between 0% and 5% in 2014. Site 100265 remained at 0% in 2016, however site 110624 (Marsden Bank) increased to 50%.

The outer harbour sites encompass different settings and sediment types. Site 100268 is away from the main Whangarei Harbour channel, while site 100190 (Mair Bank) is on the edge of this channel. Site 100126 had a reasonably consistent very fine to medium sand content over this time period, but mud reduced from 23% in 2012 to 2% in 2016, which is in contrast to coarse sand and gravel, which increased from 4% to 17% over this time. Site 100190 (Mair Bank) underwent a significant increase in coarse sand and gravel, increasing from <1% to 94%. This may have been a contributing factor to reduction in pipi populations at this site in 2014 and 2016 compared to 2010.

<u>Toxicants</u>

Between 2012 and 2016, metal/metalloid sediment concentrations were relatively consistent and showed no clear spatial or temporal patterns. Furthermore, all metal/metalloid sediment concentrations were well below (generally <20% of) Canadian Council of Ministers of the Environment (CCME) sediment quality guideline values (SGVs).

Total PAH sediment concentrations were always below detection limits. Following conservative principles, data were set to the detection limit before being normalised to 1% TOC. Despite this, total PAH concentrations were less than 0.025% of the ANZ SGV.

TPH sediment concentrations normalised to 1% TOC were generally elevated across all sites in 2012, ranging from 45% to 150% of the SGV. Highest concentrations were generally away from the mixing zone, at inner harbour and outer harbour sites. TPH concentrations were markedly

reduced in 2014 and 2016, at less than 25% of the SGV. Virtually all TPH concentrations in 2014 and 2016 were below detection limits. TPH in receiving environment sediment does not appear to correlate with Refining NZ SWB sediment TPH concentrations.

Temporal trends for arsenic, chromium, lead and zinc sediment concentrations at NRC sediment quality sites (2002 to 2016) were assessed with Time Trends. All sediment metal concentrations reduced over the period 2002 to 2016, and virtually all decreases were meaningful (i.e. > 1% annual change).

Process chemicals

Refining NZ uses a multitude of process chemicals as part of the operation of the plant. Many of the chemicals contained within each formulation are not "traditional" contaminants (such as presented above). Important distinctions between "traditional" contaminants and process chemicals are:

- "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 normally measured (in both water and sediment) routinely in the SWB and at receiving environment sites, while (due to lack of analytical capabilities) process chemicals are not.

However, process chemicals may enter the SWB, from where they may ultimately be discharged to the marine receiving environment, potentially leading to adverse ecological effects. Therefore, a risk assessment procedure that is different to that used for "traditional" contaminants is needed for the process chemicals (see conclusions later in this executive summary).

Most of the process chemical formulations assessed are used on a daily basis, however special scenarios depicting a site shutdown, unintended chemical spills and fire training foams were included.

The risk assessment methodology applied to process chemicals was as follows.

- 1. Identification of process chemical formulations used at the Refinery, including usage data, location, and physical and chemical properties.
- 2. Identification of individual chemicals within each formulation. The identity of many chemicals was restricted under a non-disclosure agreement. For these restricted proprietary chemicals, generic codes are used in this report.
- 3. Identification of ecotoxicological effects. Data were extracted from material safety data sheets and ecotoxicological databases: the United States Environmental Protection Agency (USEPA) Ecotox knowledgebase database⁶, and the European Chemicals Agency (ECHA)⁷ information on chemicals database. Using the most conservative approach (representing the worst-case scenario), the lowest marine water ecotoxicological value the predicted no-effects concentration (PNEC) was used in the risk assessment.
- 4. The risk assessment was undertaken using a tiered approach.

⁶ <u>https://cfpub.epa.gov/ecotox/search.cfm</u>

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

- a) A worst-case SWB concentration of each chemical within each formulation was calculated through mass balance.
- b) An assessment was made of the worst-case scenario SWB concentration against the lowest ecotoxicological guideline by calculating a risk quotient. The risk quotient (RQ1) was calculated by dividing SWB concentration by the ecotoxicological guideline concentration, with a value >1 indicating a potential ecotoxicological effect. The RQ indicates the dilution required to reduce the concentration of the chemical to below ecotoxicological guidelines.
- c) Where RQ1 was >1, allowance for oil and water partitioning was undertaken, and an updated risk quotient (RQ2) calculated.
- d) Where RQ2 was >1, the dilution outside the mixing zone was calculated from 3D hydrodynamic modelling of various scenarios (MetOcean Solutions, 2020). An updated risk quotient (RQ3) was calculated.
- e) Where RQ3 was >1, potential for long-term effects involving persistence and/or bioaccumulation within the receiving environment was assessed by reference to (a) biodegradation data and (b) a bioaccumulation concentration factor (BCF).

A summary table of process chemicals is shown later in this executive summary.

Assessment of effects of SWB contaminants on marine receiving environment water quality

Hydrodynamic modelling

Hydrodynamic modelling (MetOcean Solutions, 2019: appended to this report as Appendix 5) consisted of running year-long simulations within two contrasting historical contexts (El Niño/La Niña episodes), actual events and extreme events:

- El Niño/La Niña episodes (June 2010–June 2011, and June 2015–June 2016, respectively), where the outfall from the diffuser is continuous (baseline conditions).
- Actual events based on 12 historical events, where the outfall from the diffuser was continuous and the SWB overflow was open and closed during specific times.
- Extreme events consisted of different spillway overflows combined with various tidal states (low tide and high tide), wind speeds (4, 8 and 15 m/s) and wind directions (northeast and southeast). Each combination of tide and wind was simulated in combination with a 100-year average recurrence interval (ARI) rainfall event, which generated fluvial discharges from rivers and streams entering the harbour. In addition, the 100-year ARI rainfall generated wastewater discharges from the Refinery's three outfalls.

Additionally, the hydrodynamic modelling considered two scenarios:

- An "existing" scenario, based on the actual bathymetry of the harbour, and;
- a "reclaim" scenario, with an additional proposed berth at Northport Marina (known as Berth 4) and an alternative lower Whangarei Harbour channel design (known as Option 4.2).

Results for the "existing" scenario only are discussed in this report as the "reclaim" scenario results were virtually identical.

<u>Dilutions</u>

Time series of dilutions⁸ of the SWB discharge for each scenario were extracted from the model at specific locations:

- C1–C4 (4 corners of the current mixing zone), and;
- P1-P9 (receiving environment sites around the lower Whangarei Harbour that are of specific ecological interest see De Luca, 2019).

Three dilutions were calculated from the model for each site:

- practical worst-case (lowest) dilution (5th percentile);
- practical normal-case dilution (median), and;
- practical best-case (highest) dilution (95th percentile).

An analysis of time series data for a period of almost two years between 2010-2011 and 2015-2016, under La Niña and El Niño conditions respectively, shows that the dilution at mixing zone and receiving environment sites (Figure 20) is greater than 256x for more than 99% of the time. The dominating driving force for the low dilution duration appears to be due to the background diffuser discharge (i.e. annual La Niña and El Niño data) and so the same duration statistics apply to actual and extreme events.

"Traditional" and process chemical contaminants present in the SWB that have a risk quotient >1 (indicating that they have the potential to cause adverse ecological effects) were subjected to the practical worst-case and normal dilutions.

A practical worst-case scenario for annual, actual and extreme modelled events was used, consisting of:

- lowest practical dilution at each site;
- maximum SWB contaminant concentrations;
- up to 24 hours after discharge.

A practical normal-case scenario for annual, actual and extreme modelled events was used, consisting of:

- median dilution at each site;
- median SWB contaminant concentrations;
- up to 24 hours after discharge.

⁸ MetOcean Solutions have undertaken further modelling of the dilutions in the "top" and "bottom" metre of water at all sites to better understand the dilution profile at shallow sites and how this may affect biota at the surface (e.g. mussels attached to rocks) or on the sea floor (i.e. benthic organisms). This information is being used in the marine ecology assessment (De Luca, 2019). For the purposes of assessing expected concentrations of SWB contaminants at specific receiving environment sites against water quality standards/guidelines (i.e. in this report), only depth average dilutions have been used as these are applicable to water quality guidelines.

Summary of effects on water quality

For all SWB discharges under the normal-case scenario (i.e. most of the time), all traditional contaminants had a receiving environment risk quotient <1 at all receiving environment sites. Generally, the risk quotients under this scenario were orders of magnitude smaller than 1, indicating a <u>negligible effect</u> on water quality at the edges and outside of the mixing zone.

Under worst-case scenarios, ammoniacal nitrogen (NH₄-N) and faecal coliforms (FC) are the only contaminants in the SWB that <u>may potentially lead to adverse ecological effects</u> outside the mixing zone.

 NH_4 -N in the SWB appears to have a <u>negligible effect on water quality outside the mixing zone</u> <u>most of the time</u>. However, for a small portion of the time (5%), NH_4 -N concentrations at sites outside the mixing zone may temporarily exceed water quality limits. However, these water quality limits are designed to assess effects from eutrophication and are usually based on annual median data (as is the case for pNRP and NH_4 -N). Therefore, any short-term increase in NH_4 -N concentrations (as highlighted by the worst-case scenarios) are unlikely to lead to increased risk of eutrophication due to their short duration.

Under the worst-case scenarios and at a few sites, FC risk quotients marginally exceed 1, with the greatest risk quotient being 6. The large concentrations of FC were sporadic, occurring approximately once per year. These spikes are attributed to a nesting colony of Red Billed gulls which inhabit the SWB every summer, with up to 2000 nesting pairs.

A summary of fate and risk of each process chemical formulation is shown in Table E1, which summarises RQ1, RQ2 and to RQ3 described above for each formulation. Of the 18 formulations assessed, 13 are in use every day, 2 have been associated with spill events, 2 are used in the Refinery shutdown and 1 is used for fire training at the Refinery on a routine but infrequent basis.

For everyday use process chemicals, 6 formulations showed a <u>negligible</u> ecotoxicological risk (RQ1 and/or RQ2 <1),⁹ which obviates the need for further receiving environment dilution. For the remaining 7 everyday use process chemicals, dilution in the receiving environment was sufficient to reduce the risk quotient RQ3 to less than 1 for all except Cortrol OS7780.

One everyday use formulation – Cortrol OS7780– had highest RQ3 of 4.6; however, this is based on very conservative assumptions and will unlikely lead to adverse ecological effects. Cortrol OS7780 is in the process of being replaced by RNZ with an alternative formulation (Cortrol OS5614), which will lead to a net result of the removal of the toxic component of Cortrol OS7780 (1,4-Benzoquinone) and a negligible increase to the current background concentration of NH₄-N in the SWB and receiving environment.

The process chemicals used in the Refinery shutdown led to <u>negligible</u> risk of ecological effects in the receiving environment.

⁹ This includes Klaraid IC1172, for which the active ingredient (aluminium) has no applicable marine water quality guideline.

An accidental spill of DIPA over a period of 5 days in May 2018 may, if unmanaged,¹⁰ have led to <u>short-term more-than-minor ecological effects</u> outside the mixing zone. However, the ecological effects threshold is extremely conservative, and it is <u>highly unlikely</u> that there were any <u>acute ecotoxicity effects</u> in the receiving environment as a result of the DIPA spill.

ADIP-X spills are infrequent, with the largest spill over the last 15 years being 100 L. Under this scenario, ADIP-X may have led to <u>short-term more-than-minor ecological effects</u> outside the mixing zone. However, the ecological effects threshold is extremely conservative, and it is highly unlikely that there were any acute ecotoxicity effects in the receiving environment as a result of the ADIP-X spill.

The fire training foam Solberg DoD3155 is used on a routine but infrequent basis at the Refinery. A <u>negligible ecological risk</u> was presented under the normal-use scenario but worst-case dilution in the receiving environment. The causative chemical in the formulation (CPB) is readily biodegradable.

Overall, I consider the discharges of most contaminants from the Refinery SWB to have a less than minor effect on water quality in the marine receiving environment outside the current mixing zone. A few contaminants may exhibit no more than minor <u>and</u> transitory effects: ammoniacal nitrogen (NH_4 -N); faecal coliforms (FC); and the every-day process formulation Cortrol OS7780 (in the process of being replaced by a more benign formulation Cortrol OS5614)

Formulation	Toxic Component ¹	RQ1	RQ2	Highest RQ3 ²				
Everyday use								
BetzDearborn Isoparaffins		86	86	0.5				
Cortrol OS7780	1,4-Benzoquinone	797	797	4.6				
Embreak 2021	NP	10,296	0.02					
Klaraid IC1172	Aluminium	Not applicable						
Spectrus NX1100	Bronopol	2.2	0.1					
Inhibitor AZ8104	Sodium Tolyltriazole	1.9	0.03					
Crystalfloc Cationic Emulsions	Adipic acid	6.2	6.2	0.04				
Embreak 2050	DGME	0.5						
Steammate NA0880	MEA	142	142	0.8				
Genguard GN8220	Gen2	9.4	9.4	0.05				
Spectrus BD1501E	GE1	1.1	1.1	0.02				
Optispearse ADJ5150	Sodium hydroxide	0.6						
Optispearse HP2650	Sodium hydroxide	3.4	3.4	0.02				
	Spill e	vent						
ADIP-X	MDA	1945	1945	11				
DIPA	DIPA	1417	1412	8				
	Refinery shutdown							
CC Eliminator	Lauramine Oxide	4454	2.4	0.01				
CC 414P	d-Limonene	324	0.01					

¹⁰ The risk assessment in this report assumes worst-case, i.e. no management intervention was implemented for a spill event. However, Refining NZ have a range of process to avoid and respond to accidental spills and in my opinion the risks from these spills would have been mitigated at the time.

Formulation	Toxic Component ¹	RQ1	RQ2	Highest RQ3 ²			
CC 414P	Diethanolamine	76	75	0.4			
Fire training							
Solberg DoD3155 CPB 106 0.6							
Solberg DoD3155	DGMBE	15	15	0.2			

¹ NP=Formaldehyde Polymer With 4-Nonylphenol And Oxirane; Aluminium=Aluminium Chlorohydrate; DGME=Diethylene Glycol Monobutyl Ether; MEA=Monoethanolamine; Copolymer=Ethylene/Propylene Oxides Copolymer; MDA=Methyldiethanolamine; CPB=Cocoamido propyl betaine; DGMBE= Diethylene glycol mono butyl ether.

² For all, based on worst-case La Niña annual event.

³ Colour codes: < 1 = green; 1-10 = orange; >10 = red.

Cumulative effects on the receiving environment from all sources are low with good water, sediment and shellfish quality in Whangarei Harbour. Whole effluent testing of the SWB integrates all contaminants against relevant marine species and the marine ecology assessments are made on the worst-case scenario. Although some contaminants in the Refinery SWB have the potential to bioaccumulate, there is no evidence of bioaccumulation to higher trophic species levels. All process chemicals present in the Refinery SWB have extremely low bioaccumulation potential.

Groundwater quality

<u>Summary of the current groundwater condition</u>

Tonkin & Taylor Ltd (2019) has developed a hydrogeological conceptual site model of groundwater contamination at the Refinery.

Aspects of relevance to this report are:

- review of reports and data sources regarding contaminant sources, geological setting, hydrogeological conditions and the marine environment;
- completion of one round of groundwater sampling in June 2019 to assess per- and polyfluoroalkyl substances (PFAS) contamination at the location of the current onsite fire training area;
- completion of one round of groundwater sampling in September 2019 to provide recent data for potential contaminants that had either not been previously analysed or not analysed for some years.

Tonkin & Taylor Ltd (2019) compared the groundwater analytical results to guidance values adopted from the following:

- ANZECC 2000¹¹, 80% level of protection for marine ecosystems (95% level of protection for benzene);
- Ministry of Health 2018 Drinking-Water Standards for New Zealand 2005 (Revised 2018) (Ministry of Health, 2018); and
- for PFAS, the Australian Department of Health *Health-Based Guidance Values for PFAS for Use in Site Investigations in Australia* (accepted by the Ministry of Health in 2017 as interim guidance levels) (Australian Department of Health, 2017).

¹¹ The ANZECC 2000 guidelines have been revised (Australian and New Zealand Governments, 2018).

The current groundwater condition was summarised by Tonkin & Taylor (2019) as follows:

- LNAPL (a light non-aqueous phase liquid), sourced from historic losses at the site, is contained by the continuously operating hydraulic containment system.
- Dissolved phase hydrocarbons, sourced from the LNAPL plume, are also contained by the system such that there are <u>no exceedances of the ANZECC Guidelines for dissolved phase</u> <u>TPH, BTEX, PAH or phenol constituents in wells outside of the hydraulic containment</u> area.
- While there is limited groundwater quality data for chlorinated solvents, if a loss of solvents had occurred historically, it would have been in an area where groundwater is captured by the containment system.
- There are concentrations of dissolved metals (arsenic, copper, iron, manganese and zinc) in some of the groundwater wells outside of the containment area that exceed the ANZECC Guidelines. The exceedances may be due to naturally occurring concentrations rather than a specific source (or sources).
- There are concentrations of nitrate-nitrogen (NO $_3$ -N) above the adopted guideline 80% value in six perimeter wells outside of hydraulic containment. The nitrate appears likely to be at least partially sourced from the former land farms and potentially from the stormwater retention basins.
- PFAS have been detected in groundwater near the fire training ground. The reported concentrations did not exceed the ANZECC Guidelines 95% level of protection, but do exceed the 99% level of protection, in some cases because the laboratory level of detection was raised due to interference from other PFAS. The initial PFAS assessment focussed on the potential worst-case location (the current fire training area where fluorinated firefighting foams may have been used for up to 30 years of firefighting training).

Sampling of groundwater and surface water at Bream Bay beach was undertaken by Refining NZ in November 2019 to provide additional data down-gradient of the Refinery. This is summarised later.

Potential effects of groundwater contaminants on marine receiving environment

Some groundwater ecological guidelines are different to the corresponding marine receivingenvironment SWQG. As the receiving environment for groundwater outside the hydraulic containment is the marine receiving environment, groundwater contaminant concentrations were compared against SWQG. Following a conservative approach, maximum groundwater contaminant concentrations were compared against applicable SWQG. Of note, nitrate-nitrogen was not included in SWQG used to assess surface water quality, as receiving environment NO_3 -N data are sporadic. As NO_3 -N in groundwater from the Refinery is a potential issue, and recent sampling included NO_3 -N, it was included in this assessment.

Cadmium, chromium, copper, lead, nickel and zinc maximum <u>total</u> groundwater concentrations exceeded applicable SWQG (RQ >1), with only arsenic below the SWQG.

Maximum <u>dissolved</u> arsenic, cadmium, lead, mercury, nickel and vanadium groundwater concentrations were below applicable SWQG (RQ < 1). RQ exceeded 1 for chromium, cobalt, copper, manganese and zinc, with RQ ranging from 1.05 (chromium) to 25 (zinc).

The oNRP specifies a default coastal water quality standard concentration for nitrate-nitrogen (NO₃-N) of 0.01–0.06 mg/L. The pNRP has no coastal water quality standard for NO₃-N, but specifies an annual median nitrite-nitrate nitrogen (NNN) coastal water quality standard concentration for estuaries of <0.048 mg/L.

The maximum NO₃-N groundwater concentration (13.9 mg/L) exceeded the <u>lowest</u> value (0.01 mg/L) of the range of oNRP coastal water quality standard concentrations by 1,390x. If the <u>highest</u> value (0.06 mg/L) of the range of oNRP coastal water quality standard concentrations is used, the exceedance (RQ) is 232x.

The pNRP SWQG for nitrite-nitrate nitrogen (NNN) (0.048 mg/L) is effectively for NO_3 -N, as nitrite is a minimal component (ca. 0.2%) of NNN. This is close to the high end of the oNRP SWQG range (0.06 mg/L).

In summary, PFAS results of relevance to the marine receiving environment are:

- Total PFHxS has no relevant guidelines to assess against.
- Maximum total PFOS concentration (0.07 μ g/L) was below interim ANZECC 80% (31 μ g/L) and 95% (0.13 μ g/L) marine guidelines. The detection limit for total PFOS (0.01 μ g/L) was not sufficient to assess against the ANZECC 99% marine guideline (0.00023 μ g/L).
- Maximum PFOS + PFHxS concentration (0.22 $\mu g/L)$ was ca. 10x below the recreational water guideline;
- Total PFOA concentrations were well below all relevant criteria.

Groundwater dilution in receiving environment

Groundwater outflow from the Refinery was estimated by Tonkin & Taylor to be 458,525 m³/year, or 1,256 m³/day. If the Refinery is estimated to occupy 3 km of coastline, then the outflow will be 419 m³/day/km of coastline, or 0.419 m³/day/m of coastline. In contrast, the average discharge from the stormwater basin in 2018 was 6,369 m³/day. Therefore, groundwater discharge from the Refinery (when considered as a diffuse discharge over 3 km) is orders of magnitude below the surface water discharge (when considered as a point source discharge). Although tidal flushing has not been modelled at the open-ocean sites, it is expected to be large, leading to high dilution of groundwater discharges.

Beach groundwater and surface water sampling, November 2019

Refining NZ undertook groundwater and surface water sampling along the beach side of the Refinery (at the open-ocean sites). Nine groundwater sites on the beach and nine surface water sites 3–4 m immediately adjacent on the ocean side were collected at the same time. These sites were close to the NRC open-ocean site 100629 (Bream Bay). Dissolved metals (arsenic, cadmium, chromium, copper, lead, nickel, and zinc) and nitrogen species (total nitrogen, total ammoniacal-nitrogen, nitrite-N, nitrate-N+nitrite-N [NNN] and total Kjeldahl nitrogen [TKN]) were measured.

Dissolved metal/metalloid concentrations in groundwater samples and surface water samples were below applicable SWQG, with one exception. Dissolved zinc in 6 out of the 9 groundwater samples exceeded the SWQG (0.015 mg/L) by a maximum of 4.4x. However, surface water zinc concentrations 3–4 m immediately adjacent on the ocean side were all below the detection limit

(0.004 mg/L) and less than 30% of the SWQG. Perimeter groundwater wells within the Refinery, sampled in September 2019, had dissolved chromium, copper and zinc concentrations at 1.05x, 20x and 25x applicable SWQG, respectively. This suggests that groundwater is being rapidly diluted as it moves from within the Refinery to groundwater beach sites and further to surface water. Since 2015, the NRC open-ocean site 100629 (Bream Bay) has only been measured in September 2015; all metal/metalloid concentrations (total not dissolved) were below applicable SWQG.

The maximum nitrate-nitrogen (NO₃-N) groundwater concentration (0.026 mg/L) exceeded the <u>lowest</u> value (0.01 mg/L) of the range of oNRP coastal water quality standard concentrations by 2.6x, however maximum surface water NO₃-N concentrations were 10% of the same standard. For context, the maximum groundwater NO₃-N concentration at perimeter wells of the Refinery was 1,390x this standard. High NO₃-N concentrations in groundwater are likely to be from a mixture of historic contamination (the Refinery is predominantly hard surface now) and current catchment leaching. However, the extent of historic and current catchment contamination is unknown.

Nitrite-nitrate nitrogen (NNN) also followed the same trend of concentration reduction, with maximum risk quotient of 295, 0.9, and 0.04 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively.

Ammoniacal-nitrogen (NH_4 -N) followed the same trend of concentration reduction with maximum risk quotients (assessed against the oNRP value of 0.005 mg/L) of 176, 126, and 8 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively. When assessed against the pNRP value of 0.023 mg/L, the maximum risk quotient was 38, 27, and 1.7 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively. However, these water quality limits are designed to assess effects from eutrophication and are usually based on annual median data (as is the case for pNRP and NH_4 -N). Although based on a single monitoring event (and not annual data), median risk quotients were calculated for NH_4 -N in beach groundwater and beach surface water sites when assessed against the oNRP, and 4.6 and 1.0, respectively, for beach groundwater and beach surface water sites when assessed against the pNRP.

Since 2014, the NRC open-ocean site 100629 (Bream Bay) has been measured annually, with NH_4 -N concentrations ranging from 0.003 – 0.017 mg/L. These values are comparable with sites within Whangarei Harbour, but all are below the pNRP SWQG (0.023 mg/L).

In summary, the results of the groundwater perimeter sampling at the Refinery, along with the single beach sampling event in November 2019, show a clear reduction in concentrations of all toxicants as groundwater migrates from the Refinery to beach groundwater and into nearby surface water. There are minor localised effects at the beach groundwater sites for NH_4 -N, however this is based on a single monitoring event and effects were less than minor at beach surface water sites (when assessed against the pNRP) and there is no evidence that effects are seen at the NRC water quality site at Bream Bay.

1. Introduction

Streamlined Environmental Ltd (SEL) has been commissioned by The New Zealand Refining Company Ltd (trading as Refining NZ, and referred to herein as "Refining NZ") to undertake a water quality assessment to support the application for renewal of existing resource consents for the Marsden Point Refinery site at Ruakaka ("the Refinery"). The current resource consents are described in the Assessment of Environmental Effects (AEE) to which this report is attached.

The water quality assessment assesses potential effects on the receiving environment water quality associated with contaminants contained in both surface water and groundwater discharges produced as part of the refining process. The assessment of effects on water quality draws on information from hydrodynamic modelling of surface water (MetOcean Solutions, 2019, appended in Appendix 5) and a groundwater conceptual model (Tonkin & Taylor Ltd, 2019), which feeds into potential downstream effects on ecological health (De Luca, 2020) and on human health through shellfish body burden (Environmental Medicine Limited, 2020).

1.1 Surface and groundwater infrastructure

1.1.1 Surface water

There are two types of drainage system employed by the Refinery: the Continuously Oil Contaminated System ("the COC") and the Accidentally Oil Contaminated System ("the AOC"). The COC and AOC systems are described in detail in the AEE. A summary is provided here.

The COC intercepts process water, stormwater and tank drainage water that is likely to be contaminated from processing and treatment activities at the site. The COC consists of five sewer networks and oil interceptors, oil sumps and pumps. The oil that is collected in the interceptors is directed back to the slops processing unit for recycling. The separated water is then pumped to the water treatment unit (the biotreater unit) for further treatment. Separated water from the interceptors (for rainfall events of up to 6 mm/h) is also pumped back to the biotreater for further treatment. When rainfall intensity exceeds 6 mm/h the treated water from the interceptors is discharged into the AOC.

The AOC typically collects water that is unlikely to be contaminated by process activities or chemicals, but may, as a consequence of contact, be potentially contaminated. The AOC is effectively the stormwater system for the site. The reticulated stormwater network drains to the open channel drains within the site that all flow to the stormwater retention ponds and eventually discharge to the stormwater storage basin ("the SWB"). Stormwater from the SWB is pumped through a pipe along the No. 2 (western) Oil Jetty to an outfall. The stormwater discharge is tested for a range of water quality parameters in accordance with the consent conditions.

The impacts on the lower Whangarei Harbour marine receiving environment associated with contaminants discharged to <u>surface water</u> (as opposed to groundwater) from the Refinery SWB were assessed. The assessment addressed impacts on water and sediment in the marine receiving environment.

For this assessment, it was necessary to separate contaminants into those that are considered to be "traditional" (for example, petroleum hydrocarbons, metals, ammoniacal-nitrogen) and those that are considered to be "non-traditional", which encompasses many chemicals contained

within formulations (hereafter called "process chemicals") used in the refinery process. "Traditional" contaminants are those that are routinely measured in the SWB and receiving environment. These are covered in Section 2. The majority of process chemicals have not been measured in the SWB or in the receiving environment. Therefore, a risk assessment approach was used, which is covered in Section 3.

1.1.2 Groundwater

A hydraulic containment system has operated at the site since 1983 to manage hydrocarbon contamination of groundwater. The current extraction system comprises recovery wells and operates continuously. Recovered product is pumped to the COC and slops system for separation and treatment.

The impacts on the lower Whangarei Harbour marine receiving environment associated with contaminants discharged to <u>groundwater</u> after discharge to surface water and subsequent flow of that surface water to the marine receiving environment. Groundwater assessment is covered in Section 4.

2. Surface Water Quality

2.1 Assessment criteria

2.1.1 Consent limits

Resource consent AUT.008319.01.04 provides limits on SWB discharge volumes and concentrations and effects at the edge of the receiving environment. These are summarised in the respective sections below, to provide commentary on compliance of the refinery.

2.1.2 Northland Regional Plan

The proposed Regional Plan for Northland (pNRP) is currently undergoing revision. The timeframe for the pNRP to become operative is not known at the time of writing. Therefore, and until the pNRP is implemented, assessment of effects will be made against coastal water quality standards (CWQS), coastal sediment quality guidelines (CSQG) and groundwater quality guidelines (GWQG), where present, in both the current operative Regional Plan (oNRP) and the pNRP (most recent decisions version)¹².

The approach used in this assessment is to summarise standards/guidelines from both the oNRP and the pNRP (most recent decisions version) and compare receiving environment values against both sets of standards/guidelines. Where these are markedly different – for example, a parameter complying with a guideline/standard from the oNRP but not complying with a guideline/standard from the pNRP – comment will be provided.

<u>Coastal water quality standards</u>

CWQS from both the oNRP and the pNRP (most recent decisions version) are summarised in Table 1.

The oNRP differentiates between natural quality standards (CN), general quality standards (CA) and contact recreation standards (CB). CN standards provide for the protection of natural state, CA standards provide for virtually all uses and protection of marine ecosystems, and CB standards provide for contact recreation in coastal waters.

CA standards are the most relevant for this assessment (see Figure 1). CN standards are too restrictive – they state that values "shall not be altered" – presumably to protect pristine coastal environments. Most CB standards are not applicable, except for faecal coliforms, which are discussed later in this section.

¹² At the time of writing, the most recent decisions version of the proposed NRP is June 2020.



Figure 1. Coastal water quality classifications in the oNRP.

The most recent online¹³ decision version (May 2019) of the pNRP separates CWQS by coastal water quality management units.

Coastal water quality management units of relevance to this application are for estuaries (coloured teal in Figure 2) and open coastal water (coloured grey in Figure 2). All water quality sites (see Figure 13) are classed as estuarine except for Bream Bay (100269), which is open coastal water.

In the pNRP, estuaries and open coastal water have different water quality standards for some attributes (Table 1). For dissolved oxygen and ammoniacal nitrogen, the WQS for open coastal water states "no discernible change" after allowing for reasonable mixing. This suggests these standards are of relevance to discharges directly to open coastal waters only. The Refining NZ SWB discharges to estuarine water and any defined mixing zone is far from site 100269. As the hydrodynamic modelling (MetOcean Solutions, 2020) shows, dilution of the SWB discharge at site 100269 is >10,000 under all scenarios, and any effects on water quality from the discharge will therefore be negligible¹⁴ (see Section 5.2 for figures showing discharge plumes). Therefore, although site 100269 is included in the receiving environment comparison with estuarine sites, it

¹³ <u>https://nrcgis.maps.arcgis.com/apps/webappviewer/index.html?id=a8e411843cc749d3af8eab5a7b26f196</u>

¹⁴ Water quality at site 100269 is more likely to be influenced by Bercich Drain, which drains a predominantly rural catchment with stormwater discharges from Laminated Veneer Lumber Plant (LVL) and treated industrial wastewater discharge from the Air Liquide carbon dioxide and liquid oxygen plant (Riaan Elliot, Refining NZ, personal communication).

is not included in the assessment of modelled SWB dilutions against WQS. These are assessed against the estuarine sites only.



Figure 2. Boundary between estuary (teal colour) and open coastal water (grey colour) management units in the pNRP with respect to water quality sites around the refinery discharge.

Many of the attributes in Table 1 are not <u>consistently</u> measured at NRC receiving environment sites monitored as part of the assessment of effects from the refinery discharge. The following parameters present in the oNRP or pNRP CWQS were not provided in the receiving environment monitoring data or were only measured sporadically. For these parameters, no assessment could be made. Parameters not included were:

- oNRP natural visual clarity; natural hue; natural eutrophic depth; oil/grease film; scum; foam; odour; dissolved reactive phosphorus (DRP); nitrate (NO₃-N).
- pNRP turbidity; secchi depth; chlorophyll-a; total phosphorus; total nitrogen; nitratenitrite nitrogen; enterococci.

Furthermore, many contaminants measured at both NRC receiving environment sites and in the SWB (see Section 2.2 for the full list) are not current attributes in either the oNRP or the pNRP.

Therefore, water quality ecological guidelines used in this assessment are derived from a wider range of information, as described in Section 2.1.3.

Table 1. Comparison of water quality standards for ecosystem health in coastal waters for the Proposed NRP (Policy H.3.3) and the Operative NRP (as Appendix 4 of PNRP).

Attribute	Unit	Proposed NRP ¹		Operative NRP Standard		
		Compliance Metric	Estuaries	Open Coastal Water	Compliance Metric	General Quality Standard ²
Dissolved Oxygen	mg/L	Annual median	>6.9	No discernible change	Not stated	>6.63
		Minimum	4.6	4.6		
Temperature	°C	Maximum change	3	3	Maximum change	3
рН		Annual minimum and annual maximum	7.0-8.5	8.0-8.4	Maximum change	0.2
Ammoniacal Nitrogen	mg/L	Annual median	<0.023	No discernible change	Not stated	<0.005
Total Arsenic	mg/L	No data	No data	No data	Not stated	0.050
Total Cadmium	mg/L	No data	No data	No data	Not stated	0.002
Total Chromium	mg/L	No data	No data	No data	Not stated	0.050
Total Copper	mg/L	Maximum	0.0013	0.0003	Not stated	0.005
Total Lead	mg/L	Maximum	0.0044	0.0022	Not stated	0.005
Total Zinc	mg/L	Maximum	0.0150	0.0070	Not stated	0.050
		Median	≤14	≤14	Median ³	<14
Faecal coliforms⁴	MPN/100mL	Annual 90 th percentile	≤43	≤43	90 th percentile⁵	<43

¹Apply after allowing for reasonable mixing.

² Provides for virtually all uses and protection of marine ecosystems.

³ Operative NRP units % saturation (80%). Converted to mg/L (<u>http://www.waterontheweb.org/under/waterquality/dosatcalc.html</u>) for comparison with Proposed NRP. ⁴ Faecal coliforms were different for contact recreation standard (CB) and based on not fewer than 5 samples within any 30-day period. Median < 150/100mL. 80%ile <600/100mL.

⁵ Based on not fewer than 10 samples within any 30-day period.

Coastal sediment quality guidelines

The oNRP does not contain any coastal sediment quality guidelines (CSQG). The most recent decisions version (29 July 2019) of the pNRP contains CSQG for six (6) metals, under Policy H.3.4 (Table 2). CSQG for other contaminants monitored as part of this assessment are not present in the pNRP. Therefore, ecological guidelines used to assess sediment quality are derived from a wider range of information, as described in Section 2.1.3.

Attribute	Unit	Compliance Metric	Coastal water quality management unit Estuaries and Open coast
Cadmium	mg/kg	Maximum	0.68
Chromium	mg/kg	Maximum	52.3
Copper	mg/kg	Maximum	18.7
Lead	mg/kg	Maximum	30.2
Nickel	mg/kg	Maximum	15.9
Zinc	mg/kg	Maximum	124

Table 2. Coastal sediment quality guidelines provided in June 2020 decision version of the pNRP.

2.1.3 Ecological guidelines

Surface water quality guidelines (SWQG) used in this assessment are a combination of coastal water quality standards from both the oNRP and the pNRP, the Australian and New Zealand (ANZ) Guidelines for Fresh and Marine Water Quality¹⁵ 95%¹⁶ marine default guideline values (DGV) (Australian and New Zealand Governments, 2018), and water quality indices from Auckland Council (Vaughan, 2017) (Table 3).

Generally, the <u>most restrictive ecological values</u> were used for the assessment, except for NH_4 -N, for which both oNRP and pNRP CWQS were assessed. Although oNRP states NH_4 -N must be <0.005 mg/L (4.6x lower than the pNRP value of <0.023 mg/L), there is no specific compliance metric associated with this value. In contrast, pNRP states an NH_4 -N annual median of <0.023 mg/L.

 $^{^{\}rm 15}$ The guidelines were updated in 2018, and they replace a previous set of guidelines commonly referred to as the ANZECC 2000 guidelines.

¹⁶ The 95% DGV was used over the 99% DGV, based on the definitions below:

^{95%:} Ecosystems in which aquatic biological diversity may have been adversely affected to a relatively small but measurable degree by human activity. The biological communities remain in a healthy condition and ecosystem integrity is largely retained. Freshwater systems would typically have slightly to moderately cleared catchments or reasonably intact riparian vegetation. For example, rural streams receiving runoff from land disturbed to varying degrees by grazing or pastoralism. Marine systems would typically have largely intact habitats and associated biological communities. For example, marine ecosystems lying immediately adjacent to metropolitan areas.

^{99%:} Effectively unmodified or other highly valued ecosystems, typically (but not always) occurring in national parks and conservation reserves, or in remote and inaccessible locations. While there are no aquatic ecosystems in Australia and New Zealand entirely without some human influence, the ecological integrity of our high conservation or ecological value systems is regarded as 'intact'. (<u>https://www.waterquality.gov.au/anz-guidelines/resources/key-concepts/level-of-protection#slightly-to-moderately-disturbed-systems</u>).

Table 3. Surface water quality guidelines (SWQG) used in this assessment with their sources.¹⁷

Parameter	Unit	Compliance metric	Value	Source
DO	100 g / I	Annual median	>6.9	mNDD1
DO	mg/L	Minimum	4.6	- pNRP ¹
Temperature	°C	Maximum change	3	pNRP/oNRP ²
рН	unitless	Annual minimum/maximum	7.0-8.5	pNRP ¹
Ammoniacal nitrogen (NH ₄ -N) ³	mg/L	Not stated	<0.005	oNRP
Ammoniacal nitrogen (NH ₄ -N) ³	mg/L	Annual median	<0.023	pNRP
Faecal coliforms (FC)	MPN/100mL	Median	≤14	pNRP/oNRP ²
raecai comornis (rc)	MPN/100IIL	Annual 90 th percentile	≤43	pNRP/oNRP ²
Phenol	mg/L	Maximum	0.400	ANZ ⁴
Pentachlorophenol	mg/L	Maximum	0.022	ANZ ⁴
Arsenic	mg/L	Maximum	0.050	oNRP⁵
Cadmium	mg/L	Maximum	0.0020	oNRP ⁶
Chromium ⁹	mg/L	Maximum	0.0044	ANZ ^{4,7}
Copper	mg/L	Maximum	0.0013	ANZ ^{4,7}
Lead	mg/L	Maximum	0.0044	ANZ ^{4,7}
Mercury ¹⁰	mg/L	Maximum	0.0001	ANZ ^{4,8}
Nickel	mg/L	Maximum	0.0700	ANZ ^{4,8}
Zinc	mg/L	Maximum	0.015	ANZ ^{4,5}
Sulphide	mg/L	Maximum	ID	None
TSS	mg/L	Average	20	Auckland Council ¹¹

¹ pNRP more restrictive and contains more descriptive metrics than oNRP.

² Metrics identical for oNRP and pNRP.

³ NH₄-N metrics are significantly different between oNRP and pNRP so will be assessed separately.

⁴ 95% marine trigger value.

⁵ Insufficient data to derive a reliable ANZ marine trigger value.

 $^{\rm 6}$ oNRP more restrictive than ANZ (no data for pNRP).

 7 ANZ more restrictive than oNRP (no data for pNRP).

⁸ No value in oNRP.

 $^{\rm 9}$ Based on Cr(VI), the more toxic valency state for chromium.

¹⁰ Inorganic mercury.

¹¹ Auckland Council use TSS as one of 7 water quality parameters to produce water quality indices of marine water quality (Vaughan, 2017).

Sediment quality guideline values (SGVs) used in this assessment are the Canadian Council of Ministers of the Environment (CCME) Sediment Quality Guidelines for the Protection of Aquatic Life (metals) and the ANZ DGV for TPH and PAHs¹⁸ (Table 4). CCME sediment guidelines for metals have been proposed by NRC in the pNRP.¹⁹ Importantly, organic contaminants (TPH and PAHs) are normalised to 1% total organic carbon (TOC) content of the sediment.

¹⁷ Benzene has ANZ 95% marine DGV of 0.7 mg/L (Toluene, Ethylbenzene and Xylene have ID). BTEX is not measured routinely in the receiving environment so was not included in this table.

¹⁸ ANZ DGV replaced the ANZECC Interim Sediment Quality Guidelines (ISQG) in 2018.

 $^{^{19}}$ The only minor difference is cadmium with pNRP 0.68 mg/L and CCME 0.70 mg/L.

Parameter	Unit ¹	Value	Source
Arsenic	mg/kg	7.24	CCME ²
Cadmium	mg/kg	0.68	pNRP/CCME ³
Chromium	mg/kg	52.3	pNRP/CCME ³
Copper	mg/kg	18.7	pNRP/CCME ³
Lead	mg/kg	30.2	pNRP/CCME ³
Mercury	mg/kg	0.13	CCME ²
Zinc	mg/kg	124	CCME ²
ТРН	mg/kg	280	ANZ DGV ⁴
Total PAH	mg/kg	10	ANZ DGV ⁴

Table 4. Sediment quality guidelines used in this assessment, with sources of information.

¹Metals are dry weight. Organics (TPH/PAH) are dry weight and normalised to 1% TOC.

² Canadian Council of Ministers of the Environment. CCME more restrictive than ANZ.

 3 pNRP/CCME values are essentially identical. The only minor difference is cadmium with pNRP 0.68 mg/L and CCME 0.70 mg/L.

⁴ Australian and New Zealand guidelines for fresh and marine water quality (Australian and New Zealand Governments, 2018).

2.1.4 Defining the mixing zone

The appropriateness of the size of the mixing zone was questioned by Dr Rob Bell in his review of the consultative drafts of the hydrodynamic modelling report (MetOcean Solutions, 2020) and this water quality report. This has subsequently been addressed in a memo to NRC (Appendix 6) and is summarised below.

Several applicable planning documents contain provisions that are relevant to the concept of mixing zones, including the issue of mixing zone size. Relevant provisions from the New Zealand Coastal Policy Statement 2010 (NZCPS), the oNRP ("Operative Regional Plan"), and the pNRP are summarised below with respect to mixing zone size:

- The NZCPS defines "mixing zone" as "the area within which 'reasonable mixing' of contaminants from discharges occurs in receiving waters and within which the relevant water quality standards do not apply".
- The pNRP definition of "zone of reasonable mixing" states that for the purposes of activities that require resource consents the zone of reasonable mixing will be determined "consistent with" the zone of reasonable mixing applying to permitted discharges (being 20m from the point of discharge) "unless the nature and scale of the discharge requires that a case-by-case basis determination is more appropriate, in which case the extent of departure from the zone... will be determined in accordance with Policy D.4.4 Zone of reasonable mixing."
- The NZCPS (Policy 23) and the pNRP (Policy D.4.4(1)) provide that mixing zones used shall be the smallest size necessary to achieve the required water quality in the receiving environment.

The mixing zone that is proposed to apply to Refining NZ's coastal discharges associated with the re-consenting proposal is the same mixing zone that is identified under Refining NZ's current resource consent, which is also the mixing zone identified in the planning maps for both the oNRP (Figure 1) and the pNRP (Figure 2). The water quality assessment undertaken for the re-consenting proposal (this report) assesses effects on water quality outside the current mixing zone. The method used for the assessment calculates concentrations of stormwater basin contaminants at specific sites (including the four corners of the current mixing zone) after dilution in the receiving environment.

Based on the water quality assessment in this report and the marine ecology assessment (De Luca, 2020), in my opinion the mixing zone proposed/used (being the *status quo* of maintaining the mixing zone at the current size) is appropriate. Reasons include:

- The mixing zone proposed/used is the smallest extent necessary to achieve the required water quality in the receiving environment.²⁰
- Within the proposed mixing zone, effects on the life-supporting capacity of water will be minimised and are appropriate (being minor at worst).²¹ In particular, the mixing zone contaminant concentrations and levels of dissolved oxygen will not cause acute toxicity effects on aquatic ecosystems.²²
- After reasonable mixing, significant adverse effects on ecosystems and habitats will be avoided;²³ and overall water quality will be maintained.²⁴

2.2 Refining NZ SWB discharge water and sediment quality status

2.2.1 SWB sample collection and analysis methodology

Samples are collected by staff from Refining NZ from a continuously pressurised line fed by a small pump which is located next to the larger discharge pumps and as such the water in the line will be representative of what is being discharged to the harbour. The typical minimum daily SWB discharge is 5,000m³/day. The volume of SWB discharge is incorporated into the hydrodynamic modelling undertaken by MetOcean Solutions (2019), see Section 4.1 for a summary of modelling outputs and Appendix 5 for the full hydrodynamic modelling report.

The prop sample consists of sub-samples based on volume discharged and so is representative of the discharge over the day. The prop sample is collected at 8.00am each morning. The sample container is kept under refrigeration. The sample is taken to an on-site IANZ accredited independent laboratory (IPL^{25}) so no transportation issues.

Laboratory analysis methods are in Appendix 1 of the discharge consent and summarised below.

²⁰ NZCPS Policy 23(e) and Proposed Regional Plan Policy D.4.4(1).

²¹ NZCPS Policy 23(f).

²² Proposed Regional Plan Policy D.4.4(2).

²³ NZCPS Policy 23(d).

²⁴ Proposed Regional Plan Policy D.4.1(1).

²⁵ https://www.ipl.co.nz/

- Ammonia in Water: APHA Method 4500-NH3E Ammonia-Selective Electrode Using Known Addition.
- Biological Oxygen Demand (BOD): APHA Method 4500-0 G and APHA 5210 B
- Chemical Oxygen Demand (COD): Hach Method 8000, LOD= 50 mg/L
- Faecal Coliforms: APHA 9222 D Faecal Coliform Membrane Filter Procedure
- Hydrocarbons (Total) in Water: ENV001-WATER13 (in house designation), LOD = 0.2mg/L
- Phenol in Water: GS-MS (in-house designation), LOD= 0.05mg/L, or
- ASTM D1783 (Total Steam Distillable) LOD = 0.1 mg/L
- Sulphide (Total) in Water and Soil: Conservation Act 1967 APHA 4500-S²-D, LOD (total sulphide concentration in sample) = 0.03 mg/L
- Total Suspended Solids: APHA Method 2540 D Total Suspended Solids Dried at 103-105° C
- Salinity: APHA Method 2520 B Electrical Conductivity Method.

Data were provided for the Refining NZ SWB in two formats:

- 1. Daily data for 2018²⁶;
- 2. Quarterly data for the period 2014–2019.

The daily 2018 data were used to assess fine-scale variability for the most recent completed year and compliance with resource consent conditions for discharge from the SWB (AUT.008319.01.04). Parameters measured were temperature (°C), pH, 5-day biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total organic carbon (TOC), total petroleum hydrocarbon (TPH), total phenols, ammoniacal-nitrogen (NH₄-N), sulphides and salinity.

The quarterly data were included with receiving environment site data from NRC monitoring and were used to assess the status and temporal trends of the SWB water quality over the last 5 years.

Parameters consistently measured²⁷ are:

- 16 polycyclic aromatic hydrocarbons (PAHs) acenaphthene; acenaphthylene; anthracene; benzo(a)anthracene; benzo(a)pyrene²⁸; benzo(b)fluoranthene; benzo(ghi)perylene; benzo(k)fluoranthene; chrysene; dibenzo(ah)anthracene; fluorene; fluoranthene; indeno(1,2,3,c,d)pyrene; naphthalene; phenanthrene; pyrene.
- 14 phenols phenol; 2-methylphenol; 4-methylphenol; 2-chlorophenol; 2-nitrophenol; 4chloro-3-methylphenol; 2,4-dimethylphenol; 2,4-dichlorophenol; 2,6-dichlorophenol; 2methyl-4,6-dinitrophenol; 2,4,5-trichlorophenol; 2,4,6-trichlorophenol; 2,3,4,6tetrachlorophenol; pentachlorophenol.
- Total metals/<u>metalloids</u> <u>arsenic</u>; cadmium; chromium; copper; lead; mercury; nickel²⁹; zinc.

²⁶ Some parameters were measured approximately every 2 days.

²⁷ Some parameters (TN, TP, DRP, turbidity and secchi depth) have been measured sporadically (twice over 5 years and not all sites). These have not been assessed due to lack of consistent data. Furthermore, they are nutrients and indicators of water clarity and not of toxicological concern.

²⁸ Benzo(a)pyrene equivalent was also reported, however there was no methodology around how this was derived.

²⁹ Although nickel has been measured routinely in the SWB, it has not been measured routinely at receiving environment sites.

- Ammoniacal-nitrogen (NH₄-N).
- Biochemical oxygen demand (5-day).
- Dissolved oxygen (DO).
- Faecal coliforms.
- pH.
- Salinity.
- Sulphide.
- Temperature.
- Total petroleum hydrocarbon (TPH).
- Total suspended solids (TSS).

With the exception of BOD_5 , all of these parameters are measured at NRC receiving environment water quality sites (see Section 2.5).

2.2.2 Discharge water quality compliance (2018)

Consent compliance standards (AUT.008319.01.04) are show in Table 5.

Parameter	Unit	Daily maximum	Daily maximum – 30-day rolling average
Temperature	°C	37	
рН		6 to 9	
BOD ₅	mg/L	70	40
TSS	mg/L	50	30
COD	mg/L	540	280
ТРН	mg/L	12	6
Total Phenols	mg/L	0.5	0.15
NH ₄ -N	mg/L	85	40
Sulphides	mg/L	0.5	0.15

Table 5. Consent	compliance wate	r quality standards fo	or Refining NZ SWB discharge.
	1	1 2	0 0

Temperature and pH

Temperature is not permitted to exceed 37°C on any day. For 2018, the maximum temperature was 34.5°C on 29th December (Figure 3).

The permitted pH range is 6–9 on any day. The maximum permissible pH of 9 was never exceeded, however, over the second half of 2018, it was close to being exceeded (Figure 3). The 75th percentile of the maximum daily pH was 8.04 for the full year, and 8.46 from July to December, 2018. The minimum permissible pH of 6 was never reached, with the 25th and 5th percentile of the minimum pH being 7.11 and 6.81, respectively.



Figure 3. Refining NZ SWB daily temperature and pH data for 2018.

BOD₅, COD, and TOC

The daily maximum concentration of BOD_5 (52 mg/L) was well below the consent limit of 70 mg/L (Figure 5). Importantly, the 30-day rolling-average daily maximum concentration was generally below 10 mg/L, and less than 25% of the corresponding consent limit of 40 mg/L.

COD followed a similar pattern, with daily maximum and 30-day rolling-average daily maximum concentrations up to an order of magnitude (10x) below the corresponding consent limits (Figure 5).


Figure 4. Refining NZ SWB daily BOD₅ data for 2018.



Figure 5. Refining NZ SWB daily COD data for 2018.

Total petroleum hydrocarbon (TPH) was measured approximately every 2 days. TPH concentration was generally very low and below the detection limit (1.0 mg/L) (Figure 6). On four occasions, TPH was above the detection limit, with the daily maximum concentration (2.7 mg/L) approximately 5x below the corresponding consent limit (12 mg/L).



Figure 6. Refining NZ SWB "daily" TPH data for 2018.

<u>Total phenols</u>

Total phenols was measured approximately every 2 days and was below the detection limit (0.1 mg/L) in every sample measured. By using a conservative approach of setting the concentration to the detection limit (0.1 mg/L), total phenol concentration was 5x lower than the corresponding consent limit (0.5 mg/L).

Ammoniacal-nitrogen

Ammoniacal-nitrogen (NH₄-N) was measured approximately every 2 days and was above the detection limit (1.0 mg/L) on 3 occasions, with values of 1.3, 1.1, and 10.1 mg/L (Figure 7). The 30-day rolling-average daily maximum (based on setting <DL to DL) was 1.0 mg/L for the majority of the year, rising to around 1.6 mg/L (due to a spike of 10.1 mg/L) in December, which is still 25x below the corresponding consent limit of 40 mg/L.



Figure 7. Refining NZ SWB "daily" NH₄-N data for 2018.

<u>Sulphides</u>

Sulphides were measured approximately every 2 days and were above the detection limit (0.03 mg/L) for around 15 days in 2018. However, the maximum concentration detected (0.12 mg/L) was approximately 4x lower than the corresponding consent limit (0.5 mg/L) (Figure 8). The 30-day rolling-average daily maximum (based on setting <DL to DL) of 0.032 mg/L was nearly 5x lower than the corresponding consent limit (0.15 mg/L).



Figure 8. Refining NZ SWB "daily" sulphides data for 2018.

<u>Salinity</u>

Measurement of salinity is not required by the consent conditions; however, it gives an indication of periods of saltwater ingress into the SWB. Salinity ranged from 0.8 (near freshwater) to 14.4 ppt (approx. 40% seawater) with a median of 3.4 ppt. The major saltwater ingress was in the first 2 weeks of January 2018 (Figure 9).



Figure 9. Refining NZ SWB "daily" salinity data for 2018.

2.2.3 Discharge water quality status (2014–2019)

NRC monitor the SWB as part of their receiving environment monitoring. A summary of discharge data for the period 2014–2019 is presented in Table 6.

For the period 2014–2019, total phenols, total PAHs and benzene/toluene/ethylbenzene/xylene (BTEX) were below detection limits in all samples (Table 6). TPH ranged from 0.37 to 0.99 g/m³ (mg/L)³⁰. Note that the detection limit (0.3-0.5 mg/L) used by NRC for these analyses is lower than that used for the daily measurements (1.0 mg/L) (see previous section).

For the period 2014–2019, sulphides were below the detection limit (0.1 mg/L). pH ranged from 7.4 to 8.5, within the consent limit range of 6 to 9. Maximum BOD_5 was 18.0 mg/L, well below the consent limit of 70 mg/L. TSS ranged from 2.0 to 23.0 mg/L, with a median of 12.5 mg/L (Table 6).

For the period 2014–2019, NH₄-N concentration ranged from 0.02 to 15.0 mg/L, with a median of 0.41 mg/L (Table 6).

Metal and metalloid concentrations have been measured since 2015. These are discussed in relation to SWQG in the following section.

 $^{^{30}}$ Analytical laboratories report water concentrations as g/m³ or mg/L. These are effectively the same units (notwithstanding a minor correction between pure water and seawater of 1.025). For clarity, all data in this report will be reported as mg/L.

For the period 2014–2019, FC concentration ranged from <10 to 5,300 CFU/100 mL, with a median of 155 CFU/100 mL (Table 6). The large concentrations of FC were sporadic, occurring approximately once each year (Figure 10). These spikes are attributed to a nesting colony of Red Billed gulls which inhabit the SWB every summer, with up to 2000 nesting pairs (Riaan Elliot, Refining NZ, personal communication).³¹

Parameter	Units	Minimum	Maximum	Median	Mean
Total Phenols (<dl=dl)<sup>1</dl=dl)<sup>	mg/L	<0.016	<0.018	NA	NA
Total PAHs (<dl=dl)< td=""><td>mg/L</td><td><0.0016</td><td><0.0074</td><td>NA</td><td>NA</td></dl=dl)<>	mg/L	<0.0016	<0.0074	NA	NA
BTEX (<dl=dl)< td=""><td>mg/L</td><td><0.0004</td><td><0.008</td><td>NA</td><td>NA</td></dl=dl)<>	mg/L	<0.0004	<0.008	NA	NA
ТРН	mg/L	0.37	0.99	0.68	0.68
Sulphides	mg/L	<0.1	<0.1	NA	NA
рН	-	7.4	8.5	8.1	8.0
BOD ₅	mg/L	2.9	18.0	7.5	8.0
TSS	mg/L	2.0	23.0	12.5	12.2
NH ₄ -N	mg/L-N	0.02	15.0	0.41	2.26
Arsenic Total	mg/L	0.0014	0.0041	0.0020	0.0025
Cadmium Total	mg/L	0.0001	0.0001	0.0001	0.0001
Chromium Total	mg/L	0.0005	0.0019	0.0013	0.0013
Copper Total	mg/L	0.0009	0.0046	0.0027	0.0028
Lead Total	mg/L	0.0002	0.0015	0.0006	0.0007
Mercury Total	mg/L	0.0001	0.0002	0.0001	0.0001
Nickel Total	mg/L	0.0018	0.0067	0.0036	0.0042
Zinc Total	mg/L	0.0079	0.18	0.0420	0.0559
Faecal Coliforms	CFU/100mL	<10	5300	155	1111

Table 6. Refining NZ SWB discharge status summary data (2014–2019).



Figure 10. Refining NZ SWB faecal coliform concentrations between 2014 and 2019.

³¹ There are no sources of human sewage to the SWB as this is all reticulated and processed by Ruakaka WWTP.

The SWB data (Table 6) serves two main purposes:

- 1) As an early warning of contaminants present in the SWB that may potentially cause adverse effects in the receiving environment, indicated by the SWB contaminant concentration being above an applicable ecological guideline.
- 2) As inputs (maximum, mean, median values) into hydrological modelling (MetOcean Solutions, 2020) to assess associated receiving environment dilution under different scenarios (e.g., different combinations of winds and tides), from which potential adverse effects on water quality can be inferred (see Section 4).

Regarding point (1) above, the ratio of each SWB contaminant concentration to the relevant SWQG (see Table 3) was calculated and presented as a risk quotient (RQ) (Table 7), which is <u>the dilution required to reduce the SWB concentration to below the applicable receiving environment SWQG.</u> A risk quotient >1 indicates <u>potential</u> for ecological effects. It is important to note that the RQs in Table 7 do not include nearfield or far-field dilution, which may reduce contaminant concentrations in the receiving environment. Hence, this is akin to a "traffic light" approach to identifying contaminants in the SWB of potential concern. As shown in Table 7, contaminants with the greatest <u>potential</u> to cause adverse effects in the receiving environment are ammoniacal-nitrogen (NH_4 -N), copper, zinc and faecal coliforms. For those contaminants with a risk quotient in the SWB of >1, potential ecological effects after dilution in the receiving environment are assessed (see Section 4.4).

 NH_4 -N concentrations are highly elevated in the SWB compared with SWQG (Table 7). However, NH_4 -N concentrations in the SWB have been reducing significantly since an upgrade in 2014 (see Section 2.3). Since 2015, the median NH_4 -N concentration (0.28 mg/L) is 68% of the median NH_4 -N concentration since 2014 (0.41 mg/L) (Table 7).

The maximum copper and zinc concentrations are 3.5x and 12x above SWQG, respectively (Table 7).

Median and maximum faecal coliform (FC) concentrations are above SWQG (Table 7). Although FC are not required to be measured by the discharge consent, their measurement in the receiving environment is a requirement (see Section 2.5). As stated earlier, the maximum FC concentrations are due to a nesting colony of Red Billed gulls.

Parameter	Minimum SWB concentration	Median SWB concentration	Maximum SWB concentration	SWQG
Benzene	0.001	ND	0.01	0.7
TSS	0.1	0.63	1.2	20
NH ₄ -N (oNRP) (2014-2019)	4.0	82	3000	0.005
NH ₄ -N (pNRP) (2014-2019)	0.87	18	652	0.023
NH ₄ -N (oNRP) (2015-2019)	4.0	56	360	0.005
NH ₄ -N (pNRP) (2015-2019)	0.87	12	78	0.023
Arsenic Total	0.03	0.04	0.08	0.05
Cadmium Total	0.05	0.05	0.05	0.002
Chromium Total	0.11	0.3	0.43	0.0044

Table 7. Risk quotient of minimum, median and maximum Refining NZ SWB concentrations for selected contaminants with applicable SWQG.

Parameter	Minimum SWB concentration	Median SWB concentration	Maximum SWB concentration	SWQG
Copper Total	0.69	2.1	3.5	0.0013
Lead Total	0.05	0.14	0.34	0.0044
Mercury Total	0.01	0.01	0.01	0.015
Nickel Total	0.03	0.05	0.1	0.07
Zinc Total	0.53	2.8	12	0.015
Faecal coliforms	0.23	3.6	123	43
Faecal coliforms	0.71	11	379	14

¹ Colour codes: < 1 = green; 1-10 = orange; >10 = red

2.2.4 Discharge sediment quality status

SWB sediment quality was assessed using data from three sampling events: 2012, 2014 and 2016. Sediment concentrations were compared with applicable sediment quality guidelines (SQG), namely, CCME or pNRP for metals/metalloids, and ANZ DGV for TPH and total PAH (see Table 4). Organic data (TPH and PAH) were corrected to 1% TOC.

Only a few individual PAH congeners were above detection limits in the SWB sediments (ranging from 0.005 to 0.031 mg/kg, dry weight). For the purposes of calculating total PAH, these were set to the detection limit. There is no DGV for phenols, so potential effects could not be assessed. All phenol concentrations were below detection limits (0.5-3.1 mg/kg) over the 3 sampling events.³²

Results (Figure 11) show that sediment concentrations were stable between 2012 and 2016, with the possible exception of total PAH (see temporal trend analysis, Section 2.3). The contaminants with greatest potential for adverse effects in the receiving environment – i.e. those contaminants that exceed SQG by the largest margin – are mercury; zinc; copper; and TPH.

Although some SWB sediment contaminant concentrations exceed SQG, SQG are designed to be applied to the receiving environment. SWB sediment concentrations were input into a 3D-hydrodynamic model to estimate the receiving environment sediment concentrations, against which SQG can be compared for a more robust assessment (see Section 4.3).

 $^{^{\}rm 32}$ 4-methylphenol was detected in 2014 (260 mg/kg), however this is likely a spurious result as no other phenol was above detection limit (0.8 mg/kg) in this analysis.



Figure 11. Refining NZ SWB sediment quality assessment against SQG. Note the log scale on the lower figure.

2.2.5 Whole-effluent toxicity testing

The SWB water has been assessed for marine species toxicity in September 2017 by NIWA (Thompson, 2017), May 2019 by Cawthron (Champeau, 2019a) and September 2019 by Cawthron (Champeau, 2019b). All three tests were under normal Refinery operating conditions.

NIWA ran the toxicity screen against three test species in 2017: 48-hour blue mussel bivalve (*Mytilus galloprovincialis*) embryo development; 96-hour wedge shell bivalve (*Macomona liliana*) survival and morbidity (reburial); and marine alga (*Dunaliella tertiolecta*) 72-hour growth. They reported the no-toxicity dilution of the stormwater samples, which is the dilution at which the sample would be expected to exhibit no toxicity to the organisms tested after a chronic exposure. The most sensitive organism was the marine alga, with a definitive no-toxicity dilution of 8.8x. Blue mussels were the least sensitive with a definitive no-toxicity dilution of 1.7x. Wedge shell bivalve had a no-toxicity dilution of <15x.

Cawthron ran the toxicity screen against four test species in both 2019 tests: 48-hour blue mussel bivalve (*Mytilus galloprovincialis*) embryo development; pipi (*Paphies australis*) 96-hour survival/reburial; Amphipod (*Paracorophium excavatum*) 96-hour mortality; and marine

alga (*Dunaliella tertiolecta*) 96-hour growth. The no-toxicity dilution was consistent amongst the species ranging from ≥1.10x (amphipod) to ≥1.23x (pipi and blue mussel).

Across the three sampling events there were two species in common, marine alga and blue mussel. By comparison of data for these two species, the September 2019 SWB discharge appears to have been more toxic than the May 2019 and September 2017 discharges. The September 2019 SWB discharge required a no-toxicity dilution of 11.3x for green alga and >256x for blue mussel. In comparison, the May 2019 SWB discharge required an 8.8x dilution in September 2017 and 1.15x dilution in May 2019 for marine alga, and a 1.7x dilution in September 2017 and 1.23x dilution in May 2019 for blue mussel. The September 2019 SWB sampling was after 5 mm of rain in the preceding 24 hours, the May 2019 SWB sampling was after a period of dry weather, and the September 2017 SWB sampling was after 6 mm of rain in the preceding 24 hours. Notwithstanding the weather at the time, the maximum dilution required to reduce the toxicity of the SWB discharge water to a no-toxicity threshold is 256x, which is the worst-case scenario for the most sensitive marine species.

Effects on pipi were measured only by Cawthron, so assessment is restricted to the May 2019 and September 2019 results. There is evidence that pipi populations have been declining at Mair Bank since 2010 (Pawley, 2016). However, the pipi no-toxicity dilution of the SWB discharge was \geq 1.23x in May 2019 and <1.3x in September 2019. This suggests that SWB water is non-toxic *acutely* to pipi at almost no dilution.³³

2.3 Refining NZ SWB discharge water quality trends

A temporal trend analysis of selected parameters routinely measured in the SWB was undertaken to provide a longer-term view of all potential contaminants discharged, which will assist in informing the future setting of limits in consents.

Data were supplied in Excel format by Refining NZ. Water quality data were from the period May 2014 to February 2019 (up to 18 sampling events). Sediment quality data were from the period December 2012 to December 2016 (3 sampling events).

Trends for all discharge data were estimated using a Mann-Kendall trend test (Time Trends, NIWA, 2019). A Mann-Kendall trend test was considered to be more appropriate than using seasonally adjusted data (Seasonal Kendall test, which is used commonly for river quality trends), as the majority of the SWB data did not exhibit obvious seasonal bias. However, where there was apparent seasonal bias, a Seasonal Kendall test was also undertaken.³⁴ Seasons used in this analysis were: Dec – Feb; Mar – May; Jun – Aug; and Sep – Nov. Censored data, i.e. data below detection limits is treated by Time Trends by setting all data below detection limit to the detection limit. This can influence the significance of trends where there are large numbers of censored data. Any effect this may have on the significance of trends is discussed below.

Non-seasonally adjusted temporal water quality trends are summarised in Table 8, with graphs in Appendix 1. Statistically significant trends were indicated by p<0.05. The median annual Sen slope is the direction and rate of change, which was normalised by dividing by the raw data

³³ A chronic toxicity test for pipi is not practical as they are relatively long lived (Champeau (Cawthron), personal communication).

 $^{^{34}}$ BOD₅ data appeared to show a seasonal bias however a seasonal Kendall test was also insignificant.

median to give the relative SKSE (RSKSE). I have followed Scarsbrook (2006) in denoting a "meaningful" trend as one for which the RSKSE is statistically significant (p < 0.05) and the absolute magnitude is >1% per year. Meaningful trends are highlighted in red (increasing) and blue (decreasing) (Table 8).

Between 2014 and 2019, pH increased significantly (p = 0.003) by 0.15 annually and meaningfully (+1.9% annually) (Table 8). Although the second half of 2018 showed relatively high pH (but still within consent limits) (Section 2.2.2), the increase has been consistent over the last 5 years (see Appendix 1 for graph).

NH₄-N decreased significantly (p = 0.000) by -0.44 mg/L-N annually and meaningfully (-108% annually) between 2014 and 2019. However, large contributors to the decrease are high NH₄-N concentrations in 2014 and early 2015 (1.6 to 15 mg/L-N) (Figure 12). When the temporal trend analysis was repeated on data for the period June 2015 to February 2019, the decreases were still significant (p = 0.004) and very large (-0.23 mg/L-N annually) and meaningful (-80% annually). However, the maximum and median NH₄-N concentrations for the period June 2015 to February 2019 were 1.8 mg/L-N and 0.28 mg/L-N, respectively. The marked decrease in NH₄-N concentration since June 2015 is attributed to a plant upgrade³⁵, which has a significant impact on the potential worst-case risk of NH₄-N to the receiving environment (see Section 4.4).

For the data used in this assessment a high number of censored data was present for BOD_5 (33% censored data), cadmium (71% censored data), mercury (64% censored data), lead (50% censored data), and chromium (50% censored data) (Table 8). For BOD_5 , cadmium, mercury and lead, this corresponded to non-significant or zero trends. However, chromium increased significantly (p = 0.005) by 0.001 mg/L annually and meaningfully (+50% annually) between 2014 and 2019. When substituting censored data with 0.5 times the detection limit, chromium increased significantly (p = 0.01) by 0.0004 mg/L annually and meaningfully (+23% annually) between 2014 and 2019.

Non-significant (p > 0.05) increases between 2014 and 2019 include TSS (14% annually, p = 0.184), faecal coliforms (FC) (26% annually, p=0.208) and copper (18% annually, p=0.169).

Non-significant (p > 0.05) decreases between 2014 and 2019 include arsenic (-17% annually, p = 0.267), mercury (-2.5% annually, p = 0.592), and zinc (-2.4% annually, p = 0.869).

No temporal trends were observed for BOD_5 , cadmium, nickel and lead.

Sediment quality temporal trend data were not significant (p = 1.0) and are not shown.

³⁵ Refining NZ operate two sour water strippers which remove hydrogen sulphide and ammonia from process water. Some treated water is used as wash water in the desalters before being sent to the biotreater for final treatment. The project removed constraints (in 2015) within the 2nd sour water stripper which allowed the combined units to remove substantially more ammonia from the treated water. The reduced ammonia content improved the performance of the desalters, substantially improved the quality of the desalter effluent to the biotreater and reduced the ammonia load on the biotreater (Jack Stewart, Refining NZ, personal communication).

Parameter	Median value	Unit	% censored data	Р	Median annual Sen slope	RSKSE	Trend ¹
рН	7.9		0	0.003	0.15	1.9	1
TSS	12.5	g/m ³	0	0.184	1.78	14.2	1
NH ₄ -N (2014-2019)	0.41	g/m³-N	0	0.000	-0.44	-108.1	\mathbf{A}
NH ₄ -N (2015-2019)	0.28	g/m³-N	0	0.004	-0.23	-80.4	\mathbf{A}
BOD ₅	6.1	g/m ³	33	0.939	0	0	→
FC	77	CFU/100mL	11	0.208	20.25	26.3	1
Total Arsenic	0.0020	g/m ³	0	0.267	-0.0003	-16.5	$\mathbf{+}$
Total Cadmium	0.045	g/m³	71	0.368	0	0	→
Total Chromium ²	0.002	g/m ³	50	0.005	0.001	50.0	↑
Total Copper	0.003	g/m³	14	0.169	0.0005	18.0	^
Total Mercury	0.12	g/m ³	64	0.592	-0.003	-2.5	\mathbf{A}
Total Nickel	0.004	g/m ³	0	0.660	0	0	→
Total Lead	0.001	g/m³	50	0.457	0	0	→
Total Zinc	0.042	g/m ³	0	0.869	-0.001	-2.4	4

Table 8. Refining NZ SWB discharge water quality temporal trends summary (2014-2019).

¹ Meaningful and significant trends are highlighted red (increasing) and blue (decreasing).

 2 Censored data were 50% of total data. When censored data were substituted with 50% of the detection limit, the temporal trend was still significant (p = 0.01) and meaningful (+23% annually).



Figure 12. Ammoniacal nitrogen concentrations in Refining NZ SWB from May 2014 to February 2019 (top) and from June 2015 to February 2019 (bottom). Note the different concentration scales.

2.4 Northport SWB discharge quality

Under Resource Consent CON20090505532, Northport Limited discharges stormwater from Marsden Maritime Holdings (MMH) and the Port after passing through a storage and settlement pond system (combined SWB). The Northport combined SWB is discharged into Whangarei Harbour near the Refining NZ SWB discharge (see Figure 13 for location). Therefore, the contaminants discharged from Northport contribute to the current receiving environment. Water quality data from MMH and the Port were provided for the period July 2014 to November 2017 (up to 24 sampling events) by Refining NZ in Excel format.

To provide an understanding of potential point source "hotspots", a statistical summary analysis of Northport and Refining NZ SWB data for contaminants in common was undertaken (Table 9).

- TSS concentration is higher in the Northport discharge (median 34 mg/L) compared with Refining NZ (median 13 mg/L) by a factor of around 3.
- The minimum, median and mean pH in Northport (6.40, 7.00, and 7.06, respectively) is lower compared with Refining NZ (7.40, 8.10, 8.00, respectively) by around 1 pH unit.
- Copper and lead concentrations are similar between Northport (median 0.0021, 0.0006 mg/L, respectively) and Refining NZ (median 0.0027, 0.0006 mg/L, respectively).
- Zinc concentrations are higher at Refining NZ (median 0.0420 mg/L) than Northport (median 0.0178 mg/L) by a factor of around 2. Implications of the zinc SWB concentrations to the marine receiving environment are discussed in Section 4.4.1.
- Total PAHs were below the detection limit in both discharges.

Test		Northport (2014-2017)		Refining NZ (2014-2019)			
	Min	Max	Median	Mean	Min	Max	Median	Mean
TSS	6	89	34	40	2	23	13	12
рН	6.40	8.50	7.00	7.06	7.40	8.50	8.10	8.00
Total Copper	0.0008	0.0042	0.0021	0.0023	0.0009	0.0046	0.0027	0.0028
Total Lead	0.0002	0.0021	0.0006	0.0008	0.0002	0.0015	0.0006	0.0007
Total Zinc	0.0050	0.1700	0.0178	0.0250	0.0079	0.1800	0.0420	0.0559
Total PAHs ¹	<0.0001	<0.0036	NA	NA	<0.0016	<0.0074	NA	NA

Table 9. Comparison of Northport and Refining NZ SWB pond contaminants.

 1 (<DL=DL). Note 9 PAHs measured at Northport and 16 at Refining NZ.

2.5 Receiving environment water and sediment quality

NRC carry out monitoring of water, sediment and shellfish at sites within Whangarei Harbour. Water quality sites used in the assessment of potential effects are shown in Figure 13. Water quality sites coloured white are receiving environment sites monitored by NRC, while the Refining NZ SWB at Marsden Point oil refinery is coloured purple. The corners of the mixing zone are shown by red markers. The site associated with discharge from Northport (Resource Consent # CON20090505532) is coloured yellow. This is placed here for reference and has been discussed

in Section 2.4. Sediment quality sites used for status and trend analysis are summarised in Section 2.5.4 and 0.

2.5.1 Receiving environment water quality sites

Relevant to this assessment, NRC monitor nine (9) water quality sites in Whangarei Harbour, including 4 sites in the inner harbour (100263, 100270, 100264, and 100537), 2 sites at the edge of the mixing zone (100265 and 100266), and 3 sites in the outer harbour (100268, 100190, and 100269) (see Figure 13 and Table 10 for locations and following tables for water quality data).

Site Code	Name	Region	Latitude	Longitude
100263	One Tree Point	Inner Harbour	-35.817634	174.453832
100270	Snake Bank	Inner Harbour	-35.819312	174.471507
100264	Blacksmiths Creek	Inner Harbour	-35.834636	174.474646
100537	Tug wharf	Inner Harbour	-35.834085	174.489316
100265	Mix Zone - inner	Mix Zone	-35.835179	174.495614
100266	Mix Zone - outer	Mix Zone	-35.838516	174.502707
100268	Inner channel	Outer Harbour	-35.843414	174.502468
100190	Mair Bank	Outer Harbour	-35.842826	174.512687
100269	Bream Bay	Open Ocean	-35.849654	174.493694
105105	SW Basin	Refinery	-35.838936	174.497268

Table 10. Receiving environment water quality site code, name, region and coordinates.



Figure 13. Receiving environment <u>water quality</u> sites monitored by Northland Regional Council (in white), with SWB (purple), Northport discharge site (yellow: see Section 2.4) and four corners of the mixing zone (red markers).

Quarterly NRC receiving environment water quality monitoring data for the period May 2014 to February 2019 were provided by Refining NZ in Excel format.

Parameters consistently measured³⁶ at water quality sites are:

- physical DO, pH, temperature, salinity, and;
- toxicants phenols, metals/metalloids, NH₄-N, BOD₅, FC, sulphide, TPH, and TSS.

These parameters were assessed against the applicable surface water quality guideline (SWQG) summarised in Table 3.

Physical parameters

The SWQGs defined by the pNRP (Table 3) are for a minimum dissolved oxygen (DO) of 4.6 mg/L and annual median DO of >6.9 mg/L. Organic material present in point source and diffuse discharges (usually measured as BOD_5) can cause adverse effects by reducing DO to unacceptable levels. The surface water at Whangarei Harbour sites monitored by NRC have been consistently well oxygenated in the period assessed (2014–2019), with minimum DO across all sites and years of 6.3 mg/L (Table 11), which was observed at mixing zone site 100266 in 2014, and lowest annual median of 7.4 mg/L, at inner harbour site 100264 in 2016 (Table 12).

Table 11. Minimum dissolved oxygen concentration at NRC water quality sites from 2014 to 2019, and comparison with proposed Northland Regional Plan surface water quality guideline.

Region	Site ¹	Unit	2014	2015	2016	2017	2018	2019
	100263	mg/L	7.6	7.3	7.0	7.3	7.9	6.9
Inner Harbour	100270	mg/L	6.4	7.4	6.9	7.1	8.0	7.1
Inner narbour	100264	mg/L	6.5	7.2	7.0	6.5	8.0	7.0
	100537	mg/L	6.4	7.2	6.9	7.1	8.2	7.0
Miring Zono	100265	mg/L	6.5	8.1	6.9	7.1	8.2	7.1
Mixing Zone	100266	mg/L	6.3	7.2	7.0	7.1	8.2	7.1
	100268	mg/L	6.4	7.3	6.9	7.2	8.2	7.1
Outer Harbour	100190	mg/L	6.7	7.3	6.9	7.3	8.3	7.1
	100269	mg/L	6.6	7.4	7.0	7.2	8.4	7.1
pNRP minir	num	mg/L	4.6					

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

³⁶ Some parameters have been measured sporadically. These have not been assessed due to lack of consistent data.

Table 12. Annual median dissolved oxygen concentration at NRC water quality sites from 2014 to 2019, and comparison with proposed Northland Regional Plan surface water quality guideline.¹

Region	Site ²	Unit	2014	2015	2016	2017	2018
	100263	mg/L	8.2	8.2	7.9	8.1	8.2
Inner Harbour	100270	mg/L	8.1	8.0	7.6	7.9	8.2
Inner Harbour	100264	mg/L	7.9	8.2	7.4	7.8	8.2
	100537	mg/L	8.1	7.9	7.5	7.8	8.3
Mixing Zono	100265	mg/L	8.0	8.3	7.6	7.8	8.4
Mixing Zone	100266	mg/L	8.0	8.0	7.6	7.8	8.4
	100268	mg/L	8.0	8.0	7.7	7.9	8.4
Outer Harbour	100190	mg/L	8.2	8.2	7.7	7.8	8.4
	100269	mg/L	8.1	8.2	7.8	8.0	8.4
pNRP annual median mg/L >6.9							

¹Only 1 datapoint in 2019 so data not included.

² Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

The SWQGs defined by the pNRP are for a pH range between 7 and 8.5. Acidic (low pH) or alkaline (high pH) discharges may impact on receiving environment pH, leading to adverse environmental effects. For NRC Whangarei Harbour sites monitored between 2014 and 2019, pH was well within the required range of 7 to 8.5 (Table 13 and Table 14).

Furthermore, there was no more than 0.1 pH unit difference between inner harbour sites, mixing zone sites and outer harbour sites (Table 13 and Table 14).

Table 13. Minimum pH at NRC water quality sites from 2014 to 2019, and comparison with
pNRP SWQG.

Region	Site ¹	2014	2015	2016	2017	2018	2019
	100263	ND	6.3	7.9	8.1	8.1	8.2
Inner Harbour	100270	8.1	8.1	8.0	8.1	8.2	8.2
inner harbour	100264	8.1	8.1	8.0	8.0	8.1	8.2
	100537	8.1	8.0	8.0	8.1	8.1	8.2
Miving Zono	100265	8.1	8.1	8.0	8.1	8.2	8.2
Mixing Zone	100266	8.2	8.1	8.0	8.1	8.1	8.2
	100268	8.1	8.1	8.0	8.0	8.2	8.2
Outer Harbour	100190	8.1	8.1	8.0	8.0	8.2	8.2
	100269	8.2	8.1	8.0	8.1	8.2	8.2
pNRP mini	imum			2	7		

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green. ND = no data.

Region	Site ¹	2014	2015	2016	2017	2018	2019
	100263	ND	8.2	8.1	8.1	8.2	8.2
Inner Harbour	100270	8.2	8.2	8.2	8.2	8.2	8.2
Inner Harbour	100264	8.2	8.1	8.1	8.1	8.2	8.2
	100537	8.2	8.2	8.2	8.1	8.2	8.2
Mining Zono	100265	8.2	8.2	8.1	8.1	8.2	8.2
Mixing Zone	100266	8.2	8.2	8.2	8.1	8.2	8.2
	100268	8.2	8.2	8.2	8.1	8.2	8.2
Outer Harbour	100190	8.2	8.1	8.2	8.1	8.2	8.2
	100269	8.2	8.2	8.2	8.1	8.2	8.2
pNRP max	imum			8	.5		

Table 14. Maximum pH at NRC water quality sites from 2014 to 2019, and comparison with Northland Regional Plan surface water quality guideline.

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green. ND = no data.

The SWQGs defined by the oNRP and pNRP are for a maximum temperature change of 3 °C at the edge of the mixing zone. Across the NRC water quality sites monitored, there was very little difference in temperature (generally less than 1 °C: see Table 15 and Table 16). Furthermore, the two sites in closest proximity to the mixing zone showed even less variability (generally less than 0.2 °C: see rows shaded grey in Table 15 and Table 16), suggesting that temperature variation in Whangarei Harbour surface water is not influenced by the Refining NZ SWB discharge.

Table 15. Minimum temperature at NRC water quality sites from 2014 to 2019, and comparison with pNRP and oNRP SWQGs.

Region	Site ¹	Unit	2014	2015	2016	2017	2018	
	100263	°C	14.20	14.90	14.50	14.80	13.90	
Inner Harbour	100270	°C	13.20	15.20	14.50	15.10	14.10	
Inner narbour	100264	°C	13.80	14.70	14.80	15.20	14.10	
	100537	°C	13.80	14.60	14.50	15.00	14.60	
Mixing Zono	100265	°C	13.70	14.80	14.50	15.00	14.30	
Mixing Zone	100266	°C	13.80	14.60	14.50	15.00	14.50	
	100268	°C	14.00	14.70	15.20	15.10	14.50	
Outer Harbour	100190	°C	14.00	14.70	14.70	15.00	14.40	
	100269	°C	14.10	14.80	14.60	15.00	14.50	
oNRP/pNRP	maximum change	°C	3.00					

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

Table 16. Maximum temperature at NRC water quality sites from 2014 to 2019, and comparison with pNRP and oNRP SWQGs.

Region	Site ¹	Unit	2014	2015	2016	2017	2018
	100263	°C	19.40	22.20	23.50	23.70	17.60
Inner Harbour	100270	°C	16.70	21.90	22.70	22.60	17.20
Inner Harbour	100264	°C	17.10	22.30	23.70	23.70	17.50
	100537	°C	16.60	22.00	22.50	22.50	17.00
Mining Zono	100265	°C	16.50	21.80	22.60	22.60	17.00
Mixing Zone	100266	°C	16.60	22.20	22.60	22.40	17.00
	100268	°C	17.00	22.50	22.60	22.60	17.10
Outer Harbour	100190	°C	16.60	22.10	22.50	22.10	16.90
	100269	°C	16.80	22.50	22.80	22.90	17.30
oNRP/pNRP	maximum change	°C	3.00				

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

<u>Toxicants</u>

Elevated NH₄-N concentrations can cause adverse acute environmental effects. The SWQG defined by the pNRP is for annual median ammoniacal-nitrogen (NH₄-N) concentration of <0.023 mg/L. The oNRP defines an NH₄-N concentration of <0.005 mg/L; however, there is no compliance metric associated with this SWQG. Between 2014 and 2018, all NRC water quality sites had median annual NH₄-N concentrations below the pNRP SWQG (Table 17), with one exception: site 100263 (One Tree Point) marginally exceeded the pNRP SWQG in 2014 (0.027 mg/L). Although the oNRP SWQG for NH₄-N compliance metrics is not defined, the receiving environment annual median NH₄-N concentrations were also compared with the oNRP SWQG (underlined in Table 17). This shows that all sites exceeded the oNRP SWQG of 0.005 mg/L for the majority of the time. Of particular importance to this assessment, sites on the edge of the mixing zone (100265 and 100266) had low NH₄-N concentrations (generally <0.010 mg/L) compared with NRC monitoring sites in the inner harbour and the outer harbour (Table 17).

Region	Site ³	Units	2014	2015	2016	2017	2018
	100263	mg/L	0.027	<u>0.018</u>	0.008	0.006	<u>0.007</u>
Inner Harbour	100270	mg/L	0.003	<u>0.009</u>	0.007	0.003	<u>0.010</u>
Inner narbour	100264	mg/L	<u>0.008</u>	<u>0.013</u>	<u>0.018</u>	<u>0.021</u>	<u>0.017</u>
	100537	mg/L	<u>0.009</u>	<u>0.014</u>	0.003	<u>0.006</u>	0.003
Mixing Zone	100265	mg/L	0.003	<u>0.008</u>	0.003	0.003	<u>0.006</u>
WIIXINg Zone	100266	mg/L	<u>0.006</u>	<u>0.021</u>	<u>0.006</u>	<u>0.006</u>	<u>0.006</u>
	100268	mg/L	0.003	<u>0.017</u>	0.003	<u>0.006</u>	0.003
Outer Harbour	100190	mg/L	0.003	0.011	0.003	0.003	<u>0.019</u>
	100269	mg/L	<u>0.006</u>	<u>0.011</u>	0.003	<u>0.006</u>	<u>0.017</u>
	pNRP SWQG (annual median)	mg/L			<0.023		
	oNRP SWQG	mg/L			<0.005		

Table 17. Annual median ammoniacal-nitrogen concentrations at NRC water quality sites from 2014 to 2018, and comparison with pNRP and oNRP SWQGs.^{1,2}

¹Only 1 datapoint in 2019 so data not included.

² NH₄-N concentrations exceeding pNRP SWQG are bolded and exceeding oNRP SWQG underlined.

³ Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

Metals / metalloids

Elevated metal and metalloid concentrations can lead to adverse environmental effects. SWQG used for assessment of potential adverse effects are provided in Table 3. These are oNRP SWQG (arsenic and cadmium) and ANZ SWQG (chromium, copper, lead, mercury, and zinc).

Metal/metalloid concentrations are summarised in Table 18. Arsenic (a metalloid) was the only metal/metalloid consistently above detection limits, however, concentrations were never greater than 11% of the oNRP SWQG. There was no apparent inter-site or inter-annual variation in arsenic concentrations at these sites. Furthermore, the Refining NZ SWB maximum arsenic concentration between 2015 and 2019 was 0.0041 mg/L (see Table 6), which is virtually identical to the receiving environment arsenic concentrations.

The detection limits in the analytical methods for chromium, copper and mercury were not sufficient to accurately assess potential temporal or spatial ecological effects of these toxicants. Chromium detection limits range from 0.001 to 0.005 mg/L. There appears to have been a reduction in the quality of the analytical method over time, with the lower detection limit presented in 2015 and the higher detection limit presented in 2018/2019. This could be due to a change in analytical laboratory or change in methods within a specific laboratory. A chromium detection limit of 0.005 mg/L is not sufficient to assess against the ANZ marine DGV (0.0044 mg/L). Copper (0.020 mg/L) and mercury (0.0005 mg/L) detection limits were consistent but higher than the applicable ANZ marine DGVs of 0.0013 mg/L and 0.0001 mg/L for copper and mercury, respectively. This prevents a robust assessment of temporal and spatial copper and mercury concentrations are elevated in mixing zone sites in comparison with inner and outer harbour sites. However, dilution modelling (see Section 4.2) addresses any potential effects on the receiving environment bese contaminants.

As summarised in Section 0 (Table 7), maximum copper and zinc SWB concentrations exceeded the ANZ marine DGVs. Median concentrations also exceeded the same trigger values. Although this suggests a *potential* for point source discharges of these metals to have an adverse effect on the receiving environment, there is no evidence that this is occurring. Zinc in the discharge was especially high, however it was below detection limits at all receiving environment sites. Copper in the discharge was up to 3.5x the ANZ marine DGV, but only detected at 2 receiving environment sites, neither of which was a mixing zone site. Dilution modelling (see Section 4.2) addresses any potential effects on the receiving environment water quality from these contaminants.

Region	Site ³	Date	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
	100263	Nov-18	0.0028	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
Inn	100263	Apr-19	0.0032	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
er H	100270	Sep-15	0.0042	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
Inner Harbour	100264	Sep-15	0.0044	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
our	100264	May-16	ND	ND	ND	0.0062	<0.001	ND	ND	<0.01
	100537	Sep-15	0.0044	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
	100265	Sep-15	0.0041	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
	100265	Oct-18	0.0011	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
	100265	Nov-18	0.0011	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
Mi	100265	Feb-19	0.0032	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
xing	100265	Apr-19	0.0025	<0.0005	<0.002	<0.0020	<0.001	<0.0005	<0.001	<0.01
Mixing Zone	100266	Sep-15	0.0053	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
ne	100266	Oct-18	<0.0010	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
	100266	Nov-18	<0.0010	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
	100266	Feb-19	0.0039	<0.0005	<0.005	<0.0020	<0.001	<0.0005	<0.001	<0.01
	100266	Apr-19	0.0028	<0.0005	<0.002	<0.0020	<0.001	<0.0005	<0.001	<0.01
Out	100268	Sep-15	0.0043	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
Outer Harbour	100190	Sep-15	0.0038	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
Iarb	100190	May-16	ND	ND	ND	0.0091	<0.001	ND	ND	<0.01
our	100269	Sep-15	0.0049	<0.0005	<0.001	<0.0020	<0.001	<0.0005	ND	<0.01
	Maximum		0.0053	<0.0005	<0.005	0.0091	<0.001	<0.0005	<0.001	<0.01
	Median		0.0039	NA	NA	NA	NA	NA	NA	NA
(sour	SWQG ce – see Ta	ble 3)	0.050 (oNRP)	0.002 (oNRP)	0.0044 (ANZ)	0.0013 (ANZ)	0.0044 (ANZ)	0.0001 (ANZ)	0.07 (ANZ)	0.015 (ANZ)
Maxin	num % of S	SWQG ⁴	11	25	114	700	23	500	1	67
Med	ian % of S	WQG	8	NA	NA	588	NA	NA	NA	NA

Table 18. Metal/metalloid concentrations $(mg/L)^1$ at NRC water quality sites from 2015 to 2019, with maximum and median and comparison with ANZ marine DGV.²

¹ As = arsenic; Cd = cadmium; Cr = chromium; Cu = copper; Pb = lead; Hg = mercury; Ni = nickel; Zn = zinc. ND = No data.

² Data above ANZECC 95% marine trigger value are bolded.

³ Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green.

⁴Where concentration is below detection limit it is set at detection limit.

Fourteen (14) individual phenol congeners were measured at all sites over the whole period. Detection limits are analyte specific and ranged between 0.001 mg/L and 0.004 mg/L. All results were below detection limits.

ANZ marine DGVs exist for phenol and pentachlorophenol only (see Table 3), and are 0.40 mg/L and 0.022 mg/L for phenol and pentachlorophenol, respectively.

By using a conservative approach consisting of setting the water concentration at the detection limit, phenol (0.002 mg/L) was less than 2% of the ANZ marine DGV (0.40 mg/L). Similarly, pentachlorophenol (0.001 mg/L) was 18% of the ANZ marine DGV (0.022 mg/L).

Table 19. Phenol concentrations at NRC water quality sites from 2014 to 2019, and comparison with ANZ marine DGV.¹

	Units	Phenol	Pentachlorophenol
All sites	mg/L	<0.002	<0.001
ANZ DGV	mg/L	0.4	0.022

 $^{\rm 1}$ ANZ marine DGV only available for phenol and pentachlorophenol.

Annual maximum TPH concentrations at NRC receiving environment sites for the period 2014 to 2018 were generally very low and below detection limits (0.3 mg/L) (Table 20). The main exception was 2016, when maximum TPH concentration ranged between 0.4 and 1.7 mg/L. Over this time there were no apparent differences between mixing zone sites and sites in the inner harbour and the outer harbour, suggesting that Refining NZ SWB is not causing any elevation of TPH concentrations in the marine receiving environment.

The value of 1.7 mg/L at Outer Harbour site was an annual maximum value. For the other sites the annual maximum ranged from <0.3 to 0.6 mg/L, no more than 2 times the detection limit of 0.3 mg/L. NRC monitor 4 times per year, and for Outer Harbour TPH concentrations in 2016 were <0.3, <0.3, 0.5, and 1.7 mg/L. Similarly, for other sites many concentrations were <0.3 mg/L.

However, it is possible that something has occurred in 2016 to cause, what appears to be a small but consistent increase in TPH, at all receiving environment sites. Refining NZ state that short lived TPH "spike" discharges from the Refinery are highly unlikely as they consider the SWB to be reasonably well mixed, any free phase hydrocarbon will be at the surface of the SWB and the pumps take from the bottom of the SWB.

Although the cause of this small and consistent increase in TPH in receiving environment sites is unknown, there are no applicable marine water quality guidelines for TPH from which to assess potential effects of this "spike" in TPH in 2016. However, 2016 appears to be an anomaly (years 2014, 2015, 2017 and 2018 have TPH concentrations mostly below detection limits).

Region	Site ¹	2014	2015	2016	2017	2018
	100263	ND	<0.3	<0.3	<0.3	<0.3
Inner Harbour	100270	<0.3	<0.3	0.4	0.3	<0.3
IIIIei nai ooui	100264	<0.3	<0.3	0.5	<0.3	<0.3
	100537	<0.3	<0.3	0.5	<0.3	<0.3
Miving Zono	100265	<0.3	<0.3	0.4	<0.3	<0.3
Mixing Zone	100266	<0.3	<0.3	0.6	<0.3	<0.3
	100268	<0.3	<0.3	0.5	<0.3	<0.3
Outer Harbour	100190	<0.3	<0.3	0.4	0.4	<0.3
	100269	<0.3	<0.3	1.7	<0.3	<0.3

Table 20. Annual maximum TPH concentrations at NRC water quality sites from 2014 to 2018.

¹Sites in closest proximity to the mixing zone are shaded grey, while 100269 (open costal water) is shaded green. ND = no data.

Sulphide was measured at all sites over the whole period, with all results below detection limit (0.1 mg/L). There are no ANZ marine DGVs for sulphide.

Annual-average total suspended sediment (TSS) concentration for each of the years 2014 to 2018 is shown in Figure 14. There are no TSS guidelines provided by the either the oNRP or pNRP, and neither is there an ANZ marine DGV. Auckland Council (AC) use TSS as one of 7 parameters to calculate a water quality index, which is a relative measure of marine water quality compared with reference sites (Vaughan, 2017). AC use an average TSS concentration of 20 mg/L. Generally, annual-average TSS concentrations at NRC receiving environment sites were around 20 mg/L (see Figure 14 for a pictorial comparison), ranging from 4 to 35 mg/L. This suggests suspended solid concentrations at these sites are not excessively high.



Figure 14. Annual-average TSS concentration at NRC water quality sites from 2014 to 2018. Auckland Council average water quality TSS concentration of 20 mg/L designated by dashed red line.

Sediment from the Refining NZ SWB discharge was modelled (MetOcean Solutions, 2020) to estimate potential receiving environment concentrations of sediment (effectively TSS). Results of this modelling are discussed in Section 5.

2.5.3 Receiving environment water quality trends

Temporal trends for selected parameters at NRC water quality sites were assessed with Time Trends (see Section 2.3 for summary and methodology). The parameters selected for analysis were NH_4 -N, DO, pH and temperature. For each of these parameters, there were consistent data and the concentrations were predominantly above detection limits, i.e. very few censored data.

 NH_4 -N was assessed using a Mann-Kendall trend test and a Seasonal Trend test, as there was potential seasonal bias in the data. All temporal trends were not significant and independent of season: p = 0.10 to 0.97 for Mann-Kendall and p = 0.15 to 1.00 for Seasonal Trend test.

DO was assessed using a Seasonal Trend test, as there was clear seasonal bias in the data. All temporal trends were not significant (p = 0.12 to 1.00).

pH showed no obvious seasonal bias and was assessed using a Mann-Kendall trend test. All temporal trends were not significant (p = 0.36 to 1.00).

Temperature was assessed using a Seasonal Trend test, as there was clear seasonal bias in the data. Inner harbour site trends were not significant (p = 0.12 to 0.19). However, the mixing zone and outer harbour sites were either significant (p = 0.04) or borderline significant (p = 0.05 - 0.06), with all showing an increase in temperature between 2014 and 2019 (Table 21 and Appendix 1).

Table 21. Temperature temporal trends summary (2014-2019) in mixing zone and outer harbour receiving environment sites.¹

Region	Site	Median value	Р	Median annual Sen slope	RSKSE	Trend ²
Mixing	100265	17.0	0.04	0.25	1.5	↑
Zone	100266	16.9	0.04	0.21	1.2	^
	100268	17.0	0.06	0.10	0.6	^
Outer Harbour	100190	16.8	0.06	0.23	1.4	^
	100269	16.8	0.05	0.20	1.2	^

¹ Inner Harbour site trends were not significant and are not presented.

² Meaningful (RSKSE > 1.0) and significant (p<0.05) trends are highlighted red (increasing).

2.5.4 Receiving environment sediment quality sites

Seven (7) NRC sediment quality sites in Whangarei Harbour have been monitored reasonably consistently. See Table 22 and Figure 15 for site locations. There are 3 sites in the inner harbour (109265, 100127, 110593), 2 sites at the mixing zone boundary (100605 and 110624) and 2 sites in the outer harbour (100268 and 100190)³⁷. The Refining NZ SWB was also monitored (site 100532). Three sites have been monitored from 2002 to 2016: 100127 (6 times), 100605 (8 times), and 100268 (8 times). The other 4 sites (and the Refining NZ SWB) have been monitored 3 times: in 2012, 2014 and 2016. All 7 sites were assessed for current status sediment quality (2012, 2014 and 2016), while temporal trends for 4 selected metals/metalloids were undertaken on data from the long-term sites (see Section 0).

 $^{^{\}rm 37}$ The outer harbour sites – 100268 and 100190 – are also water quality sites.



Figure 15. Receiving environment <u>sediment</u> quality sites monitored by Northland Regional Council (in white), with SWB (purple), and four corners of the mixing zone (shown as red markers). Inset is expanded view around mixing zone, including 2019 Refining NZ soft-sediment sites (De Luca, 2020).

Table 22. Receiving environment sediment quality site code, name, region and coordinates.

Site ID	Site Name	Region	Latitude	Longitude
109265	Parua Bay intertidal flat between Manganese Point and Motukiore Island	Inner Harbour	-35.791321	174.444656
100127	Whangarei Harbour @ Snake Bank North side	Inner Harbour	-35.809154	174.473511
110593	Whangarei Harbour at Adjacent fishing jetty.	Inner Harbour	-35.835527	174.491536
100605	Between NHB and NZRC jetty	Mix Zone	-35.836066	174.493848
110624	Lower Whangarei harbour at Marsden Bank	Mix Zone	-35.839242	174.503086
100268	Inner Channel	Outer Harbour	-35.843414	174.502468
100190	Lower Whangarei Harbour a2913,b265 at Mair Bank Outer Marker Pile	Outer Harbour	-35.842826	174.512687
100532	NZRC Stormwater basin at discharge - sampling point	Refinery	-35.837712	174.49781

2.5.5 Receiving environment sediment quality status

The same suite of PAHs, phenols, TPH and metals/metalloids as measured at the water quality sites and the Refining NZ SWB was measured in receiving environment sediments. Additional total organic carbon (TOC) and grainsize (sediment texture, or particle size) analyses were undertaken at the sediment sites.

Refining NZ have also undertaken a one-off sediment quality analysis of eight (8) soft-sediment sites around the mixing zone in May 2019 (see insert in Figure 15). This analysis is described in detail by De Luca (2020).

<u>Sediment texture</u>

Sediment texture was classified³⁸ as:

- <63 µm mud
- 63–250 µm very fine and fine sand
- 250–500 µm medium sand
- >500 μm coarse sand and gravel

Between 2012 and 2016, sediment texture at some NRC sediment sites was highly variable. NRC sampling protocol states that a single surficial sediment sample is collected at each site and samples are analysed for grain size by either Watercare or University of Waikato. Therefore, the high variability may be in part due to the lack of replicate samples and a single laboratory used for analysis.

Inner harbour sites (Table 23) were predominantly sandy between 2012 and 2016, with very low coarse gravel and mud (<10%). The exception was a high mud content at site 110593 (64%), but this was observed only in 2012 and was 3% in 2014 and 2016.

³⁸ Following the classification from Waikato Regional Council

⁽http://www.waikatoregion.govt.nz/environment/natural-resources/coast/coastal-monitoring/regional-estuarymonitoring-programme/methods/sediment-properties/sediment-classification/)

Site	2012	2014	2016
109265			
100127			
110593			
Legend	 mud very fine and 	fine sand 🛛 medium sand	coarse sand and gravel

Table 23. Inner harbour sites sediment texture proportions from 2012 to 2016.

Mixing zone sites were also predominantly sandy over this time period with a consistently low mud content but variable coarse sand and gravel (Table 24). In 2012, mixing zone sites had a coarse sand and gravel of between 12% and 14%, which reduced to between 0% and 5% in 2014. Site 100265 remained at 0% in 2016, however site 110624 (Marsden Bank) increased to 50%.

Site	2012	2014	2016
100605			
110624			
Legend	mud very fine and	fine sand 🛛 🔹 medium sand	coarse sand and gravel

Table 24. Mixing Zone sites sediment texture	e proportions from 2012 to 2016.
--	----------------------------------

The outer harbour sites encompass different settings and sediment types. Site 100268 is away from the main Whangarei Harbour channel, while site 100190 (Mair Bank) is on the edge of this channel.

Site 100126 had a reasonably consistent very fine to medium sand content over this time period, but mud reduced from 23% in 2012 to 2% in 2016, which is in contrast to coarse sand and gravel, which increased from 4% to 17% over this time.

Between 2012 and 2016, site 100190 (Mair Bank) underwent a significant increase in coarse sand and gravel, increasing from <1% to 94% (Table 25. This may have been a contributing factor to reduction in pipi populations at this site in 2014 and 2016 compared to 2010 (Pawley, 2016).

Site	2012	2014	2016
100268			
100190			
Legend	mud very fine and	fine sand 🛛 🖬 medium sand	coarse sand and gravel

Table 25. Outer harbour sites sediment texture proportions from 2012 to 2016.

<u>Toxicants</u>

Between 2012 and 2016, metal/metalloid sediment concentrations were consistent and showed no clear spatial or temporal patterns (see Appendix 2 for graphs). Furthermore, all metal/metalloid sediment concentrations were well below (generally <20% of) Canadian Council of Ministers of the Environment (CCME) sediment quality guideline values (SGVs) (see Table 4 for SGVs).

The NRC sediment monitoring data appear to show that mercury is the metal closest to the SGV, with up to 35% of the SGV observed. However, virtually all sediment mercury concentrations in the receiving environment were below the detection limit of 0.022 to 0.045 mg/kg, so this is not likely to be associated with any adverse effects. The practice (adopted here) of replacing values that are below the detection limit with the detection limit is very conservative, and it is possible that mercury concentrations are well below the detection limit and, as such, are actually much less than 35% of the SGV.

Only arsenic, chromium and lead were consistently above detection limits. Zinc was above detection limits for around 50% of samples. The detection limits for cadmium, copper, and mercury are sufficient to assess sediment quality regarding these toxicants but are not sufficient to assess spatial or temporal trends.

Total PAH sediment concentrations were always below detection limits. Data were set to the detection limit before being normalised to 1% TOC. Despite this, total PAH concentrations were less than 0.025% of the ANZ SGV.

TPH sediment concentrations normalised to 1% TOC were generally elevated across all sites in 2012, ranging from 45% to 150% of the SGV (Figure 16). Highest concentrations were generally away from the mixing zone, at inner harbour and outer harbour sites. TPH concentrations were markedly reduced in 2014 and 2016, at less than 25% of the SGV. Virtually all TPH concentrations in 2014 and 2016 were below detection limits.

TPH in receiving environment sediment does not appear to correlate with Refining NZ SWB sediment TPH concentrations. Although receiving environment sediment TPH concentrations in 2012 were markedly higher than in 2014 and 2016 (Figure 16), SWB sediment TPH concentrations were markedly lower in 2012 (450 mg/kg, normalised to 1% TOC) compared with 2014 (2714 mg/kg, normalised to 1% TOC) and 2016 (1723 mg/kg, normalised to 1% TOC) (Figure 11). Unexplained "spikes" in TPH in receiving environment sediment have occurred previously. Mortimer Consulting (2010) noted that for site 100605 (mixing zone), TPH in sediment was <60; <70; 157; and <60 mg/kg, for 2005; 2007; 2008 and 2009, respectively. They stated that the 2008 TPH concentration was notable but unexplained. No other receiving environment sites were included in this TPH assessment.





2.5.6 Receiving environment sediment quality trends

Temporal trends for arsenic, chromium, lead and zinc sediment concentrations at NRC sediment quality sites (2002 to 2016) were assessed with Time Trends (see Section 2.3 for summary and methodology). All sediment metal concentrations reduced over the period 2002 to 2016, and virtually all decreases were meaningful (i.e. RSKSE greater than 1% per year) (Table 26). For the inner harbour site, arsenic, chromium and lead reductions were also significant (p < 0.05).

Table 26. Receiving environment sediment metal/metalloid temporal trends summary(2002-2016).

Site	Parameter	Median value	Р	Median annual Sen slope	RSKSE (%)	Trend
	Arsenic	1.75	0.05	-0.13	-7.1	•
100127	Chromium	4.25	0.02	-0.40	-9.4	•
(Inner Harbour)	Lead	0.77	0.01	-0.08	-9.9	•
	Zinc	6.03	0.14	-0.35	-5.9	¥
	Arsenic	2.40	0.01	-0.10	-4.3	•
100605	Chromium	7.85	0.14	-0.59	-7.5	¥
(Mixing Zone)	Lead	1.20	0.07	-0.08	-6.4	•
	Zinc	9.35	0.14	-0.58	-6.1	¥
	Arsenic	2.45	0.45	-0.01	-0.4	¥
100268	Chromium	5.10	0.59	-0.07	-1.4	¥
(Outer Harbour)	Lead	0.81	0.03	-0.02	-2.1	•
	Zinc	6.26	0.41	-0.07	-1.1	•

3. Process Chemicals

3.1 Introduction

Refining NZ Marsden Point Refinery uses a multitude of process chemicals as part of the operation of the plant. Uses are varied and include:

- flocculant;
- oxygen scavenger;
- emulsion breaker;
- biocide;
- pH modifier/alkalinity builder;
- boiler water treatment;
- acid gas removal;
- biodispersant, and;
- removal of benzene, hydrogen sulphide and pyrophoric iron.

Many of the chemicals contained within each formulation are not "traditional" contaminants (such as presented in Section 2). Important distinctions between "traditional" contaminants and process chemicals are:

- "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 normally measured (in both water and sediment) routinely in the SWB and at receiving environment sites, while (due to lack of analytical capabilities) process chemicals are not.

However, process chemicals may enter the SWB, from where they may ultimately 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 3.2. Results are discussed in Section 3.3. Formulation and individual chemical data are provided in Appendix 3.

3.2 Risk assessment methodology

3.2.1 Identification of process chemical formulations used at Marsden Point Refinery

Refining NZ provided a simplified flow scheme of process chemical formulations used within the refinery (Figure 17), along with Chemwatch³⁹ Safety Data Sheets (SDS) for each formulation. Some of the SDS were incomplete regarding the exact individual chemical components and amounts of each component within the formulation. For these formulations, further information required to complete the identification of components and amounts was obtained from the manufacturer.

³⁹ https://www.chemwatch.net/

For each <u>formulation</u>, where possible, the following physical and chemical properties were obtained:

- form (liquid or solid);
- water solubility (miscible or immiscible);
- pH (as supplied);
- logP;^{40,41}
- logD (at pH 5.5 and pH 7.4);^{40,41}
- BCF (at pH 5.5 and pH 7.4).⁴⁰

3.2.2 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.

3.2.3 Identification of ecotoxicological effects

Ecotoxicological information was extracted from Chemwatch SDS for the formulation and individual chemicals within the formulation (if this exists). Where ecotoxicological data were not provided in the Chemwatch SDS, these were sourced primarily from a Sigma Aldrich⁴² SDS for the chemical, or from an SDS from another manufacturer, where the chemical is not available at Sigma Aldrich.

To provide a more robust assessment, two international ecotoxicology databases were searched, using the unique chemical identifier (CASRN). These were:

1. the Unites States Environmental Protection Agency (USEPA) Ecotox knowledgebase database⁴³, extracting lowest LC_{50}/EC_{50}^{44} for marine species (where present), or freshwater species (where no marine species data);

⁴³ <u>https://cfpub.epa.gov/ecotox/search.cfm</u>

 $^{^{40}}$ LogP, logD and bioaccumulation concentration factor (BCF) generated by ACD Labs (in the first instance) or ChemAxon (if not available). LogD and BCF values at pH 5.5 and 7.4. If only one value present, then it is pH independent.

⁴¹ The partition coefficient, P, is a measure of the differential solubility of a compound in two immiscible solvents. The most commonly used solvent system is octanol/water. The partition coefficient is the descriptor of lipophilicity for neutral compounds, or where the compound exists in a single form. For ionizable solutes, the compound may exist as a variety of different species in each phase at any given pH. D, the distribution coefficient, is the appropriate descriptor for ionizable compounds since it is a measure of the pH-dependent differential solubility of all species in the octanol/water system. P and D are typically used in the logarithmic form, logP and logD (https://www.acdlabs.com/download/app/physchem/logp_vs_logd.pdf)

⁴² https://www.sigmaaldrich.com/new-zealand.html

 $^{^{44}}$ LC $_{50}$ is the concentration at which 50% of the test population dies, while EC $_{50}$ is the concentration at an effect is recorded for 50% of the test population.

2. the European Chemicals Agency (ECHA)⁴⁵ information on chemicals database, extracting the lowest predicted no-effects concentration (PNEC) for marine water.

Using the most conservative approach (representing the worst-case scenario), the <u>lowest marine</u> <u>water ecotoxicological value</u> (PNEC) was used for the majority of chemicals in the risk assessment mass balance calculation.

However, when a PNEC was not available, it was estimated from toxicity data following guidelines from ECHA (2008). ECHA guidelines suggest the use of assessment factors that put a weighting on the appropriateness of the toxicity data. The toxicity data are divided by the assessment factor to estimate a marine PNEC. Assessment factors range from 10 to 10,000 (Table 27). Generally, acute (short-term) toxicity data corresponds with higher assessment factors (1,000 and 10,000) with chronic (long-term) toxicity data corresponding with lower assessment factors (10 to 1,000).

Where acute or chronic toxicity data are converted to a marine PNEC in this report, justification is provided for the assessment factor used.

Table 27. Assessment factors proposed for deriving marine PNEC for different data sets (Table R.10-5 from ECHA, 2008).

Data set	Assessment factor
Lowest short-term $L(E)C_{50}$ from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels	10,000
Lowest short-term $L(E)C_{50}$ from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels, + two additional marine taxonomic groups (e.g. echinoderms, molluscs)	1,000
One long-term result (e.g. EC_{10} or NOEC) (from freshwater or saltwater crustacean reproduction or fish growth studies)	1,000
Two long-term results (e.g. EC_{10} or NOEC) from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish)	500
Lowest long-term results (e.g. EC_{10} or NOEC) from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels	100
Two long-term results (e.g. EC_{10} or NOEC) from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish) + one long-term result from an additional marine taxonomic group (e.g. echinoderms, molluscs)	50
Lowest long-term results (e.g. EC_{10} or NOEC) from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels + two long-term results from additional marine taxonomic groups (e.g. echinoderms, molluscs)	10

⁴⁵ <u>https://echa.europa.eu/information-on-chemicals</u>



Figure 17. Simplified flow scheme of process chemicals used at Marsden Point Refinery.

The risk assessment was undertaken using a tiered approach.

- 1. A worst-case SWB concentration of each chemical within each formulation was calculated through mass balance.
- 2. An assessment was made of the worst-case scenario SWB concentration against the lowest ecotoxicological guideline by calculating a risk quotient. The risk quotient (RQ1) was calculated by dividing SWB concentration by the ecotoxicological guideline concentration, with a value >1 indicating a potential ecotoxicological effect. The RQ indicates the dilution required to reduce the concentration of the chemical to below ecotoxicological guidelines.
- 3. Where RQ1 was >1, allowance for oil and water partitioning was undertaken, and an updated risk quotient (RQ2) calculated.
- 4. Where RQ2 was >1, the dilution outside the mixing zone was calculated from 3D hydrodynamic modelling of various scenarios (MetOcean Solutions, 2020). An updated risk quotient (RQ3) was calculated.
- 5. Where RQ3 was >1, the potential for long-term effects involving persistence and/or bioaccumulation within the receiving environment was assessed by reference to (a) biodegradation data and (b) a bioaccumulation concentration factor (BCF).

Worst-case SW basin concentration scenario (RQ1)

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

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

The worst-case scenario assumes that the concentration in the SWB is then discharged to the marine receiving environment without further dilution.

Assessment of worst-case SWB concentration against lowest ecotoxicological guideline

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

 $\begin{array}{l} Adjusted \ ecotoxicological \ guideline \ \left(\frac{mg}{L}\right) = \\ \hline \\ \underline{Lowest \ ecotoxicological \ guideline \ for \ individual \ chemical \left(\frac{mg}{L}\right)} \\ proportion \ of \ formulation \ (\%) \end{array}$

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

RQ1 = SWB formulation worst-case" concentration (mg/L)/Adjusted ecotoxicological guideline (mg/L)

Where RQ1 <1 (i.e. the concentration being discharged from the SWB is below the lowest ecological guideline), the chemical (and therefore formulation) is flagged as "no ecological risk".

No further action is undertaken. This needs to be valid for $\underline{all \ chemicals}$ assessed within each formulation.

Where RQ1 >1 (i.e. the concentration being discharged from the SWB is above the lowest ecological guideline), the chemical (and therefore formulation) is flagged as "potential ecological risk". This needs to be valid for <u>at least one</u> chemical assessed within each formulation. For each chemical with RQ1 >1, oil/water partition calculations were undertaken.

Oil/water partition calculation

As most⁴⁶ process chemicals come into contact with the crude oil refinery process, their fate is determined by the equilibrium between the oil and water phases.⁴⁷ Lipophilic (lipid loving) chemicals will preferentially associate with the oil phase and be retained, while hydrophilic (water loving) chemicals will preferentially associate with the water phase and be discharged to the SWB. In practice, chemicals will sit somewhere between these two extremes, in which case the proportion of each chemical in oil or water can be calculated based on the partition coefficient (P) for neutral chemicals, or the dissociation coefficient (D) for ionisable chemicals (see footnote 41).

The percentage of each chemical in the oil phase was calculated by:

$$oil \ percentage = (\frac{P}{P+1}) * 100$$

By the conservation principle, the percentage of each chemical in the water phase was calculated by:

water
$$percentage = 100\% - oil percentage$$

For example:

- If P = 100,000⁴⁸ then the oil percentage will be (100,000/100,000+1)*100 = 99.999%. The water percentage will be 100%-99.999% = 0.001%.
- If P = 1.0^{49} then the oil percentage will be (1/1+1)*100 = 50%. The water percentage will be 100%-50% = 50%.
- If P = 0.03⁵⁰ then the oil percentage will be (0.03/0.03+1)*100 = 3.07%. The water percentage will be 100%-3.07% = 96.93%.

The same formulas apply for the dissociation coefficient (D) used for ionisable chemicals. The oil/water proportions were calculated for all chemicals subjected to this process for <u>both P and D</u> and the most conservative value used.

⁴⁶ Chemicals that do not come into contact with hydrocarbons through the refinery process are not subjected to oil and water partitioning calculations. These are highlighted individually in Section 3.3.

⁴⁷ Notwithstanding other processes, such as thermal or hydrological degradation, in the absence of any contradictory information, <u>conservation of each chemical was assumed</u>. These other processes were only assessed where specific information was available (see, for example, hydroquinone).

⁴⁸ logP = 5, which are properties of a highly lipophilic chemical.

⁴⁹ logP = 0, which are properties of a balanced lipophilic/hydrophilic chemical.

 $^{^{50}}$ logP = -1.5, which are properties of a highly hydrophilic chemical.
Dilution (after correction for oil/water partition) that is required to meet lowest ecological guideline (RQ2), was calculated from the formula:

RQ2 = RQ1 * percentage of each chemical in water phase

Dilution required within mixing zone (RQ3)

Dilution of the SWB discharge in the receiving environment was modelled (MetOcean Solutions, 2020). Each process chemical with RQ>2 had the worst-case scenario dilution applied to assess whether receiving environment concentrations may lead to adverse effects, which is indicated by RQ3 > 1.

Environmental fate (RQ3 > 1)

Formulation biodegradation data were obtained, where available, in the first instance from SDS. Where data were not available, biodegradation data were obtained from the ECHA database.

The bioaccumulation concentration factor (BCF) was calculated for each chemical. US EPA⁵¹ define a chemical with BCF <1000 as having a low bioconcentration potential. ECHA⁵² 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 are presented in Appendix 4.

3.3 Results and discussion

3.3.1 Comment on non-disclosure

Some of the formulations used at the Refinery have chemicals contained within that are proprietary and therefore commercially sensitive. Refining NZ and Streamlined Environmental Ltd (SEL) have signed non-disclosure agreements (NDA) with Suez Water Technologies and Solutions and Solberg Asia Pacific Ltd. The result of these NDAs is that SEL have the required information to undertake a robust risk assessment however, 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.

3.3.2 BetzDearborn AE1115P

BetzDearborn is a flocculant used in the following processes: biological treatment, DAF, bug tank, clarification (Figure 17). BetzDearborn does not come into contact with petroleum hydrocarbons as part of the refining process. It is applied at an average rate of 4.6 kg/day. The formulation has a pH of 7. No ecotoxicological data were available in the Chemwatch SDS.

⁵¹ US EPA Sustainable Futures / P2 Framework Manual 2012 EPA-748-B12-001 Chapter 5. Estimating Physical / Chemical and Environmental Fate Properties with EPI Suite™.

⁵² ECHA Report. Guidance on Information Requirements and Chemical Safety Assessment Part C: PBT/vPvB assessment Version 3.0 June 2017.

There are four components of BetzDearborn, not including water (Appendix 3). Three components are restricted under an NDA and are given generic codes. The four components are:

- Isoparaffins petroleum hydrotreated HFP (ICP solvent) (22.4% by weight: CASRN 64742-47-8).
- Betz1 (30% by weight: CASRN restricted).
- Betz2 (0.04% by weight: CASRN restricted).
- Betz3 (0.7% by weight: CASRN restricted).

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

A potential ecological risk was identified for ICP solvent component only. ICP solvent has a long-term no-observable-effects concentration (NOEC) for crustacea of 0.024 mg/L,⁵³ plus long-term no-observable-effects concentration (NOEL) of 0.098 mg/L for fish,⁵⁴ and long-term NOEL of 0.48 mg/L for an aquatic invertebrates.⁵⁴ Based on ECHA criteria for estimating a PNEC based on two long-term results representing two trophic levels (crustaceans and fish) plus one long-term result from an additional marine taxonomic group (Table 27), an assessment factor of 50 was used to estimate a marine PNEC of 0.00048 mg/L Furthermore, AE1115P formulation is only injected upstream of the FFU (DAF). The hydrocarbon removal efficiency of the DAF is in the 80 to 90% range (Phillip Shoebridge, Refining NZ, personal communication). Using a conservative removal rate of 80% and a proportion in the formulation of 22.4% by weight, an RQ1 was calculated as 86. As the formulation does not come into contact with petroleum hydrocarbons, an oil/water correction (i.e. RQ2) was not valid and therefore not applied. Therefore, RQ1 = RQ2.

As RQ2 (86) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Sections 4.4.2 and 4.5.2).

3.3.3 Cortrol OS7780

Cortrol OS7780 is a dissolved oxygen scavenger/metal passivator used in the western Accidentally Oil Contaminated (AOC) trench (Figure 17). Cortrol OS7780 does not come into contact with petroleum hydrocarbons as part of the refining process. It is applied at an average rate of 13.7 kg/day. The formulation has a pH of 7.5. No ecotoxicological data were available in the Chemwatch SDS.

There are six components of Cortrol OS7780, not including water (Appendix 3). 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).

⁵³ Chemwatch SDS.

⁵⁴ https://echa.europa.eu/registration-dossier/-/registered-dossier/15375/6/2/1

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

A potential ecological risk was identified for hydroquinone only, for which RQ1 = 1202, based primarily on a marine PNEC of 0.000057 mg/L. However, the process converts hydroquinone to 1,4-benzoquinone in quantitative yield (i.e. 100% conversion). 1,4-benzoquinone has a NOEC from a freshwater fish (Zebra fish: *Danio rerio*) of 0.086 mg/L. An assessment factor of 1,000 was used to estimate a marine PNEC of 0.000086 mg/L (Table 27). Based on a derived marine PNEC of 0.000086 mg/L, a RQ1 of 797 was calculated for 1,4-benzoquinone .

As the formulation does not come into contact with petroleum hydrocarbons, an oil/water correction (i.e. RQ2) was not valid and therefore not applied. Therefore, RQ1 = RQ2.

As RQ2 (797was>1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Sections 4.4.2 and 4.5.2).

3.3.4 Cortrol OS5614 (alternative to OS7780)

As Cortrol OS7780 may be causing more than minor effects outside the mixing zone (see Sections 4.4.2 and 4.5.2). An alternative oxygen scavenger/metal passivator formulation was assessed, Cortrol OS5614. Cortrol OS5614 would not come into contact with petroleum hydrocarbons as part of the refining process. It would be applied at an average rate of 13.7 kg/day. The formulation has a pH of 9.

There are two components of Cortrol OS5614, not including water (Appendix 3). Both components are restricted under an NDA and are given generic codes. The two components are:

- Cort6 (11.97% by weight: CASRN restricted).
- Cort7 (0.006% by weight: CASRN restricted).

The major active ingredient (Cort6) decomposes to ammonia (NH₄-N), nitrogen (N₂), and carbon dioxide (CO₂) above 200 °C. At a dose rate of formula of 1 mg/L, the concentration of Cort6 in the formula is 11.97% of 1 mg/L, or 0.12 mg/L. Assuming 100% decomposition, and with N₂ and CO₂ being lost as gases, around 60% of the mass is removed through gas boil-off which results in around a 60% reduction of the original 0.12 mg/L concentration of Cort6. Therefore, the remaining NH₄-N concentration would 40% of 0.12 mg/L, or 0.048 mg/L. Further reduction of NH₄-N would be achieved at alkaline pH (pH>7), where a proportion of NH₄-N will be as ammonia (NH₃), which is in the gas form and would be removed through gas boil-off, as for N₂ and CO₂. The formulation has pH 9, but there are no data on the pH during the process. Therefore, following conservative principles, I have assumed for the purposes of this risk assessment that all NH₄-N is in the non-gaseous form (ammonium: NH₄⁺), and none is lost as NH₃ gas.

Therefore, the use of Cortrol OS5614 would lead to a net result of the removal of the toxic component of Cortrol OS7780 (1,4-Benzoquinone) and a negligible increase (0.048 mg/L) to the current background concentration of NH_4 -N in the SWB and receiving environment. The potential for additive effects with other NH_4 -N sources is discussed in Section 4.5.2.

3.3.5 Embreak 2021

Embreak 2021 is an emulsion breaker used in deoiled water from Tilted Plate Interceptors (TPIs) and process water (Figure 17). Embreak 2021 comes into contact with petroleum hydrocarbons as part of the refining process. It is applied at an average rate of 128.7 kg/day. The formulation is miscible with water, and has an undisclosed pH. No ecotoxicological data were available in the Chemwatch SDS.

There are fourteen components of Embreak 2021, not including water (Appendix 3). Ten components are restricted under an NDA and are given generic codes. Nine components are hydrocarbons: Emb1; Emb2; naphthalene; Emb3; Emb4; solvent naphtha, petroleum, heavy aromatic; light aromatic naphtha; Emb8; Emb9. All of these have been discounted from further assessment. Five other components are:

- Nonylphenol (technical) (1.175% by weight, CASRN 84852-15-3).
- Emb5 (0.1152% by weight, CASRN restricted).
- Emb6 (40.47% by weight, CASRN restricted).
- Emb7 (0.235% by weight, CASRN not supplied).
- Emb10 (4.4775% by weight, CASRN restricted).

One note can be made from the above chemical list. Emb6 contains nonylphenol (already present as a separate component) but the SDS did not state the proportion. Using conservative principles, the amount of 4-nonyphenol in Emb6 was set at 40.47%, i.e. the full amount.

A potential ecological risk was identified for nonylphenol (technical) and Emb6.

An RQ1 of 302 was calculated for nonylphenol (technical), based primarily on a marine PNEC of 0.001 mg/L. An RQ1 of 10,280 was calculated for Emb6, based on the same PNEC and a proportion of 40.47%.

By performing a correction for oil and water partitioning, RQ2 for nonylphenol (technical) was 0.001 and RQ2 for Emb6 was 0.016. Both chemicals are highly lipophilic, with 99.9996% retained in the hydrocarbon phase.

As the largest RQ2 (0.016) was < 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was not undertaken. Potential effects are summarised in Section 4.5.2.

3.3.6 Klaraid IC1172

Klaraid is a water treatment additive used in biological treatment, dissolved air flotation (DAF), activated sludge plant, and clarification processes (Figure 17) at an average application rate of 156.7 kg/day. The formulation is a 40% by weight solution of aluminium chlorohydrate (CASRN 12042-91-0) (Appendix 3). Klaraid is not restricted under an NDA.

There are no applicable marine ecological guidelines for aluminium. In 2000, ANZECC reported a low-reliability marine trigger value of 0.0005 mg/L ($0.5 \mu g/L$) for aluminium, but acknowledged that it should be used as an indicative interim working level only, until more data are available. Recent ANZ DGV (2018) for aluminium are available for freshwater only. This is consistent with other jurisdictions where marine guidelines for aluminium have not been set. US EPA have

aquatic life criteria for aluminium in freshwater only, revised in 2018.⁵⁵ The European Chemicals Agency (ECHA) identified no hazard in marine waters for aluminium chlorohydrate.⁵⁶

With no applicable marine ecological guideline, further assessment through mass balance was not undertaken. However, a significant amount of aluminium is potentially entering the marine receiving environment and may affect sediment-dwelling organisms or bioaccumulate in shellfish. Aluminium was measured in water from the Refining NZ clarifier outlet and SWB on a single sample of each collected on 25th June 2019.⁵⁷ The single aluminium concentration was 0.130 mg/L and 0.083 mg/L for the clarifier and SWB, respectively.

An assessment of marine sediment aluminium concentrations was undertaken in 2019 by De Luca (2019), who stated that aluminium⁵⁸ does not have a DGV or GV and is not a metal commonly included in contaminant analyses. Aluminium was detected at an average concentration of 2,030 mg/kg within the mixing zone, 3,300 mg/kg outside of the reasonable mixing zone, and between 4,000 mg/kg and 6,700 mg/kg at reference sites. It is not uncommon to have high aluminium concentrations in marine sediment, with Waikato Regional Council results (2008) ranging from 8,100 to 15,000 mg/kg in Aotea Harbour, and 13,000 to 26,000 mg/kg in Kawhia Harbour⁵⁹. Both Aotea Harbour and Kawhia Harbour have predominantly rural catchments, with little urban/industrial landuse.

Therefore, there appears to be no evidence for aluminium accumulation within the mixing zone and concentrations are generally below baseline.

3.3.7 Spectrus NX1100

Spectrus NX1100 is a biocide used on deoiled water from Tilted Plate Interceptors (TPIs) (Figure 17). It is applied at an average rate of 0.2 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 3.0. No ecotoxicological data were available in the Chemwatch SDS.

There are six components of Spectrus NX1100, not including water (Appendix 3). Two components are restricted under an NDA and are given generic codes. The six components are:

- Bronopol (5.544% by weight, CASRN 52-51-7).
- Magnesium nitrate (3.68% by weight, CASRN 13446-18-9).
- Isothiazolinones, mixed (Kathron 886) (2.576% by weight, CASRN 55965-84-9).
- Magnesium chloride (1.656% by weight, CASRN 7786-30-3).
- Spec1 (0.98% by weight, CASRN restricted).
- Spec2 (0.1903% by weight, CASRN restricted).

All 6 components have the required chemical information (CASRN) to assess risk.

⁵⁵ https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table

⁵⁶ <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/15326/6/1</u>

⁵⁷ Measurement was undertaken by Suez Customer Analytical Services Laboratory, Singapore on request by Refining NZ.

⁵⁸ Aluminium occurs ubiquitously in natural waters as a result of weathering of rocks that contain aluminium.

⁵⁹ Data supplied by Waikato Regional Council.

A potential ecological risk was identified for bronopol only, with RQ1 = 2.2, based primarily on a marine PNEC of 0.001 mg/L. By performing a correction for oil and water partitioning, RQ2 for bronopol was 0.10. Bronopol is lipophilic, with 95.6% retained in the hydrocarbon phase.

As the RQ2 (0.1) was < 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was not undertaken. Potential effects are summarised in Section 4.5.2.

3.3.8 Inhibitor AZ8104

Inhibitor AZ8104 is used in internal boiler treatment on deoiled water from Tilted Plate Interceptors (TPIs) (Figure 17). It is applied at an average rate of 5.5 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 12.7. No ecotoxicological data were available in the Chemwatch SDS.

There are five components of Inhibitor AZ8104, not including water (Appendix 3). 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 so no information could be obtained. As (i) there are 2 other chemicals related to AZ1 which can be used to calculate risk and (ii) these are highly lipophilic (and so will be retained in the petroleum phase), no further information was requested.

A potential ecological risk was identified for sodium tolytriazole only, with RQ1 = 1.93, based primarily on a marine PNEC of 0.008 mg/L. By performing a correction for oil and water partitioning, RQ2 for sodium tolytriazole was 0.03. Sodium tolytriazole is lipophilic, with 98.4% retained in the hydrocarbon phase.

As the RQ2 (0.03) was < 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was not undertaken. Potential effects are summarised in Section 4.5.2.

3.3.9 Embreak 2050

Embreak 2050 is used as an emulsion breaker in process water after desalting (Figure 17). It is applied at an average rate of 5.2 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The pH of the formulation and ecotoxicological data were not available in the Chemwatch SDS.

There are four components of Embreak 2050, not including water (Appendix 3). Three components are restricted under an NDA and are given generic codes. The four components are:

- Diethylene glycol monobutyl ether (4.95% by weight, CASRN 112-34-5).
- Emb11 (0.025% by weight, CASRN restricted).
- Emb12 (0.015% by weight, CASRN restricted).

• Emb13 (32% by weight, CASRN restricted).

All four components have the required chemical information (CASRN) to assess risk. None of the components presented a potential ecological risk, with the largest RQ1 (0.5) for diethylene glycol monobutyl ether based primarily on a marine PNEC of 0.11 mg/L.

As the RQ1 (0.5) was < 1, an assessment of potential effects after oil partitioning (RQ2) or dilution in the receiving environment (RQ3) was not undertaken. Potential effects are summarised in Section 4.5.2.

3.3.10 Steammate NA0808

Steammate NA0808 is a blend of neutralising amines used on the western AOC trench (Figure 17). It is applied at an average rate of 16.1 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 12.7. No ecotoxicological data were available in the Chemwatch SDS.

There are three components of Steammate NA0808, not including water (Appendix 3). 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 (DMAP) (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, and all presented a potential ecological risk, with RQ1 = 142, 92 and 3.2 for monoethanolamine, 3-dimethylaminopropylamine, and SM1, respectively, based primarily on marine PNEC of 0.009 mg/L, 0.007 mg/L, 0.002 mg/L for monoethanolamine, 3-dimethylaminopropylamine, and SM1, respectively.

The components in Steammate NA0808 are hydrophilic and partition primarily to the water phase (>99.8%). Therefore, oil/water partition corrections had no effect on the risk quotients, with RQ2 = 142, 92 and 3.2 for monoethanolamine (MEA), 3-dimethylaminopropylamine (DMAP), and SM1, respectively.

As the largest RQ2 (142) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

3.3.11 Genguard GN8220

Genguard GN8220 is used for internal boiler treatment on deoiled water from Tilted Plate Interceptors (TPIs) (Figure 17). It is applied at an average rate of 6.03 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 2.1. No ecotoxicological data were available in the Chemwatch SDS.

There are seven components⁶⁰ of Genguard GN8220, not including water (Appendix 3). Five components are restricted under an NDA and are given generic codes. The seven components are:

- Maleic acid (0.279% by weight, CASRN 110-16-7).
- Phosphoric acid (3.8983% by weight, CASRN 7664-38-2).
- Gen1 (9.3% by weight, CASRN restricted).
- Gen2 (0.125% by weight, CASRN restricted).
- Gen3 (0.2059% by weight, CASRN restricted).
- Gen4 (0.4325% by weight, CASRN restricted).
- Gen5 (5.4643% by weight, CASRN restricted).

All seven components have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for Gen2 and maleic acid, with RQ1 = 9.4 and 4.7, respectively, based primarily on marine PNECs of 0.005 mg/L, and 0.01 mg/L, respectively. Gen2 is inorganic so will partition 100% to the water phase. Maleic acid is hydrophilic with 99.9% expected to partition to the water phase. Therefore, oil/water partition for these chemicals will have no effect on ecological risk quotients (i.e. RQ2 = 9.4 and 4.7 for Gen2 and maleic acid, respectively).

As the largest RQ2 (9.4) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

3.3.12 GE Spectrus BD1501E

GE Spectrus BD1501E is used as a biodispersant on deoiled water from TPIs (Figure 17). It is applied at an average rate of 0.05 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 6.7. No ecotoxicological data were available in the Chemwatch SDS.

There are two components⁶¹ of GE Spectrus BD1501E, not including water (Appendix 3). One component is restricted under an NDA and has been given a generic code. The two components are:

- Alcohols, C10, alkoxylated (14% by weight, CASRN 166736-08-9).
- GE1 (13.8873% by weight, CASRN restricted).

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

Neither component presented a potential ecological risk, with the largest RQ1 = 0.0001, for GE1, based on a US EPA toxicity value of 12.5 mg/L (mortality, saltwater, algae). By applying a worst-case scenario and converting the US EPA toxicity value to a marine PNEC, i.e. applying an assessment factor of 10,000, would equate to a RQ1=1.1 for GE1. There were no available physico-chemical data to apply an oil/water correction to GE1 (i.e. RQ2). Therefore, RQ1 = RQ2.As RQ2 (1.1),

 $^{^{60}}$ Ingredients making up <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

 $^{^{61}}$ Ingredients making up <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

based on a derived marine PNEC, was >1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2)..

3.3.13 Optisperse ADJ5150

Optisperse ADJ5150 is an alkalinity builder used in boiler blowdown and discharges to the western AOC trench (Figure 17). It is applied at an average rate of 0.05 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 14. No ecotoxicological data were available in the Chemwatch SDS.

There are two components⁶² of Optisperse ADJ5150, not including water (Appendix 3). 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, with the largest RQ1 = 0.0001, for sodium hydroxide, based on an acute (48 hour) EC_{50} of 40.4 mg/L for crustacea. By applying a worst-case scenario and converting the EC_{50} value to a marine PNEC, i.e. applying an assessment factor of 10,000, would equate to a RQ1=0.6 for sodium hydroxide.

As the RQ1, based on a derived marine PNEC, was 0.6, an assessment of potential effects after oil partitioning (RQ2) or dilution in the receiving environment (RQ3) was not undertaken. Potential effects are summarised in Section 4.5.2.

3.3.14 Optisperse HP2650

Optisperse HP2650 is used for internal boiler treatment on the western AOC trench (Figure 17). It is applied at an average rate of 2.3 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of >13. No ecotoxicological data were available in the Chemwatch SDS.

There are two components 63 of Optisperse HP2650, not including water (Appendix 3). One component is restricted under an NDA and has been given a generic code. The two components are:

- Sodium hydroxide (3% by weight, CASRN 1310-73-2).
- HP1 (5% by weight, CASRN restricted).

Neither component presented a potential ecological risk, with the largest RQ1 = 0.0003, for sodium hydroxide, based on an acute (48 hour) EC_{50} of 40.4 mg/L for crustacea. By applying a worst-case scenario and converting the EC_{50} value to a marine PNEC, i.e. applying an assessment factor of 10,000, would equate to a RQ1=3.4 for sodium hydroxide.

 $^{^{62}}$ Ingredients making up <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

 $^{^{\}rm 63}$ Ingredients making up <0.1% of formulation were restricted under an NDA. Due to extremely low proportions these were not assessed further.

As the RQ1, based on a derived marine PNEC, was 3.4, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

3.3.15 Crystalfloc Cationic Emulsions

Crystalfloc cationic emulsions is a processing aid for industrial applications and used in S 3901 Above Ground TPI (Figure 17). It is applied at an average rate of 20 kg/day and comes into contact with petroleum hydrocarbons as part of the refining process. The formulation has a pH of 4-6. The SDS supplied by the manufacturer (Ixom Operations) contained ecotoxicological data for the formulation: EC_{50} 10-100 mg/L (*Daphnia magna*, 48 h) and LC_{50} 10-100 mg/L (fish, 96 h), suggesting slight to low ecotoxicity.

Crystalfloc cationic emulsions is not restricted under an NDA and has three 3 components⁶⁴, not including water (Appendix 3), namely:

- Branched tridecyl alcohol, ethoxylated (0-<5% by weight, CASRN not available).
- Fatty alcohol alkoxylate (0-<5% by weight, CASRN not available).
- Adipic acid (0-<2% by weight, CASRN 124-04-9).

With no available CASRN for the first 2 components, no further ecological risk assessment could be made on these, and the assessment was based on adipic acid only.

Adipic acid presented a potential ecological risk, with RQ1 = 6.2, based primarily on a marine PNEC of 0.013 mg/L. Adipic acid is hydrophilic and partitions primarily to the water phase (>99.99%). Therefore, oil/water partition corrections had no effect on the risk quotients, with RQ2 = 6.2.

As the RQ2 (6.2) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) is undertaken in Section 4.4.2 and 4.5.2.

3.3.16 Special case scenarios

Aside from the use of process chemicals during normal operation of the Refinery, there are special cases where the Refinery undergoes a shutdown procedure or where unintended spills of process chemicals occur. Special case scenarios are described below.

3.3.17 Special case scenario – site shutdown

Between 3rd May 2018 and 21st May 2018, the refinery underwent a total shutdown. To facilitate the shutdown, two process formulations were used: CC Eliminator and CC414P, which are used for the removal of benzene, hydrogen sulphide and pyrophoric iron.

<u>CC Eliminator</u>

CC Eliminator is not restricted under an NDA and was used in S 3901 Above Ground TPI (Figure 17). During the shutdown process it was applied at an average rate of 222.7 kg/day and came into

⁶⁴ Ingredients making up <0.1% of formulation were: Sodium chlorate (0.0001%), Sodium carbonate (0.0018%), Sodium silicate (0.0066%), Sodium chloride (0.0600%). Due to extremely low proportions these were not assessed further.

contact with petroleum hydrocarbons. The formulation has an unknown pH. No ecotoxicological data were available in the Chemwatch SDS.

There are three components of CC Eliminator, not including water (Appendix 3), namely:

- Lauramine oxide (25-30% by weight, CASRN 1643-20-5).
- Alcohols C12-16 ethoxylated (0-5% by weight, CASRN 68551-12-2).
- Sodium hydroxide (45-50% by weight, CASRN 1310-73-2).

All four components have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for lauramine oxide and alcohols C12-16 ethoxylated, with RQ1 = 4454 and 2.2, respectively. The high RQ1 for lauramine oxide was primarily a result of the low marine PNEC of 0.003 mg/L. The RQ1 for alcohols C12-16 ethoxylated was based on a lowest toxicity value, which is a long-term (72h) NOEC for algae of 1 mg/L. As data are also present for 2 other trophic species (higher toxicity concentrations), an assessment factor of 1,000 was used to estimate a marine PNEC of 0.001 mg/L (Table 27). Based on a derived marine PNEC of 0.001 mg/L, RQ1 for alcohols C12-16 ethoxylated is 2,200. Lauramine oxide partitions primarily to oil (99.95%), with a calculated RQ2 = 2.4. There were no available data on logP or logD for alcohols C12-16 ethoxylated from any literature sources. However, as these are highly lipophilic long chain alkanes, they will partition predominantly to oil. A substitute chemical isododecanol⁶⁵ was used to approximate oil partitioning. Isododecanol has a logP of 4.94 and logD of 4.03. RQ2 was calculated to be 0.21 for alcohols C12-16 ethoxylated – based on the conservative substitute isododecanol.

As the RQ2 (2.4) for lauramine oxide was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

<u>CC 414P</u>

CC414P is not restricted under an NDA and was also used in the total shutdown, but in lower amounts than CC Eliminator. During the shutdown process it was applied at an average rate of 15.1 kg/day and came into contact with petroleum hydrocarbons. The formulation has a pH of 8-8.5. No ecotoxicological data were available in the Chemwatch SDS.

There are seven components of CC414P, not including water (Appendix 3), namely:

- d-Limonene (5-15% by weight, CASRN 5989-27-5).
- Dodecylbenzenesulfonic acid (5-15% by weight, CASRN 27176-87-0).
- Methoxypropoxypropanol (5-10% by weight, CASRN 34590-94-8).
- Propylene glycol n-butyl ether (5-10% by weight, CASRN 5131-66-8).
- Diethanolamine (0-5% by weight, CASRN 111-42-2).
- Nonylphenol ethoxylate (0-5% by weight, CASRN 9016-45-9).
- Tetrasodium EDTA (0-5% by weight, CASRN 64-02-8).

All seven components have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for d-limonene and diethanolamine, with RQ1 = 324 and 76,

 $^{^{65}}$ Isodecanol is a C12 alkane with one hydroxyl group attached. This is a conservative substitute chemical for lipophilicity as it is (a) has the shortest carbon chain and (b) has a free hydroxyl group, i.e. no ethoylate.

respectively. d-Limonene partitions primarily to oil (>99.99%) and RQ2 = 0.01 was calculated, eliminating ecological risk associated with d-limonene. Conversely, diethanolamine partitions primarily to water (99.8%), and an RQ2 = 75 was calculated.

As the largest RQ2 (75) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

3.3.18 Special case scenarios – chemical spills

ADIP-X

ADIP-X is a gas removal solvent used on the western AOC trench (Figure 17). There has been no spill in the last 15 years that has caused the SWB to go off grade due to ADIP-X. However, there have been reported several spills to ground in the process unit which have had the potential to get into the drainage system, if unmanaged.⁶⁶ There was one in 2011 and two in 2014; the largest of these was 100 L and the smallest was 3 L (Phillip Shoebridge, Refining NZ, personal communication). Based on a 100 L spill of ADIP-X over a period of 1 day, an average 103 kg/day of formulation was released to the western AOC. ADIP-X does not come into contact with petroleum hydrocarbons as part of the refining process and is discharged directly to the SWB. The formulation has an undisclosed pH. No ecotoxicological data were available in the Chemwatch SDS.

ADIP-X is not restricted under an NDA. It has three different components, not including water (Appendix 3), namely:

- Methyldiethanolamine (MDA) (80% by weight, CASRN 105-59-9).
- Piperazine (13% by weight, CASRN 110-85-0).
- Sodium hydroxide (7% by weight, CASRN 1310-73-2).

All three compounds have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for MDA and piperazine, with RQ1 = 1945 and 10, respectively. The high RQ1 for MDA was primarily a result of a low marine PNEC (0.004 mg/L) and a high proportion in the formulation (80%). ADIP-X does not come into contact with petroleum hydrocarbons, so an oil/water partition was not undertaken (i.e. RQ1 = RQ2).

As the largest RQ2 (1945) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) is undertaken (Section 4.4.2 and 4.5.2).

DIPA (di-isopropanolamine)

A spill of DIPA occurred between $11^{\rm th}$ May 2018 and $16^{\rm th}$ May 2018, leading to 7 m 3 of 30% amine being lost to the AOC.

DIPA is not restricted under an NDA and is a base for fatty acid soaps used in polishes, textiles, cutting oils, and insecticide emulsions. It is ≥99% di-isopropanolamine (DIPA) (CASRN 110-97-4).

⁶⁶ The risk assessment in this report assumes worst-case, i.e. no management intervention was implemented for a spill event. However, Refining NZ have a range of process to avoid and respond to accidental spills and in my opinion the risks from these spills would have been mitigated at the time.

An RQ1 for DIPA was calculated as 1417, suggesting potential for ecological effects. DIPA partitions primarily to water (99.7%) and an RQ2 was calculated as 1412.

As the RQ2 (1412) was > 1, an assessment of potential effects after dilution in the receiving environment (RQ3) was undertaken (Section 4.4.2 and 4.5.2).

3.3.19 Special case scenario – Fire training

Solberg DoD3155

Fire training is undertaken on a routine but infrequent basis at the Refinery. The fire training foam used for training is Solberg DoD3155. In contrast to process chemicals used every day at the Refinery, as Solberg DoD3155 is only used infrequently, there will be virtually no residual (or legacy) foam chemicals in the SWB and retaining ponds prior to the discharge of the foam. This effectively means that dilution of firefighting foam from the fire training ground to the final receiving environment will include volumes in the retention basin and stormwater discharge basin (see Figure 18). The total volume of the retention basin and stormwater basin is 12,800 m³.

There are five components of Solberg DoD3155, not including water (Appendix 3). Two components are restricted under an NDA and have been given a generic code. The five components are:

- Diethylene glycol mono butyl ether (DGMBE) (8.6% by weight, CASRN 112-34-5).
- Alcohol sulphate C12-C14, triethanolamine salt (3.4% by weight, CASRN 90583-18-9).
- Cocoamido propyl betaine (CPB) (1.12% by weight, CASRN 61789-40-0).
- Sol1 (1.65% by weight, CASRN restricted).
- Sol2 (2.09% by weight, CASRN restricted).

All five components have the required chemical information (CASRN) to assess risk. A potential ecological risk was identified for cocoamido propyl betaine (CPB) and diethylene glycol mono butyl ether (DGMBE), with RQ1 = 106 and 15, respectively. This was based primarily on marine PNECs of 0.002 mg/L (intermittent discharge) and 0.11 mg/L, for CPB and DGMBE, respectively. No allowance was made for oil partitioning as the fire training foam is discharged directly to the retention basin. Therefore, RQ1 = RQ2.



Figure 18. Location of fire training ground, retention basin and stormwater basin at the Refinery.

3.4 Summary

Process chemicals present in the Refining NZ SWB that have a risk quotient RQ2 >1, which indicates the potential to cause adverse ecological effects in the receiving environment, are summarised in Table 28. To apply marine ecological guidelines, dilution of the chemicals in the receiving environment needs to be accounted for. Receiving environment risk quotients RQ3 were calculated from hydrodynamic modelling (Section 4.4.2) and potential effects assessed in Section 4.5.2.

Formulation	Toxic Component	RQ2
	Everyday use	
Steammate NA0880	Monoethanolamine (MEA)	142
Steammate NA0880	3-Dimethylaminopropylamine (DMAP)	92
Steammate NA0880	SM1	3.2
Genguard GN8220	Gen2	9.4
Genguard GN8220	Maleic acid	4.7
Crystalfloc Cationic Emulsions	Adipic acid	6.2
BetzDearborn AE1115P	ICP solvent	86
Cortrol OS7780	1,4-Benzoquinone	797
Spectrus BD1501E	GE1	1.1
Optispearse HP2650	Sodium hydroxide	3.4
	Spill event	
ADIP-X	Methyldiethanolamine (MDA)	1945
ADIP-X	Piperazine	10
DIPA	Di-isopropanolamine (DIPA)	1412
	Refinery shutdown	
CC Eliminator	Lauramine Oxide	2.4
CC 414P	Diethanolamine	75
	Fire training	
Solberg DoD3155	Cocoamido propyl betaine (CPB)	106
Solberg DoD3155	Diethylene glycol mono butyl ether (DGMBE)	15

Table 28. Process chemicals present in Refining NZ SWB with RQ2 > 1.

4. Assessment of effects of stormwater basin contaminants on marine receiving

environment water quality

4.1 Summary of hydrodynamic modelling

Hydrodynamic modelling (MetOcean Solutions, 2019: appended to this report as Appendix 5) consisted of running year-long simulations within two contrasting historical contexts (El Niño/La Niña episodes, June 2010–June 2011 and June 2015–June 2016, respectively), actual events and extreme events.

During El Niño conditions, New Zealand typically experiences stronger or more frequent westerly winds during summer. This leads to a greater risk of drier-than-normal conditions in east coast areas and more rain than normal in the west. In winter, colder southerly winds tend to prevail, while in spring and autumn, southwesterlies tend to be stronger or more frequent, bringing a mix of the summer and winter effects.

During La Niña conditions, more northeasterly winds are characteristic, which tend to bring moist, rainy conditions to the northeast of the North Island, and reduced rainfall to the south and southwest of the South Island.

For simulating actual events, Refining NZ provided data from 12 historical events. During those events, outfall from the diffuser was continuous in time and the SWB overflow was open and closed during specific times. Of all the 12 events modelled, only one of them includes the spillway overflow (event on 26/03/2017, Table 29).

Extreme events consisted of different spillway overflows combined with various tidal states (low tide and high tide), wind speeds (4, 8 and 15 m/s) and wind directions (northeast and southeast). Each combination of tide and wind was simulated in combination with a 100-year average recurrence interval (ARI) rainfall event, which generated fluvial discharges from rivers and streams entering the harbour. In addition, the 100-year ARI rainfall generated wastewater discharges from the Refinery's three outfalls (Table 29).

The locations of the three outfalls are shown in Figure 19.

Table 29. Summary of outfall location for each of the cases modelled (MetOcean Solutions, 2020).

Case/Location	Existing diffuser	Diffuser bypass	Overflow spillway
Year-long simulation	On	Off	Off
Actual event	On	On	On/Off
Extreme event	On	On	On

The hydrodynamic modelling considered two scenarios:

- an "existing" scenario, based on the actual bathymetry of the harbour, and
- a "reclaim" scenario, with an additional proposed berth at Northport Marina (known as Berth 4) and an alternative lower Whangarei Harbour channel design (known as Option 4.2).

Results for the "existing" scenario only are discussed in this report as the "reclaim" scenario results were virtually identical (data not shown).



Figure 19. Aerial photo of location of Refinery showing the location of the three outfalls modelled (MetOcean Solutions, 2020).

Time series of dilutions of the SWB discharge for each scenario were extracted from the model at specific locations as shown in Figure 20.

- Sites C1–C4 correspond to the corners of the mixing zone.
- Sites P1–P9 correspond to ecological sites of significance and/or sites where modelling figures suggested lowest dilution of the SWB plume (De Luca, 2020).

MetOcean Solutions (2020) noted that some of the sites of interest are in shallow water, especially those sites close to the coastline. Some sites can even be dry at times. Contaminant concentrations are averaged over water depth at each site, which can result in contaminant concentration spikes during periods of low water level. Therefore, dilution (reciprocal of contaminant concentration) at the shallowest sites should be interpreted carefully. MetOcean Solutions have undertaken further modelling of the dilutions in the "top" and "bottom" metre of water at all sites to better understand the dilution profile at shallow sites and how this may affect biota at the surface (e.g. mussels attached to rocks) or on the sea floor (i.e. benthic organisms). This information was processed along with the depth average data and is being used in the marine ecology assessment (De Luca, 2020). For the purposes of assessing expected concentrations of SWB contaminants at specific receiving environment sites against water quality standards/guidelines (i.e. in this report), only depth average dilutions have been used as these are applicable to water quality guidelines. This is discussed in further detail in Section 4.2.

Time series data were supplied in Excel format. 5^{th} percentile, median, and 95^{th} percentile dilutions were calculated for each scenario. Zeroes in the data were removed, as these indicate

the plume was not present. Minimum and maximum dilutions are potentially skewed by outliers. Therefore, 5th and 95th percentile data were used to represent the <u>practical worst-case</u> (5th percentile, lowest dilution) and the <u>practical best-case</u> (95th percentile, highest dilution) scenarios, respectively, and the median was used to represent the <u>practical-normal case</u> scenario.

To provide some context on the duration of low dilution events, an analysis of time series data for a period of almost two years between 2010-2011 and 2015-2016, under La Niña and El Niño conditions respectively, shows that the dilution at mixing zone and receiving environment sites (Figure 20) is greater than 256x for more than 99% of the time.⁶⁷ A duration of 1 hour at below 256x occurs between 0.1 and 0.6% of the time. The longest duration (3 hours) occurs up to 0.05% of the time. The dominating driving force for the low dilution duration appears to be due to the background diffuser discharge (i.e. annual La Niña and El Niño data) and so the same duration statistics apply to actual and extreme events.



Figure 20. Receiving environment sites where dilution data were extracted.

⁶⁷ A 256x dilution was chosen as the greatest dilution required (i.e. worst-case) of the whole effluent toxicity testing of the SWB (see Section 2.2.5).

4.2 Modelled dilution

4.2.1 El Niño/La Niña year-long episodes

Dilution of the SWB plume (discharged via the existing diffuser) averaged over year-long El Niño and La Niña episodes is shown in Figure 21 (full model domain) and Figure 22 (zoomed in on mixing zone). In both cases, the plume concentrates on the southern side of Marsden Point.



Figure 21. Average dilution over the year-long El Niño (top) and La Niña (bottom) episodes using the existing (left) and reclaim (right) bathymetries. Full model domain.



Figure 22. Average dilution over the year-long El Niño (top) and La Niña (bottom) episodes using the existing (left) and reclaim (right) bathymetries. Zoomed in on mixing zone.

Three metrics under each of the El Niño and La Niña episodes were calculated for each site presented in Table 30 and Table 31:

- practical worst-case (lowest) dilution (5th percentile),
- practical normal-case (median) dilution, and
- practical best-case (highest) dilution (95th percentile).

These dilutions were used in two ecological risk scenarios associated with discharge of NZ SWB contaminants <u>under baseline conditions</u>: practical worst-case and practical normal-case scenarios (see Section 4.4.1). Both scenarios were 24 hours post-discharge. The practical worst-case scenario used 5th percentile dilutions, while the practical normal-case scenario used median dilutions.

Table 30. Summary of 5th percentile, median and 95th percentile modelled contaminant dilutions for <u>El Niño episode</u> at mixing zone and at receiving environment sites.

Statistic		Mixing Z	one Sites					Receivin	g Environm	ent Sites			
	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	15,916	8,096	253	3,612	9,632	9,445	10,775	532	8,772	281	918	13,815	13,426
Median	66,566	40,581	1,622	17,542	13,014	47,391	50,018	2,577	33,360	1,690	7,450	58,283	53,760
95%ile	940,889	143,754	8,674	132,276	34,604	788,460	222,739	20,431	266,549	23,124	75,467	171,795	5,193,230

Table 31. Summary of 5th percentile, median and 95th percentile modelled contaminant dilutions for <u>La Niña episode</u> at mixing zone and at receiving environment sites.

Statistic		Mixing Z	one Sites					Receivin	g Environm	ent Sites			
	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	14,702	7,799	201	3,696	5,503	8,765	12,480	329	7,165	278	1,078	14,264	13,681
Median	68,110	34,469	1,419	18,312	13,992	45,656	39,634	2,844	28,316	2,036	8,115	51,210	51,993
95%ile	1,009,488	141,746	7,058	126,866	41,391	984,179	182,614	17,152	233,033	21,336	91,474	428,376	5,675,006

4.2.2 Actual event scenarios

An example of the SWB discharge plume dilution for the actual event scenarios is shown 24 hours and 48 hours after discharge in Figure 23 (full model domain) and Figure 24 (zoomed in on mixing zone). The plume is typical of all actual events, concentrating on the southern side of Marsden Point and mostly dissipating after 48 hours.



Figure 23. Average dilution for the first 24 hours (top) and from 24 to 48 hours (bottom) for actual event of 10/08/16 using the existing (left) and reclaim (right) bathymetries. Full model domain.



Figure 24. Average dilution for the first 24 hours (top) and from 24 to 48 hours (bottom) for actual event of 10/08/16 using the existing (left) and reclaim (right) bathymetries. Zoomed in on mixing zone.

5th percentile, median and 95th percentile dilutions were extracted from the time series data for the 12 actual event scenarios for mixing zone and receiving environment sites for 24 and 48 hours after discharge (Table 32).

Practical worst-case scenario (5th percentile) dilution at mixing zone sites (C1–C4) was between 186 (C3) and 10,054 (C1) after 24 hours, and between 220 (C3) and 11,964 (C1) after 48 hours. Worst-case scenario (5th percentile) dilution at receiving environment sites (P1–P9) was between 230 (P6) and 12,447 (P9) after 24 hours, and between 283 (P6) and 12,531 (P8) after 48 hours.

Practical normal scenario (median) dilution at mixing zone sites (C1–C4) was between 1,434 (C3) and 47,280 (C1) after 24 hours, and between 1,491 (C3) and 51,063 (C1) after 48 hours. Practical normal scenario (median) dilution at receiving environment sites (P1–P9) was between 1,809 (P6) and 53,151 (P9) after 24 hours, and between 1,883 (P6) and 49,121 (P9) after 48 hours.

Using the dilution time series data, two ecological risk scenarios associated with discharge of SWB contaminants <u>under normal operating conditions</u> were modelled: practical worst-case (5th percentile dilutions) and practical normal-case (median dilutions) scenarios (see Section 4.4.1). Both scenarios were for the first 24 hours post-discharge. The practical worst-case scenario used 5th percentile dilutions, while the practical normal-case scenario used median dilutions.

4.2.3 Extreme scenarios

An example of the SWB discharge plume dilution for an extreme event scenario 24 hours and 48 hours after discharge is shown in Figure 25. The plume is similar to that under the actual events, concentrating on the southern side of Marsden Point and dissipating after 48 hours.



Figure 25. Average dilution for the first 24 hours (top) and from 24 to 48 hours (bottom) for high-tide release during an extreme event with northeasterly wind of 15 m/s using the existing (left) and reclaim (right) bathymetries. Full model domain.



Figure 26. Average dilution for the first 24 hours (top) and from 24 to 48 hours (bottom) for high-tide release during an extreme event with northeasterly wind of 15 m/s using the existing (left) and reclaim (right) bathymetries. Zoomed in on mixing zone.

5th percentile, median and 95th percentile dilutions were extracted from the time series data for 12 extreme event scenarios for mixing zone and receiving environment sites 24, 48 and 72 hours after discharge (Table 33).

Practical worst-case scenario (5th percentile) dilution at mixing zone sites (C1–C4) was between 175 (C3) and 7,251 (C1) after 24 hours, between 213 (C3) and 12,697 (C1) after 48 hours, and between 221 (C3) and 14,974 (C1) after 72 hours. Worst-case scenario (5th percentile) dilution at receiving environment sites (P1–P9) was between 199 (P6) and 11,650 (P9) after 24 hours, between 280 (P6) and 13,418 (P9) after 48 hours, and between 284 (P6) and 13,478 (P9) after 72 hours.

Practical normal scenario (median) dilution at mixing zone sites (C1–C4) was between 1,366 (C3) and 37,543 (C1) after 24 hours, between 1,482 (C3) and 50,875 (C1) after 48 hours, and between

1,496 (C3) and 62,281 (C1) after 72 hours. Practical normal scenario (median) dilution at receiving environment sites (P1–P9) was between 1,629 (P6) and 53,977 (P9) after 24 hours, between 1,868 (P6) and 53,829 (P9) after 48 hours, and between 1,887 (P6) and 53,999 (P9) after 72 hours.

Using the dilution time series data, two ecological risk scenarios associated with discharge of SWB contaminants <u>under extreme event conditions</u> were modelled: practical worst-case (5th percentile dilutions) and practical normal-case (median dilutions) scenarios (see Section 4.4.1). Both scenarios were for the first 24 hours post-discharge. The practical worst-case scenario used 5th percentile dilutions, while the practical normal-case scenario used median dilutions.

Discharge/Statistic		Mixing Z	one Sites					Receivin	g Environm	ent Sites			
24-hours	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	10,054	3,444	186	2,115	4,918	7,607	9,913	379	6,663	230	803	12,032	12,447
Median	47,280	23,715	1,434	13,414	12,864	45,729	42,550	2,932	30,946	1,809	6,259	46,908	53,151
95%ile	993,192	142,441	8,049	131,275	41,655	826,156	221,065	19,229	256,054	23,208	85,597	264,668	6,105,457
48-hours	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	11,964	6,715	220	3,262	5,158	7,822	10,106	398	6,915	283	941	12,531	12,517
Median	51,063	31,057	1,491	16,396	12,763	35,615	39,255	2,932	28,719	1,883	7,420	44,067	49,121
95%ile	566,022	132,248	8,049	117,229	40,000	243,516	189,137	19,229	251,497	23,208	77,806	226,947	2,789,192

Table 32. Summary of 5th percentile, median and 95th percentile modelled contaminant dilutions for <u>actual event scenarios</u> at mixing zone and receiving environment sites 24-hours and 48-hours post discharge.

Table 33. Summary of 5th percentile, median and 95th percentile modelled contaminant dilutions for <u>extreme event scenarios</u> at mixing zone and receiving environment sites 24-hours, 48-hours and 72-hours post discharge.

Discharge/Statistic		Mixing Z	one Sites					Receivin	g Environm	ent Sites			
24-hours	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	7,251	2,735	175	595	4,263	7,369	8,280	324	5,932	199	471	9,784	11,650
Median	37,543	18,611	1,366	10,596	12,217	39,173	45,215	2,897	30,944	1,629	5,050	50,538	53,977
95%ile	993,192	129,425	8,049	131,275	41,655	826,156	221,065	19,229	256,052	22,418	85,597	264,668	6,105,427
48-hours	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	12,697	6,946	213	3,324	5,081	7,693	10,142	394	6,902	280	923	12,131	13,418
Median	50,875	30,506	1,482	16,066	12,303	36,344	41,426	2,897	30,548	1,868	6,818	44,896	53,829
95%ile	670,138	136,463	8,009	110,126	41,013	384,822	205,769	19,227	250,879	22,887	67,556	252,138	5,915,834
72-hours	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	14,974	7,659	221	3,554	5,257	8,200	10,823	399	7,219	284	970	13,364	13,478
Median	62,281	35,032	1,496	17,526	13,009	41,803	44,818	2,920	30,912	1,887	7,734	50,127	53,999
95%ile	908,074	141,566	8,044	130,462	41,466	610,213	218,187	19,228	255,357	23,164	84,836	261,591	6,091,883

4.3 Modelled sediment results

Dispersal of sediment in the SWB discharge was modelled under actual and extreme scenarios.⁶⁸

5th percentile (practical best-case), median (practical normal-case) and 95th percentile (practical worst-case) sediment concentrations (mg/L) at mixing zone (C1–C4) sites and receiving environment (P1–P9) sites were extracted from time series data 24 hours post discharge, (Table 34).

Modelled sediment concentrations were extremely low and there was little variation between actual and extreme modelled scenarios (Table 34). The practical worst-case sediment concentration at the edge of the mixing zone after 24 hours was 0.03 mg/L (C3, extreme scenario). For receiving environment sites, the practical worst-case sediment concentration after 24 hours was 0.02 mg/L (P6, both scenarios).

As stated in Section 2.5.2, there are no total suspended sediment (TSS) guidelines provided by either the oNRP or the pNRP, and neither is there an ANZ marine DGV. Auckland Council (AC) use TSS as one of seven parameters to calculate a water quality index that is a relative measure of marine water quality compared with reference sites (Vaughan, 2017). AC use an average TSS concentration of 20 mg/L. Generally, average annual TSS concentration at NRC receiving environment sites is around 20 mg/L. Therefore, any effect due to sediment in SWB discharge – maximum of 0.03 mg/L at the edge of the mixing zone and 0.02 mg/L at receiving environment sites – will be <u>negligible</u>.

⁶⁸ Annual scenarios were not modelled for sediment.

		Mixing Z	one Sites					Receivin	g Environm	ent Sites			
Statistic	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
						Act	ual						
5%ile	2.2E-06	4.0E-06	9.9E-07	2.7E-05	2.8E-07	1.9E-08	4.5E-09	5.4E-08	6.1E-07	4.3E-06	8.5E-06	4.2E-08	5.9E-07
Median	2.0E-05	2.1E-04	2.1E-04	1.3E-03	7.2E-06	1.4E-06	2.0E-06	1.6E-05	5.3E-06	2.0E-04	8.2E-04	2.4E-06	5.5E-06
95%ile	0.0005	0.003	0.02	0.01	0.00008	0.00004	0.00004	0.002	0.00006	0.02	0.006	0.00004	0.00006
						Extr	eme						
	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
5%ile	2.8E-13	1.0E-05	2.3E-06	6.8E-06	2.3E-09	6.5E-07	3.5E-08	7.9E-08	2.5E-06	2.5E-06	1.1E-05	8.7E-07	2.3E-06
Median	9.5E-05	1.6E-04	8.0E-05	1.2E-04	1.4E-05	2.0E-05	2.0E-05	1.1E-05	4.0E-05	1.3E-04	9.0E-05	2.7E-05	3.2E-05
95%ile	0.0008	0.004	0.03	0.03	0.0007	0.0001	0.0002	0.006	0.0003	0.02	0.02	0.0002	0.0002

Table 34. Summary of 5^{th} percentile, median and 95^{th} percentile modelled sediment concentrations (mg/L) for <u>actual and extreme event</u> <u>scenarios</u> at mixing zone and receiving environment sites 24-hours post discharge.

4.4 Dilution of Refining NZ SWB contaminants

4.4.1 "Traditional" contaminants

"Traditional" contaminants present in the SWB that have a risk quotient >1 (indicating that they have the potential to cause adverse ecological effects, see Table 7) were further assessed for ecological risk in the receiving environment using the modelled dilutions provided in Section 4.2.

A practical worst-case scenario for annual, actual and extreme modelled events was used, consisting of:

- lowest practical dilution at each site;
- maximum SWB contaminant concentrations;
- up to 24 hours after discharge.

A practical normal-case scenario for annual, actual and extreme modelled events was used, consisting of:

- median dilution at each site;
- median SWB contaminant concentrations;
- up to 24 hours after discharge.

A summary of risk quotients after 24 hours is provided in Table 35 to Table 42.

Table 35. Calculated risk quotients (worst-case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for El Niño episode.¹

Worst-case scenario		Mixing 7	Zone Sites					Receivin	g Environn	nent Sites			
El Niño	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH ₄ -N (oNRP) (2014-2019)	0.1885	0.3705	<u>11.8653</u>	0.8307	0.3114	0.3176	0.2784	<u>5.6420</u>	0.3420	<u>10.6890</u>	<u>3.2677</u>	0.2171	0.2234
NH ₄ -N (pNRP) (2014-2019)	0.0410	0.0805	<u>2.5787</u>	0.1805	0.0677	0.0690	0.0605	<u>1.2262</u>	0.0743	2.3231	0.7102	0.0472	0.0486
NH ₄ -N (oNRP) (2015-2019)	0.0226	0.0445	<u>1.4238</u>	0.0997	0.0374	0.0381	0.0334	0.6770	0.0410	<u>1.2827</u>	0.3921	0.0261	0.0268
NH ₄ -N (pNRP) (2015-2019)	0.0049	0.0097	0.3095	0.0217	0.0081	0.0083	0.0073	0.1472	0.0089	0.2788	0.0852	0.0057	0.0058
Copper Total	0.0002	0.0004	0.0138	0.0010	0.0004	0.0004	0.0003	0.0066	0.0004	0.0125	0.0038	0.0003	0.0003
Zinc Total	0.0008	0.0015	0.0475	0.0033	0.0012	0.0013	0.0011	0.0226	0.0014	0.0428	0.0131	0.0009	0.0009
Faecal coliforms (90th percentile)	0.0077	0.0152	0.4865	0.0341	0.0128	0.0130	0.0114	0.2313	0.0140	0.4382	0.1340	0.0089	0.0092
Faecal coliforms (median)	0.0238	0.0468	<u>1.4990</u>	0.1049	0.0393	0.0401	0.0352	0.7128	0.0432	<u>1.3504</u>	0.4128	0.0274	0.0282

¹ Risk quotients exceeding 1 are underlined.

Table 36. Calculated risk quotients (normal case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for El Niño episode.¹

Normal scenario		Mixing 7	Cone Sites					Receiving	g Environn	nent Sites			
El Niño	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH ₄ -N (oNRP) (2014-2019)	0.00123	0.00202	0.05054	0.00467	0.00630	0.00173	0.00164	0.03182	0.00246	0.04853	0.01101	0.00141	0.00153
NH ₄ -N (pNRP) (2014-2019)	0.00027	0.00044	0.01109	0.00103	0.00138	0.00038	0.00036	0.00698	0.00054	0.01065	0.00242	0.00031	0.00033
Copper Total	0.00003	0.00005	0.00129	0.00012	0.00016	0.00004	0.00004	0.00081	0.00006	0.00124	0.00028	0.00004	0.00004
Zinc Total	0.00004	0.00007	0.00173	0.00016	0.00022	0.00006	0.00006	0.00109	0.00008	0.00166	0.00038	0.00005	0.00005
Faecal coliforms (90th percentile)	0.00005	0.00009	0.00222	0.00021	0.00028	0.00008	0.00007	0.00140	0.00011	0.00213	0.00048	0.00006	0.00007
Faecal coliforms (median)	0.00017	0.00027	0.00678	0.00063	0.00085	0.00023	0.00022	0.00427	0.00033	0.00651	0.00148	0.00019	0.00020

Table 37. Calculated risk quotients (worst-case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for La Niña episode.¹

Worst-case scenario		Mixing	Zone Sites					Receiving	g Environn	ient Sites			
La Niña	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH ₄ -N (oNRP) (2014-2019)	0.2040	0.3847	<u>14.9501</u>	0.8116	0.5451	0.3423	0.2404	<u>9.1087</u>	0.4187	<u>10.7885</u>	<u>2.7817</u>	0.2103	0.2193
NH ₄ -N (pNRP) (2014-2019)	0.0443	0.0836	<u>3.2492</u>	0.1764	0.1185	0.0744	0.0522	<u>1.9796</u>	0.0910	<u>2.3447</u>	0.6045	0.0457	0.0477
NH ₄ -N (oNRP) (2015-2019)	0.0245	0.0462	<u>1.7940</u>	0.0974	0.0654	0.0411	0.0288	<u>1.0930</u>	0.0502	<u>1.2946</u>	0.3338	0.0252	0.0263
NH ₄ -N (pNRP) (2015-2019)	0.0053	0.0100	0.3900	0.0212	0.0142	0.0089	0.0063	0.2376	0.0109	0.2814	0.0726	0.0055	0.0057
Copper Total	0.0002	0.0004	0.0174	0.0009	0.0006	0.0004	0.0003	0.0106	0.0005	0.0126	0.0032	0.0002	0.0003
Zinc Total	0.0008	0.0015	0.0598	0.0032	0.0022	0.0014	0.0010	0.0364	0.0017	0.0432	0.0111	0.0008	0.0009
Faecal coliforms (90 th percentile)	0.0084	0.0158	0.6130	0.0333	0.0224	0.0140	0.0099	0.3735	0.0172	0.4423	0.1140	0.0086	0.0090
Faecal coliforms (median)	0.0258	0.0486	<u>1.8887</u>	0.1025	0.0689	0.0432	0.0304	<u>1.1507</u>	0.0529	<u>1.3630</u>	0.3514	0.0266	0.0277

¹ Risk quotients exceeding 1 are underlined.

Table 38. Calculated risk quotients (normal case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for La Niña episode.¹

Normal scenario		Mixing Z	one Sites					Receiving	g Environn	ient Sites			
La Niña	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH ₄ -N (oNRP) (2014-2019)	0.00120	0.00238	0.05777	0.00448	0.00586	0.00180	0.00207	0.02884	0.00290	0.04028	0.01011	0.00160	0.00158
NH ₄ -N (pNRP) (2014-2019)	0.00026	0.00052	0.01268	0.00098	0.00129	0.00039	0.00045	0.00633	0.00064	0.00884	0.00222	0.00035	0.00035
Copper Total	0.00003	0.00006	0.00148	0.00011	0.00015	0.00005	0.00005	0.00074	0.00007	0.00103	0.00026	0.00004	0.00004
Zinc Total	0.00004	0.00008	0.00197	0.00015	0.00020	0.00006	0.00007	0.00098	0.00010	0.00138	0.00035	0.00005	0.00005
Faecal coliforms (90 th percentile)	0.00005	0.00010	0.00254	0.00020	0.00026	0.00008	0.00009	0.00127	0.00013	0.00177	0.00044	0.00007	0.00007
Faecal coliforms (median)	0.00016	0.00032	0.00775	0.00060	0.00079	0.00024	0.00028	0.00387	0.00039	0.00540	0.00136	0.00021	0.00021

Table 39. Calculated risk quotients (worst-case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for actual event scenarios.¹

Worst-case scenario		Mixing	Zone Sites					Receiving	g Environm	ent Sites			
Actual events	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
NH ₄ -N (oNRP) (2014-2019)	0.2984	0.8712	<u>16.1237</u>	<u>1.4187</u>	0.6101	0.3944	0.3026	<u>7.9253</u>	0.4503	<u>13.0276</u>	<u>3.7354</u>	0.2493	0.2410
NH ₄ -N (pNRP) (2014-2019)	0.0648	0.1893	3.5042	0.3083	0.1326	0.0857	0.0658	<u>1.7224</u>	0.0979	<u>2.8313</u>	0.8118	0.0542	0.0524
NH ₄ -N (oNRP) (2015-2019)	0.0358	0.1045	1.9348	0.1702	0.0732	0.0473	0.0363	0.9510	0.0540	<u>1.5633</u>	0.4483	0.0299	0.0289
NH ₄ -N (pNRP) (2015-2019)	0.0078	0.0227	0.4206	0.0370	0.0159	0.0103	0.0079	0.2067	0.0117	0.3398	0.0974	0.0065	0.0063
Copper Total	0.0003	0.0010	0.0188	0.0017	0.0007	0.0005	0.0004	0.0092	0.0005	0.0152	0.0044	0.0003	0.0003
Zinc Total	0.0012	0.0035	0.0645	0.0057	0.0024	0.0016	0.0012	0.0317	0.0018	0.0521	0.0149	0.0010	0.0010
Faecal coliforms (90 th percentile)	0.0122	0.0357	0.6611	0.0582	0.0250	0.0162	0.0124	0.3249	0.0185	0.5341	0.1532	0.0102	0.0099
Faecal coliforms (median)	0.0377	0.1101	<u>2.0370</u>	0.1792	0.0771	0.0498	0.0382	<u>1.0012</u>	0.0569	<u>1.6458</u>	0.4719	0.0315	0.0304

¹ Risk quotients exceeding 1 are underlined.

Table 40. Calculated risk quotients (normal case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for actual event scenarios.¹

Normal scenario		Mixing Z	one Sites		Receiving Environment Sites									
Actual events	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9	
NH ₄ -N (oNRP) (2014-2019)	0.0017	0.0035	0.0572	0.0061	0.0064	0.0018	0.0019	0.0280	0.0026	0.0453	0.0131	0.0017	0.0015	
NH ₄ -N (pNRP) (2014-2019)	0.0004	0.0008	0.0125	0.0013	0.0014	0.0004	0.0004	0.0061	0.0006	0.0100	0.0029	0.0004	0.0003	
Copper Total	0.0000	0.0001	0.0015	0.0002	0.0002	0.0000	0.0000	0.0007	0.0001	0.0012	0.0003	0.0000	0.0000	
Zinc Total	0.0001	0.0001	0.0020	0.0002	0.0002	0.0001	0.0001	0.0010	0.0001	0.0015	0.0004	0.0001	0.0001	
Faecal coliforms (90 th percentile)	0.0001	0.0002	0.0025	0.0003	0.0003	0.0001	0.0001	0.0012	0.0001	0.0020	0.0006	0.0001	0.0001	
Faecal coliforms (median)	0.0002	0.0005	0.0077	0.0008	0.0009	0.0002	0.0003	0.0038	0.0004	0.0061	0.0018	0.0002	0.0002	

Table 41. Calculated risk quotients (worst-case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for extreme event scenarios.¹

Worst-case scenario		Mixing	Zone Sites		Receiving Environment Sites										
Extreme events	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9		
NH ₄ -N (oNRP) (2014-2019)	0.4137	<u>1.0969</u>	<u>17.1104</u>	<u>5.0416</u>	0.7038	0.4071	0.3623	<u>9.2594</u>	0.5057	<u>15.1019</u>	<u>6.3645</u>	0.3066	0.2575		
NH ₄ -N (pNRP) (2014-2019)	0.0899	0.2384	<u>3.7187</u>	<u>1.0957</u>	0.1529	0.0885	0.0787	2.0124	0.1099	<u>3.2821</u>	<u>1.3832</u>	0.0666	0.0560		
NH ₄ -N (oNRP) (2015-2019)	0.0496	0.1316	2.0532	0.6050	0.0845	0.0489	0.0435	<u>1.1111</u>	0.0607	<u>1.8122</u>	0.7637	0.0368	0.0309		
NH ₄ -N (pNRP) (2015-2019)	0.0108	0.0286	0.4464	0.1315	0.0184	0.0106	0.0095	0.2415	0.0132	0.3940	0.1660	0.0080	0.0067		
Copper Total	0.0005	0.0013	0.0200	0.0059	0.0008	0.0005	0.0004	0.0108	0.0006	0.0176	0.0074	0.0004	0.0003		
Zinc Total	0.0017	0.0044	0.0684	0.0202	0.0028	0.0016	0.0014	0.0370	0.0020	0.0604	0.0255	0.0012	0.0010		
Faecal coliforms (90 th percentile)	0.0170	0.0450	0.7015	0.2067	0.0289	0.0167	0.0149	0.3796	0.0207	0.6192	0.2609	0.0126	0.0106		
Faecal coliforms (median)	0.0523	0.1386	<u>2.1616</u>	0.6369	0.0889	0.0514	0.0458	<u>1.1698</u>	0.0639	<u>1.9079</u>	0.8040	0.0387	0.0325		

¹ Risk quotients exceeding 1 are underlined.

Table 42. Calculated risk quotients (normal case) for selected Refining NZ SWB "traditional" contaminants at mixing zone and receiving environment sites up to 24 hours after discharge for extreme event scenarios.¹

Normal scenario		Mixing Z	one Sites		Receiving Environment Sites									
Extreme events	C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9	
NH ₄ -N (oNRP) (2014-2019)	0.0022	0.0044	0.0600	0.0077	0.0067	0.0021	0.0018	0.0283	0.0026	0.0503	0.0162	0.0016	0.0015	
NH ₄ -N (pNRP) (2014-2019)	0.0005	0.0010	0.0132	0.0017	0.0015	0.0005	0.0004	0.0062	0.0006	0.0111	0.0036	0.0004	0.0003	
Copper Total	0.0001	0.0001	0.0015	0.0002	0.0002	0.0001	0.0000	0.0007	0.0001	0.0013	0.0004	0.0000	0.0000	
Zinc Total	0.0001	0.0002	0.0020	0.0003	0.0002	0.0001	0.0001	0.0010	0.0001	0.0017	0.0006	0.0001	0.0001	
Faecal coliforms (90 th percentile)	0.0001	0.0002	0.0026	0.0003	0.0003	0.0001	0.0001	0.0012	0.0001	0.0022	0.0007	0.0001	0.0001	
Faecal coliforms (median)	0.0003	0.0006	0.0081	0.0010	0.0009	0.0003	0.0002	0.0038	0.0004	0.0068	0.0022	0.0002	0.0002	

4.4.2 Process chemicals

Process chemicals present in the SWB that have a RQ2 >1 (indicating that they have the potential to cause adverse ecological effects, see Table 28) were further assessed for ecological risk in the receiving environment using the modelled dilutions provided in Section 4.2.

A practical worst-case scenario for annual, actual and extreme modelled events was used, consisting of:

- lowest practical dilution at each site;
- maximum SWB contaminant concentrations;
- up to 24 hours after discharge.

A practical normal-case scenario for annual, actual and extreme modelled events was used, consisting of:

- median dilution at each site;
- median SWB contaminant concentrations;
- up to 24 hours after discharge.

A summary of risk quotients after 24 hours is provided in Table 43 to Table 50.

Formulation ²	Toxic Component ³		Mixing Z	one Sites		Receiving Environment Sites									
		C1	C2	С3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9	
Steammate	MEA	0.0089	0.0175	0.5616	0.0393	0.0147	0.0150	0.0132	0.2671	0.0162	0.5059	0.1547	0.0103	0.0106	
Genguard	Gen2	0.0006	0.0012	0.0372	0.0026	0.0010	0.0010	0.0009	0.0177	0.0011	0.0335	0.0102	0.0007	0.0007	
Crystalfloc	Adipic acid	0.0004	0.0008	0.0245	0.0017	0.0006	0.0007	0.0006	0.0117	0.0007	0.0221	0.0068	0.0004	0.0005	
BetzDearborn	ICP solvent	0.0054	0.0106	0.3401	0.0238	0.0089	0.0091	0.0080	0.1617	0.0098	0.3064	0.0937	0.0062	0.0064	
Cortrol	1,4-Benzoquinone	0.0501	0.0984	<u>3.1522</u>	0.2207	0.0827	0.0844	0.0740	<u>1.4989</u>	0.0909	<u>2.8397</u>	0.8681	0.0577	0.0594	
Spectrus	GE1	0.0001	0.0001	0.0044	0.0003	0.0001	0.0001	0.0001	0.0021	0.0001	0.0039	0.0012	0.0001	0.0001	
Optispearse	Sodium hydroxide	0.0002	0.0004	0.0134	0.0009	0.0004	0.0004	0.0003	0.0064	0.0004	0.0121	0.0037	0.0002	0.0003	
ADIP-X	MDA	0.1222	0.2402	7.6927	0.5385	0.2019	0.2059	0.1805	<u>3.6579</u>	0.2217	<u>6.9300</u>	<u>2.1186</u>	0.1408	0.1449	
DIPA	DIPA	0.0887	0.1744	<u>5.5846</u>	0.3910	0.1466	0.1495	0.1310	<u>2.6555</u>	0.1610	<u>5.0310</u>	<u>1.5380</u>	0.1022	0.1052	
CC Eliminator	Lauramine Oxide	0.0002	0.0003	0.0095	0.0007	0.0002	0.0003	0.0002	0.0045	0.0003	0.0086	0.0026	0.0002	0.0002	
CC 414P	Diethanolamine	0.0047	0.0093	0.2966	0.0208	0.0078	0.0079	0.0070	0.1410	0.0085	0.2672	0.0817	0.0054	0.0056	
Solberg	СРВ	0.0067	0.0131	0.4192	0.0293	0.0110	0.0112	0.0098	0.1993	0.0121	0.3777	0.1155	0.0077	0.0079	

Table 43. Calculated risk quotients (worst-case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for El Niño episode.¹

¹ Risk quotients exceeding 1 are underlined. ² Steammate=Steammate NA0880; Genguard=Genguard GN8220; Crystalfloc=Crystalfloc Cationic Emulsions; BetzDearborn=BetzDearborn AE1115P; Cortrol=Cortrol OS7780; Spectrus=Spectrus BD1501E; Optispearse= Optispearse HP2650. ³ MEA= Monoethanolamine; MDA=Methyldiethanolamine; ICP solvent=Isoparaffins petroleum hydrotreated HFP; CPB=Cocoamido propyl betaine.
Formulation ²	Toxic Component ³		Mixing Zone Sites						Receiving	Environm	ent Sites			
		C1	C2	С3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0021	0.0035	0.0875	0.0081	0.0109	0.0030	0.0028	0.0551	0.0043	0.0840	0.0191	0.0024	0.0026
Genguard	Gen2	0.0001	0.0002	0.0058	0.0005	0.0007	0.0002	0.0002	0.0036	0.0003	0.0056	0.0013	0.0002	0.0002
Crystalfloc	Adipic acid	0.0001	0.0002	0.0038	0.0004	0.0005	0.0001	0.0001	0.0024	0.0002	0.0037	0.0008	0.0001	0.0001
BetzDearborn	ICP solvent	0.0013	0.0021	0.0530	0.0049	0.0066	0.0018	0.0017	0.0334	0.0026	0.0509	0.0115	0.0015	0.0016
Cortrol	1,4-Benzoquinone	0.0120	0.0196	0.4912	0.0454	0.0612	0.0168	0.0159	0.3092	0.0239	0.4717	0.1070	0.0137	0.0148
Spectrus	GE1	0.0000	0.0000	0.0007	0.0001	0.0001	0.0000	0.0000	0.0004	0.0000	0.0007	0.0001	0.0000	0.0000
Optispearse	Sodium hydroxide	0.0001	0.0001	0.0021	0.0002	0.0003	0.0001	0.0001	0.0013	0.0001	0.0020	0.0005	0.0001	0.0001
ADIP-X	MDA	0.0292	0.0479	<u>1.1988</u>	0.1109	0.1495	0.0410	0.0389	0.7547	0.0583	<u>1.1510</u>	0.2611	0.0334	0.0362
DIPA	DIPA	0.0212	0.0348	0.8703	0.0805	0.1085	0.0298	0.0282	0.5479	0.0423	0.8356	0.1895	0.0242	0.0263
CC Eliminator	Lauramine Oxide	0.0000	0.0001	0.0015	0.0001	0.0002	0.0001	0.0000	0.0009	0.0001	0.0014	0.0003	0.0000	0.0000
CC 414P	Diethanolamine	0.0011	0.0018	0.0462	0.0043	0.0058	0.0016	0.0015	0.0291	0.0022	0.0444	0.0101	0.0013	0.0014
Solberg	СРВ	0.0016	0.0026	0.0653	0.0060	0.0081	0.0022	0.0021	0.0411	0.0032	0.0627	0.0142	0.0018	0.0020

Table 44. Calculated risk quotients (normal case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for El Niño episode.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites				Receiving Environment Sites							
		C1	C2	С3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0097	0.0182	0.7076	0.0384	0.0258	0.0162	0.0114	0.4311	0.0198	0.5107	0.1317	0.0100	0.0104
Genguard	Gen2	0.0006	0.0012	0.0468	0.0025	0.0017	0.0011	0.0008	0.0285	0.0013	0.0338	0.0087	0.0007	0.0007
Crystalfloc	Adipic acid	0.0004	0.0008	0.0309	0.0017	0.0011	0.0007	0.0005	0.0188	0.0009	0.0223	0.0057	0.0004	0.0005
BetzDearborn	ICP solvent	0.0058	0.0110	0.4286	0.0233	0.0156	0.0098	0.0069	0.2611	0.0120	0.3093	0.0797	0.0060	0.0063
Cortrol	1,4-Benzoquinone	0.0542	0.1022	<u>3.9717</u>	0.2156	0.1448	0.0909	0.0639	<u>2.4199</u>	0.1112	<u>2.8662</u>	0.7390	0.0559	0.0583
Spectrus	GE1	0.0001	0.0001	0.0055	0.0003	0.0002	0.0001	0.0001	0.0033	0.0002	0.0040	0.0010	0.0001	0.0001
Optispearse	Sodium hydroxide	0.0002	0.0004	0.0169	0.0009	0.0006	0.0004	0.0003	0.0103	0.0005	0.0122	0.0032	0.0002	0.0002
ADIP-X	MDA	0.1323	0.2494	<u>9.6926</u>	0.5262	0.3534	0.2219	0.1558	<u>5.9055</u>	0.2715	<u>6.9946</u>	<u>1.8034</u>	0.1364	0.1422
DIPA	DIPA	0.0960	0.1811	7.0365	0.3820	0.2566	0.1611	0.1131	4.2872	0.1971	<u>5.0778</u>	<u>1.3092</u>	0.0990	0.1032
CC Eliminator	Lauramine Oxide	0.0002	0.0003	0.0120	0.0006	0.0004	0.0003	0.0002	0.0073	0.0003	0.0086	0.0022	0.0002	0.0002
CC 414P	Diethanolamine	0.0051	0.0096	0.3738	0.0203	0.0136	0.0086	0.0060	0.2277	0.0105	0.2697	0.0695	0.0053	0.0055
Solberg	СРВ	0.0072	0.0136	0.5282	0.0287	0.0193	0.0121	0.0085	0.3218	0.0148	0.3812	0.0983	0.0074	0.0077

Table 45. Calculated risk quotients (worst-case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for La Niña episode.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites						Receiving	Environn	nent Sites			
		C1	C2	С3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0021	0.0041	0.1000	0.0078	0.0101	0.0031	0.0036	0.0499	0.0050	0.0698	0.0175	0.0028	0.0027
Genguard	Gen2	0.0001	0.0003	0.0066	0.0005	0.0007	0.0002	0.0002	0.0033	0.0003	0.0046	0.0012	0.0002	0.0002
Crystalfloc	Adipic acid	0.0001	0.0002	0.0044	0.0003	0.0004	0.0001	0.0002	0.0022	0.0002	0.0030	0.0008	0.0001	0.0001
BetzDearborn	ICP solvent	0.0013	0.0025	0.0606	0.0047	0.0061	0.0019	0.0022	0.0302	0.0030	0.0422	0.0106	0.0017	0.0017
Cortrol	1,4-Benzoquinone	0.0117	0.0231	0.5615	0.0435	0.0570	0.0175	0.0201	0.2803	0.0281	0.3915	0.0982	0.0156	0.0153
Spectrus	GE1	0.0000	0.0000	0.0008	0.0001	0.0001	0.0000	0.0000	0.0004	0.0000	0.0005	0.0001	0.0000	0.0000
Optispearse	Sodium hydroxide	0.0000	0.0001	0.0024	0.0002	0.0002	0.0001	0.0001	0.0012	0.0001	0.0017	0.0004	0.0001	0.0001
ADIP-X	MDA	0.0286	0.0564	<u>1.3704</u>	0.1062	0.1390	0.0426	0.0491	0.6840	0.0687	0.9554	0.2397	0.0380	0.0374
DIPA	DIPA	0.0207	0.0410	0.9949	0.0771	0.1009	0.0309	0.0356	0.4965	0.0499	0.6936	0.1740	0.0276	0.0272
CC Eliminator	Lauramine Oxide	0.0000	0.0001	0.0017	0.0001	0.0002	0.0001	0.0001	0.0008	0.0001	0.0012	0.0003	0.0000	0.0000
CC 414P	Diethanolamine	0.0011	0.0022	0.0528	0.0041	0.0054	0.0016	0.0019	0.0264	0.0026	0.0368	0.0092	0.0015	0.0014
Solberg	СРВ	0.0016	0.0031	0.0747	0.0058	0.0076	0.0023	0.0027	0.0373	0.0037	0.0521	0.0131	0.0021	0.0020

Table 46. Calculated risk quotients (normal case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for La Niña episode.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites				Receiving Environment Sites							
		C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0141	0.0412	0.7632	0.0672	0.0289	0.0187	0.0143	0.3751	0.0213	0.6166	0.1768	0.0118	0.0114
Genguard	Gen2	0.0009	0.0027	0.0505	0.0044	0.0019	0.0012	0.0009	0.0248	0.0014	0.0408	0.0117	0.0008	0.0008
Crystalfloc	Adipic acid	0.0006	0.0018	0.0333	0.0029	0.0013	0.0008	0.0006	0.0164	0.0009	0.0269	0.0077	0.0005	0.0005
BetzDearborn	ICP solvent	0.0086	0.0250	0.4622	0.0407	0.0175	0.0113	0.0087	0.2272	0.0129	0.3735	0.1071	0.0071	0.0069
Cortrol	1,4-Benzoquinone	0.0793	0.2314	4.2835	0.3769	0.1621	0.1048	0.0804	<u>2.1055</u>	0.1196	<u>3.4610</u>	0.9924	0.0662	0.0640
Spectrus	GE1	0.0001	0.0003	0.0059	0.0005	0.0002	0.0001	0.0001	0.0029	0.0002	0.0048	0.0014	0.0001	0.0001
Optispearse	Sodium hydroxide	0.0003	0.0010	0.0183	0.0016	0.0007	0.0004	0.0003	0.0090	0.0005	0.0148	0.0042	0.0003	0.0003
ADIP-X	MDA	0.1934	0.5648	10.4535	0.9198	0.3955	0.2557	0.1962	<u>5.1382</u>	0.2919	<u>8.4462</u>	<u>2.4218</u>	0.1617	0.1563
DIPA	DIPA	0.1404	0.4100	<u>7.5889</u>	0.6677	0.2871	0.1856	0.1424	<u>3.7302</u>	0.2119	<u>6.1316</u>	<u>1.7581</u>	0.1174	0.1134
CC Eliminator	Lauramine Oxide	0.0002	0.0007	0.0129	0.0011	0.0005	0.0003	0.0002	0.0063	0.0004	0.0104	0.0030	0.0002	0.0002
CC 414P	Diethanolamine	0.0075	0.0218	0.4031	0.0355	0.0153	0.0099	0.0076	0.1981	0.0113	0.3257	0.0934	0.0062	0.0060
Solberg	СРВ	0.0105	0.0308	0.5697	0.0501	0.0216	0.0139	0.0107	0.2800	0.0159	0.4603	0.1320	0.0088	0.0085

Table 47. Calculated risk quotients (worst-case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for actual event scenarios.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites						Receiving	g Environn	nent Sites			
		C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0030	0.0060	0.0990	0.0106	0.0110	0.0031	0.0033	0.0484	0.0046	0.0785	0.0227	0.0030	0.0027
Genguard	Gen2	0.0002	0.0004	0.0066	0.0007	0.0007	0.0002	0.0002	0.0032	0.0003	0.0052	0.0015	0.0002	0.0002
Crystalfloc	Adipic acid	0.0001	0.0003	0.0043	0.0005	0.0005	0.0001	0.0001	0.0021	0.0002	0.0034	0.0010	0.0001	0.0001
BetzDearborn	ICP solvent	0.0018	0.0036	0.0600	0.0064	0.0067	0.0019	0.0020	0.0293	0.0028	0.0475	0.0137	0.0018	0.0016
Cortrol	1,4-Benzoquinone	0.0169	0.0336	0.5556	0.0594	0.0620	0.0174	0.0187	0.2718	0.0258	0.4406	0.1273	0.0170	0.0150
Spectrus	GE1	0.0000	0.0000	0.0008	0.0001	0.0001	0.0000	0.0000	0.0004	0.0000	0.0006	0.0002	0.0000	0.0000
Optispearse	Sodium hydroxide	0.0001	0.0001	0.0024	0.0003	0.0003	0.0001	0.0001	0.0012	0.0001	0.0019	0.0005	0.0001	0.0001
ADIP-X	MDA	0.0411	0.0820	<u>1.3559</u>	0.1450	0.1512	0.0425	0.0457	0.6633	0.0629	<u>1.0753</u>	0.3108	0.0415	0.0366
DIPA	DIPA	0.0299	0.0595	0.9843	0.1053	0.1098	0.0309	0.0332	0.4816	0.0456	0.7806	0.2256	0.0301	0.0266
CC Eliminator	Lauramine Oxide	0.0001	0.0001	0.0017	0.0002	0.0002	0.0001	0.0001	0.0008	0.0001	0.0013	0.0004	0.0001	0.0000
CC 414P	Diethanolamine	0.0016	0.0032	0.0523	0.0056	0.0058	0.0016	0.0018	0.0256	0.0024	0.0415	0.0120	0.0016	0.0014
Solberg	СРВ	0.0022	0.0045	0.0739	0.0079	0.0082	0.0023	0.0025	0.0362	0.0034	0.0586	0.0169	0.0023	0.0020

Table 48. Calculated risk quotients (normal case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for actual event scenarios.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites				Receiving Environment Sites							
		C1	C2	C3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0196	0.0519	0.8099	0.2386	0.0333	0.0193	0.0172	0.4383	0.0239	0.7148	0.3013	0.0145	0.0122
Genguard	Gen2	0.0013	0.0034	0.0536	0.0158	0.0022	0.0013	0.0011	0.0290	0.0016	0.0473	0.0199	0.0010	0.0008
Crystalfloc	Adipic acid	0.0009	0.0023	0.0354	0.0104	0.0015	0.0008	0.0007	0.0191	0.0010	0.0312	0.0132	0.0006	0.0005
BetzDearborn	ICP solvent	0.0119	0.0314	0.4905	0.1445	0.0202	0.0117	0.0104	0.2654	0.0145	0.4329	0.1824	0.0088	0.0074
Cortrol	1,4-Benzoquinone	0.1099	0.2914	<u>4.5457</u>	<u>1.3394</u>	0.1870	0.1082	0.0963	<u>2.4599</u>	0.1344	<u>4.0121</u>	<u>1.6908</u>	0.0815	0.0684
Spectrus	GE1	0.0002	0.0004	0.0063	0.0018	0.0003	0.0001	0.0001	0.0034	0.0002	0.0055	0.0023	0.0001	0.0001
Optispearse	Sodium hydroxide	0.0005	0.0012	0.0194	0.0057	0.0008	0.0005	0.0004	0.0105	0.0006	0.0171	0.0072	0.0003	0.0003
ADIP-X	MDA	0.2682	0.7111	<u>11.0932</u>	<u>3.2687</u>	0.4563	0.2640	0.2349	<u>6.0032</u>	0.3279	<u>9.7910</u>	<u>4.1263</u>	0.1988	0.1669
DIPA	DIPA	0.1947	0.5163	<u>8.0533</u>	<u>2.3729</u>	0.3312	0.1916	0.1705	<u>4.3581</u>	0.2380	<u>7.1079</u>	<u>2.9956</u>	0.1443	0.1212
CC Eliminator	Lauramine Oxide	0.0003	0.0009	0.0137	0.0040	0.0006	0.0003	0.0003	0.0074	0.0004	0.0121	0.0051	0.0002	0.0002
CC 414P	Diethanolamine	0.0103	0.0274	0.4278	0.1260	0.0176	0.0102	0.0091	0.2315	0.0126	0.3775	0.1591	0.0077	0.0064
Solberg	СРВ	0.0146	0.0388	0.6046	0.1781	0.0249	0.0144	0.0128	0.3272	0.0179	0.5336	0.2249	0.0108	0.0091

Table 49. Calculated risk quotients (worst-case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for extreme event scenarios.¹

Formulation ²	Toxic Component ³		Mixing Zone Sites						Receiving	; Environn	nent Sites			
		C1	C2	С3	C4	P1	P2	P3	P4	P5	P6	P7	P8	P9
Steammate	MEA	0.0038	0.0076	0.1040	0.0134	0.0116	0.0036	0.0031	0.0490	0.0046	0.0872	0.0281	0.0028	0.0026
Genguard	Gen2	0.0003	0.0005	0.0069	0.0009	0.0008	0.0002	0.0002	0.0032	0.0003	0.0058	0.0019	0.0002	0.0002
Crystalfloc	Adipic acid	0.0002	0.0003	0.0045	0.0006	0.0005	0.0002	0.0001	0.0021	0.0002	0.0038	0.0012	0.0001	0.0001
BetzDearborn	ICP solvent	0.0023	0.0046	0.0630	0.0081	0.0070	0.0022	0.0019	0.0297	0.0028	0.0528	0.0170	0.0017	0.0016
Cortrol	1,4-Benzoquinone	0.0212	0.0428	0.5835	0.0752	0.0652	0.0203	0.0176	0.2751	0.0258	0.4893	0.1578	0.0158	0.0148
Spectrus	GE1	0.0000	0.0001	0.0008	0.0001	0.0001	0.0000	0.0000	0.0004	0.0000	0.0007	0.0002	0.0000	0.0000
Optispearse	Sodium hydroxide	0.0001	0.0002	0.0025	0.0003	0.0003	0.0001	0.0001	0.0012	0.0001	0.0021	0.0007	0.0001	0.0001
ADIP-X	MDA	0.0518	0.1045	<u>1.4240</u>	0.1836	0.1592	0.0497	0.0430	0.6715	0.0629	<u>1.1942</u>	0.3851	0.0385	0.0360
DIPA	DIPA	0.0376	0.0759	<u>1.0338</u>	0.1333	0.1156	0.0360	0.0312	0.4875	0.0456	0.8669	0.2796	0.0279	0.0262
CC Eliminator	Lauramine Oxide	0.0001	0.0001	0.0018	0.0002	0.0002	0.0001	0.0001	0.0008	0.0001	0.0015	0.0005	0.0000	0.0000
CC 414P	Diethanolamine	0.0020	0.0040	0.0549	0.0071	0.0061	0.0019	0.0017	0.0259	0.0024	0.0460	0.0149	0.0015	0.0014
Solberg	СРВ	0.0028	0.0057	0.0776	0.0100	0.0087	0.0027	0.0023	0.0366	0.0034	0.0651	0.0210	0.0021	0.0020

Table 50. Calculated risk quotients (normal case) for selected Refining NZ SWB process chemicals at mixing zone and receiving environment sites up to 24 hours after discharge for extreme event scenarios.¹

4.5 Assessment of effects on water quality

4.5.1 "Traditional" contaminants

For all SWB discharges and under the normal-case scenario (i.e. most of the time) (Table 36, Table 38, Table 40, Table 42), all traditional contaminants had a receiving environment risk quotient (i.e., RQ3) <1 at all receiving environment sites. Generally, the risk quotients under this scenario were orders of magnitude smaller than 1, indicating a <u>negligible effect</u> on water quality at the edges and outside of the mixing zone.

Under worst-case scenarios, ammoniacal nitrogen (NH_4 -N) and faecal coliforms (FC) are the only contaminants in the SWB that <u>may potentially lead to adverse ecological effects</u> outside the mixing zone (Table 35, Table 37, Table 39, Table 41).

Under worst-case scenarios, NH_4 -N appears to show the greatest potential effect on the receiving environment due to risk quotients of up to 17 at some receiving environment sites. However, this needs to be explained, as follows.

Worst-case scenarios use the lowest practical dilutions (5^{th} percentile), which will occur 5% of the time. They also use maximum Refining NZ SWB contaminant concentrations.

The large risk quotients for NH_4 -N are primarily a result of the large maximum SWB concentrations between 2014 and 2019 and a low regulatory guideline in the oNRP (<0.005 mg/L). As described in Section 2.3 and shown in Table 8 and Figure 12, SWB NH_4 -N concentrations were markedly higher in 2014 and early 2015 prior to a plant upgrade. After the plant upgrade, maximum NH_4 -N concentrations (2015–2019) were ca. 8x lower than before the upgrade. When the SWB NH_4 -N concentrations for the period 2015–2019 are used (i.e. post upgrade), the maximum risk quotients under worst-case dilutions and assessing against the oNRP are <2.1.

The pNRP designates an annual median NH_4 -N concentration of <0.023 mg/L. When the regional plan process is completed and the current pNRP becomes operational, it is likely that this value for NH_4 -N (or something close to it) will be used, rather than the oNRP value of <0.005 mg/L.

Between 2014 and 2018, <u>measured</u> NH₄-N concentrations at receiving environment sites assessed in this report were all, with one exception, below the pNRP value of 0.023 mg/L. The exception was site 100263 (One Tree Point), which marginally exceeded the pNRP SWQG (0.027 mg/L) in 2014. In contrast, all sites exceeded the oNRP SWQG of 0.005 mg/L for the majority of the time (see Table 17). Of particular importance to this assessment, sites on the edge of the mixing zone (100265 and 100266) had relatively low NH₄-N concentrations (generally <0.010 mg/L) compared with NRC monitoring sites in the inner harbour and the outer harbour.

Ammoniacal-nitrogen in the SWB appears to have a <u>negligible effect</u> on water quality outside the mixing zone <u>most of the time</u>. However, for a small portion of the time (5%), ammoniacal-nitrogen concentration at sites outside the mixing zone may temporarily exceed water quality limits. However, these water quality limits are designed to assess effects from eutrophication and are usually based on annual median data (as is the case for pNRP and NH₄-N). Therefore, any short-

term increase in NH_4 -N concentration (as highlighted by the worst-case scenarios) are unlikely to lead to increased risk of eutrophication due to their short duration.

Under the worst-case scenarios and at a few sites, faecal coliforms (FC) risk quotients marginally exceed 1, with the greatest risk quotient being 2.2. The large concentrations of FC were sporadic, occurring approximately once per year (see Figure 10). These spikes are attributed to a nesting colony of Red Billed gulls which inhabit the SWB every summer, with up to 2000 nesting pairs (Riaan Elliot, Refining NZ, personal communication). It is important to note that the modelled worst-case scenarios will occur only 5% of the time. Furthermore, they do not include any attenuation of faecal coliforms that will occur in marine water.

4.5.2 Process chemicals

A summary of risk quotients for process chemicals is provided in Table 51.

Referring to Table 51, the majority of the formulations used at the Refinery on an **everyday basis** will lead to <u>negligible effects</u> on the ecology of the receiving environment.

- For two formulations –, Embreak 2050 and Optispearse ADJ5150 the risk is negligible in the SWB, even before allowing for partitioning into oil or for dilution in the receiving environment, i.e. RQ1 < 1.
- For three formulations Embreak 2021, Spectrus NX1100 and Inhibitor AZ8104 oil partitioning calculations were sufficient to reduce the risk quotient RQ2 to less than 1, indicating negligible risk in the SWB.
- For six formulations Steammate NA0880, BetzDearborn, Crystalfloc Cationic Emulsions, Genguard GN8220, Spectrus BD1501E and Optisperse HP2650 dilution in the receiving environment was sufficient to reduce the risk quotient RQ3 to less than 1 (even under worst-case dilutions and event scenarios).
- One formulation Cortrol OS7780 had RQ3 = 4.5 under worst-case dilutions and event • scenarios. As previously, I note that this may occur 5% of the time and under least favourable conditions. Under normal scenario conditions, the maximum RQ3 = 0.6 for Cortrol OS7780. Therefore, the use of Cortrol OS7780 may be causing more than minor transitory effects outside the mixing zone. As a mitigation measure, Cortrol OS7780 is in the process of being replaced by RNZ with an alternative formulation (Cortrol OS5614). As described in Section 3.3.4, the use of Cortrol OS5614 will lead to a minor increase (0.048 mg/L) in NH_4 -N to the SWB. As described in Section 4.5.1, when the SWB NH_4 -N concentrations for the period 2015–2019 are used (i.e. post upgrade), the maximum risk quotients under worst-case dilutions and assessing against the oNRP are <2.1. The additional NH₄-N load from Cortrol OS5614 would lead to a revised maximum risk quotient under worst-case dilutions and assessing against the oNRP of <2.2. Under normal-case scenario (i.e. most of the time) the additional NH₄-N load from Cortrol OS5614 would still provide a RQ3 of <1, indicating a negligible effect on water quality at the edges and outside of the mixing zone.

During the **total Refinery shutdown** between 3^{rd} May 2018 and 21^{st} May 2018, large amounts of CC Eliminator and CC 414P formulations were used (see Section 3.3.16).

- Despite the large amount of formulation used, a marginal risk (RQ = 2.4) was calculated for lauramine oxide (in CC Eliminator) in the SWB. However, after dilution in the receiving environment, the risk to receiving environment sites outside the mixing zone was negligible (RQ3 = 0.01).
- d-Limonene (in CC 414P) presented as a negligible risk in the SWB, after allowing for oil/water partitioning (RQ2 = 0.01).
- Diethanolamine (in CC 414P) presented as a negligible ecotoxicological risk outside the mixing zone (RQ3 = 0.4). Diethanolamine does not bioaccumulate (BAF = 1) and is readily biodegradable.⁶⁹

The process chemicals used in the Refinery shutdown led to <u>negligible</u> ecological effects in the receiving environment.

An **accidental spill of DIPA** over a period of 5 days in May 2018 may, if unmanaged,⁷⁰ have led to short-term more-than-minor ecological effects outside the mixing zone.

DIPA had a maximum RQ3 = 8, under worst-case dilutions and event scenarios, and • maximum RQ3 = 1.03 under normal-scenario dilutions. DIPA has low persistence in sediment/water⁷³ and does not bioaccumulate (BAF = 1). DIPA biodegradation was not reported. Therefore, DIPA would not persist in sediment or be readily taken up by biota and would be rapidly diluted further over 24-48 hours to below ecological effect thresholds. The toxicity is driven by a low marine PNEC for DIPA of 0.028 mg/L, with an assessment factor of 10,000. The large assessment factor (100x higher than monoethanolamine – see above) suggests that there are few reliable marine data from which to establish a reliable marine PNEC, leading to an extremely conservative marine PNEC value. ECHA state that there is a high probability that DIPA is not acutely toxic to fish, invertebrates, algae or cyanobacteria.⁷¹ The only specified marine species was the algae *Skeletonema costatum*, which exhibited a 72-hour EC_{50} of 240 mg/L. Therefore, despite a calculated maximum RQ3 of 8 for DIPA, this is more a function of an extremely conservative PNEC, and it is highly unlikely that there were any acute ecotoxicity effects in the receiving environment as a result of the DIPA spill.

ADIP-X spills are infrequent, with the largest spill over the last 15 years of 100 L. Under this scenario, and if unmanaged,⁷⁰ methyldiethanolamine (MDA) presented the highest risk (albeit under worst-case scenario dilutions and events) with RQ3 = 11. The highest calculated RQ3 under normal dilution scenarios was 1.4. The toxicity is driven by a low marine PNEC for MDA of 0.004 mg/L, with an assessment factor of 10,000, the same as for DIPA, suggesting an extremely conservative marine PNEC value. ECHA state that the most sensitive endpoint in marine water was the LC₅₀ of 45 mg/L after 48 hours of exposure determined for *Acartia tonsa*, suggesting very low acute toxicity for MDA to marine species.⁷² Therefore, despite a calculated maximum RQ3 of 11 for MDA, this is more a function of an extremely conservative PNEC, and it is highly unlikely that there were any acute ecotoxicity effects in the receiving environment as a result of the ADIP-

⁶⁹ Data from Sigma SDS.

⁷⁰ The risk assessment in this report assumes worst-case, i.e. no management intervention was implemented for a spill event. However, Refining NZ have a range of process to avoid and respond to accidental spills and in my opinion the risks from these spills would have been mitigated at the time.

⁷¹ https://echa.europa.eu/registration-dossier/-/registered-dossier/13889/6/2/1

⁷² https://echa.europa.eu/registration-dossier/-/registered-dossier/14521/6/2/1

X spill. Furthermore, MDA has low persistence in sediment/water and low biodegradability⁷³, but does not bioaccumulate (BAF = 1). Therefore, MDA would not persist in sediment or be readily taken up by biota and would be rapidly diluted further over 24–48 hours to below ecological effect thresholds.

The **fire training foam** Solberg DoD3155 is used on a routine but infrequent basis at the Refinery.

• A negligible ecological risk was presented under the normal-use scenario but worst-case dilution in the receiving environment (RQ3 = 0.6). The causative chemical was cocoamido propyl betaine (CPB), based primarily on a marine PNEC of 0.002 mg/L (intermittent discharge) with an associated assessment factor of 500. As stated above, this suggests that there are few reliability marine data from which to establish a reliable marine PNEC, leading to a highly conservative value. The only marine organism specified by ECHA was the marine microalgae *Ulva lactuca*, with a 48-hour EC₅₀ of 30 mg/L.⁷⁴ ECHA also state that CPB is readily biodegradable with >50% degradation after 1 day and >90% after 5 days in seawater.⁷⁵ Although freshwater was not assessed, it is highly likely that CPB will degrade at a similar rate as it proceeds through the retention pond and stormwater basin. Taking a highly conservative stance (including a highly conservative PNEC, lowest (worst-case) dilution and conservation of all chemical components), CPB will lead to negligible adverse effects on the marine receiving environment.

Formulation	Toxic Component ¹	RQ1	RQ2	Highest RQ3 ²
	Everyda	iy use		
BetzDearborn	Isoparaffins	86	86	0.5
Cortrol OS7780	1,4-Benzoquinone	797	797	4.6
Embreak 2021	NP	10,296	0.02	
Klaraid IC1172	Aluminium	Not applicable		
Spectrus NX1100	Bronopol	2.2	0.1	
Inhibitor AZ8104	Sodium Tolyltriazole	1.9	0.03	
Crystalfloc Cationic Emulsions	Adipic acid	6.2	6.2	0.04
Embreak 2050	DGME	0.5		
Steammate NA0880	MEA	142	142	0.8
Genguard GN8220	Gen2	9.4	9.4	0.05
Spectrus BD1501E	GE1	1.1	1.1	0.02
Optispearse ADJ5150	Sodium hydroxide	0.6		
Optispearse HP2650	Sodium hydroxide	3.4	3.4	0.02
	Spill e	vent		
ADIP-X	MDA	1945	1945	11
DIPA	DIPA	1417	1412	8
	Refinery sl	nutdown		
CC Eliminator	Lauramine Oxide	4454	2.4	0.01
CC 414P	d-Limonene	324	0.01	

Table 51. Summary of risk quotients for process chemical formulations.

⁷³ Data from Chemwatch SDS.

⁷⁴ <u>https://echa.europa.eu/registration-dossier/-/registered-dossier/25362/6/2/1</u>

⁷⁵ https://echa.europa.eu/registration-dossier/-/registered-dossier/25362/5/3/2

Formulation	Toxic Component ¹	RQ1	RQ2	Highest RQ3 ²							
CC 414P	Diethanolamine	76	75	0.4							
	Fire training										
Solberg DoD3155	СРВ	106	106	0.6							
Solberg DoD3155	DGMBE	15	15	0.2							

¹ NP=Formaldehyde Polymer With 4-Nonylphenol And Oxirane; Aluminium=Aluminium Chlorohydrate; DGME=Diethylene Glycol Monobutyl Ether; MEA=Monoethanolamine; Copolymer=Ethylene/Propylene Oxides Copolymer; MDA=Methyldiethanolamine; CPB=Cocoamido propyl betaine; DGMBE= Diethylene glycol mono butyl ether.

² For all, based on worst-case La Niña annual event.

³ Colour codes: < 1 = green; 1-10 = orange; >10 = red.

4.5.3 Cumulative effects

The cultural effects assessment report undertaken for the Patuharakeke Te Iwi Trust Board (Chetham and Maki-Midwood, 2020) queried two aspects of this report:

- How the mixing zone is determined, as it appears to be an arbitrary location from previous consents based more on the Marsden Point Port Zone (MPPZ) area than environmental parameters.
- What cumulative effects (in combination with past effects and temporary effects) can flow on to the mauri of the harbour, mātaitai and taonga species.

The determination of the mixing zone size was also questioned by Dr Rob Bell in his review of the hydrodynamic modelling and water quality reports. This has subsequently been addressed in a memo to NRC (Appendix 6) and is summarised in Section 2.1.4 of this report.

Further clarification on cumulative effects was obtained from the report lead author, Juliane Chetham (Riaan Elliot, Refining NZ, personal communication) and these encompass:

- Cumulative effects as a result of all sources to the harbour including from the Refinery.
- Cumulative effect of all contaminants in the Refinery discharge combined.
- Cumulative effects associated with bioaccumulation up the food chain.

These are addressed separately below.

Cumulative effects of all sources

Cumulative effects of all sources to the harbour are assessed by measurement of contaminants in water, sediment, and biota at receiving environment sites. NRC undertake routine measurement of water, sediment and biota to assess what these cumulative effects may be. Therefore, each contaminant that is measured at a receiving environment site is in effect integrating all those contaminant sources. Water and sediment quality in the receiving environment is generally good and below guideline values (this report), while oyster body burden from contaminants is low (De Luca, 2020).

Cumulative effects of all contaminants in Refinery SWB

It is not possible to accurately measure the cumulative effects that all contaminants present in the SWB at one time may have on the receiving environment by measuring each contaminant. Water quality and sediment quality standards used for assessing potential for adverse effects are for specific individual chemicals (see Section 2.1.3). Furthermore, some chemicals present in the SWB (i.e. process chemicals) are not able to be measured routinely and potential for adverse effects from these chemicals is undertaken by a risk assessment using a mass balance approach (see Section 3).

However, whole effluent toxicity tests on the SWB have been undertaken on three occasions between 2017 and 2019 and provide an integrated toxicity assessment of the Refinery stormwater at that time (see Section 2.2.5) against relevant marine species. All three tests were under normal Refinery operating conditions. In summary, the maximum dilution required to reduce the toxicity of the SWB discharge water to a no-toxicity threshold is 256x, which is the worst-case scenario based on the worst-case test result for the most sensitive marine species (blue mussel larvae) and noting the other two test results for this species were 1.7x and 1.23x. This 256x value has been used as a worst-case scenario assessment for cumulative effects from all contaminants contained in the Refinery SWB on marine ecology (De Luca, 2020).

Bioaccumulation to higher trophic species levels

Some contaminants present in the Refinery SWB have the potential to bioaccumulate through higher trophic species levels (normally referred to as "up the food chain"). These include some organic contaminants (e.g. PAHs, phenols and mercury). Bioaccumulative contaminants generally associate with organic matter in sediment rather than be in the dissolved phase. Analysis of contaminants in receiving environment sediments (see Section 2.5.5) showed generally very low concentrations of contaminants in oysters at the Jetty showed lower or similar concentrations to other sites around the harbour and effects were considered negligible (De Luca, 2020). The potential for adverse human health effects from consumption of these oysters containing bioaccumulative contaminants from the discharges are considered less than minor (Environmental Medicine Limited, 2020). Furthermore, an assessment of effects on marine mammals from bioaccumulative contaminants is considered negligible (Clement, 2020).

Some process chemicals have the potential to bioaccumulate. As stated in Section 3.2.4, any chemical with a bioaccumulation concentration factor (BCF) >1000 is likely to bioaccumulate. Of the process chemicals that enter the SWB and discharged to the receiving environment, the BCF range from 1 to 4, so do not bioaccumulate.

In summary, cumulative effects on the receiving environment from all sources are low with good water, sediment and shellfish quality in Whangarei Harbour. Whole effluent testing of the SWB integrates all contaminants against relevant marine species and the marine ecology assessments are made on the worst-case scenario. Although some contaminants in the Refinery SWB have the potential to bioaccumulate, there is no evidence of bioaccumulation to higher trophic species levels. All process chemicals present in the Refinery SWB have extremely low bioaccumulation potential.

4.5.4 Summary statement of effects on water quality

Overall, I consider the discharges of most contaminants from the Refinery SWB to have a less than minor effect on water quality in the marine receiving environment outside the current mixing zone. A few contaminants may exhibit no more than minor <u>and</u> transitory effects: ammoniacal nitrogen (NH_4 -N); faecal coliforms (FC); and the every-day process formulations Cortrol OS7780 (in the process of being replaced by a more benign formulation Cortrol OS5614).

5. Groundwater Quality

Tonkin & Taylor Ltd (2019) has developed a hydrogeological conceptual site model of groundwater contamination at the Refinery.

Aspects of relevance to this report are:

- review of reports and data sources regarding contaminant sources, geological setting, hydrogeological conditions and the marine environment;
- completion of one round of groundwater sampling in June 2019 to assess per- and polyfluoroalkyl substances (PFAS) contamination in the location of the current onsite fire training area;
- completion of one round of groundwater sampling in September 2019 to provide recent data for potential contaminants that had either not been previously analysed or not analysed for some years.

Tonkin & Taylor Ltd (2019) compared the groundwater analytical results to guidance values adopted from the following:

- ANZECC 2000⁷⁶, 80% level of protection for marine ecosystems (95% level of protection for benzene);
- Ministry of Health 2018 Drinking-Water Standards for New Zealand 2005 (Revised 2018) (Ministry of Health, 2018); and
- for PFAS, the Australian Department of Health *Health-Based Guidance Values for PFAS for Use in Site Investigations in Australia* (accepted by the Ministry of Health in 2017 as interim guidance levels) (Australian Department of Health, 2017).

5.1 Summary of the current groundwater condition (T&T)

The current groundwater condition was summarised by Tonkin & Taylor (2019) as follows:

- LNAPL (a light non-aqueous phase liquid), sourced from historic losses at the site, is contained by the continuously operating hydraulic containment system.
- Dissolved phase hydrocarbons, sourced from the LNAPL plume, are also contained by the system such that there are no exceedances of the ANZECC Guidelines for dissolved phase TPH, BTEX, PAH or phenol constituents in wells outside of the hydraulic containment area.
- While there is limited groundwater quality data for chlorinated solvents, if a loss of solvents had occurred historically, it would have been in an area where groundwater is captured by the containment system.
- There are concentrations of dissolved metals (arsenic, copper, iron, manganese and zinc) in some of the groundwater wells outside of the containment area that exceed the ANZECC Guidelines. The exceedances may be due to naturally occurring concentrations rather than a specific source (or sources).

⁷⁶ The ANZECC 2000 guidelines have been revised (Australian and New Zealand Governments, 2018).

- There are concentrations of nitrate-nitrogen (NO_3-N) above the adopted guideline 80% value in six perimeter wells outside of hydraulic containment. The nitrate appears likely to be at least partially sourced from the former land farms (where nitrate fertiliser was applied historically) and potentially from the stormwater retention basins.
- PFAS have been detected in groundwater near the fire training ground. The reported concentrations did not exceed the ANZECC Guidelines 95% level of protection, but do exceed the 99% level of protection, in some cases because the laboratory level of detection was raised due to interference from other PFAS. The initial PFAS assessment focussed on the potential worst-case location (the current fire training area where fluorinated firefighting foams may have been used for up to 30 years of firefighting training).

5.2 Potential effects of groundwater contaminants on marine receiving environment

5.2.1 Groundwater quality results

Some groundwater ecological guidelines are different to the corresponding marine receiving environment SWQG. As the receiving environment for groundwater outside the hydraulic containment is the marine receiving environment, groundwater contaminant concentrations were compared against SWQG. Following a conservative approach, maximum groundwater contaminant concentrations were compared against applicable SWQG (Table 3). Of note, nitrate-nitrogen was not included in SWQG used to assess surface water quality as receiving environment NO₃-N data are sporadic. As NO₃-N in groundwater from the Refinery is a potential issue, and recent sampling included NO₃-N, it was included in an assessment in this chapter.

Petroleum Hydrocarbons

As stated above, dissolved phase hydrocarbons, sourced from the LNAPL plume, are also contained by the system such that there are no exceedances of the ANZECC Guidelines for dissolved phase TPH, BTEX, PAH or phenol constituents in wells outside of the hydraulic containment area (for example, see TPH groundwater concentrations: Figure 27).



Figure 27. TPH groundwater concentrations from 2018-2019.

Metals/metalloids

Tonkin & Taylor (2019) measured total metal/metalloid groundwater concentrations in 2018–2019 and dissolved metal/metalloid groundwater concentrations in 2019.

Maximum <u>total</u> metal/metalloid groundwater concentrations were compared with SWQG (Table 52). Maximum metal/metalloid groundwater concentrations exceeded applicable SWQG (risk quotient RQ >1) for all metals, with only arsenic (a metalloid) below applicable SWQG (RQ < 1). Exceedances were for cadmium, chromium, copper, lead, nickel and zinc, with RQs ranging from 1.3 (chromium) to 30 (zinc).

Table 52. Total metal/metalloid concentrations (mg/L) in groundwater 2018-2019
(perimeter wells) and comparison with SWQG.

Analyte	Maximum GW concentration	GW Guideline	SWQG	SWQG Source	Maximum groundwater concentration as a percentage of SWQG	Risk Quotient ¹
Arsenic	0.027	0.0023	0.05	oNRP ³	54	0.5
Cadmium	0.0033	0.036	0.002	oNRP ⁴	165	1.7
Chromium	0.0059	0.085	0.0044	ANZ ^{2,7}	134	1.3
Copper	0.038	0.008	0.0013	ANZ ^{2,5}	2923	29

Analyte	Maximum GW concentration	GW Guideline	SWQG	SWQG Source	Maximum groundwater concentration as a percentage of SWQG	Risk Quotient ¹
Lead	0.064	0.012	0.0044	ANZ ^{2,5}	1455	15
Nickel	0.42	0.56	0.07	ANZ ^{2,6}	600	6
Zinc	0.45	0.043	0.015	ANZ ^{2,3}	3000	30

¹ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

²95% marine trigger value.

³ Insufficient data to derive a reliable ANZ marine trigger value.

⁴ oNRP more restrictive than ANZ (no data for pNRP).

⁵ ANZ more restrictive than oNRP (no data for pNRP).

⁶ No value in oNRP.

 $^{\rm 7}$ Based on Cr(VI), the more toxic valency state for chromium.

Maximum <u>dissolved</u> metal/metalloid groundwater concentrations were compared with SWQG (Table 53). Arsenic, cadmium, lead, mercury, nickel and vanadium all had RQ < 1. RQ exceeded 1 for chromium, cobalt, copper, manganese and zinc, with RQ ranging from 1.05 (chromium) to 25 (zinc).

In November 2019, Refining NZ undertook groundwater and surface water sampling along the beach side of the Refinery (at the open ocean sites) – which included dissolved metals – to assess potential effects to water quality from groundwater (see Section 5.2.3).

Table 53. <u>Dissolved metal/metalloid</u> concentrations (mg/L) in groundwater (wells outside or potentially outside of containment) September 2019 and comparison with SWQG.

Analyte	Maximum GW concentration	GW Guideline	SWQG	SWQG Source	Maximum groundwater concentration as a percentage of SWQG	Risk Quotient ¹
Arsenic	0.022	0.0023	0.05	oNRP ³	44	0.4
Cadmium	0.00023	0.036	0.002	oNRP ⁴	12	0.1
Chromium	0.0046	0.085	0.0044	ANZ ^{2,7}	105	1.05
Cobalt	0.0027	0.15	0.001	ANZ ²	270	2.7
Copper	0.026	0.008	0.0013	ANZ ^{2,5}	2000	20
Iron	11.9	0.3	-	ANZ ²	NA	NA
Lead	0.00137	0.012	0.0044	ANZ ^{2,5}	31	0.3
Manganese	0.74	0.08	0.08	ANZ ^{2,8}	925	9.3
Mercury	<0.00008	0.0014	0.0001	ANZ ^{2,9}	80	0.8
Nickel	0.0176	0.56	0.07	ANZ ^{2,5}	25	0.3
Vanadium	0.0025	-	0.1	ANZ ²	3	0.03
Zinc	0.38	0.043	0.015	ANZ ^{2,3}	2533	25

¹ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

² 95% marine trigger value.

³ Insufficient data to derive a reliable ANZ marine trigger value.

⁴ oNRP more restrictive than ANZ (no data for pNRP).

⁵ ANZ more restrictive than oNRP (no data for pNRP).

⁶ No value in oNRP.

 $^{\rm 7}$ Based on Cr(VI), the more toxic valency state for chromium.

⁸ Unknown level of protection.

⁹Inorganic mercury.

Nitrogen species

Nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N) and ammoniacal-nitrogen (NH₄-N) were measured in 2019 at wells outside or potentially outside of containment. Maximum concentrations were compared against applicable SWQGs (Table 54).

Analyte	Maximum GW concentration	GW Guideline	SWQG	SWQG Source	Maximum groundwater concentration as a percentage of SWQG	Risk Quotient ¹
Nitrate-nitrogen	13.9	6.9	0.01 - 0.06	oNRP	139,000	1,390
Nitrite-nitrogen	0.24	-	No value	-	NA	NA
NNN ²	14.14	-	<0.048	pNRP ²	29,458	295
Ammoniacal-nitrogen	0.88	7.3 (at pH 7)	0.005	oNRP	17,600	176
Ammoniacal-nitrogen	0.88	7.3 (at pH 7)	0.023	pNRP	3,826	38

Table 54. Nitrogen species concentrations (mg/L) in groundwater (wells outside or potentially outside of containment) 2019 and comparison with SWQG.

¹ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

 2 NNN = Nitrite-nitrate nitrogen. For the purposes of this assessment, maximum nitrate and nitrite concentrations were summed to give NNN.

The oNRP specifies a default coastal water quality standard concentration for NO_3 -N of 10–60 mg/m³ (0.01-0.06 mg/L). The pNRP has no coastal water quality standard for NO_3 -N, but specifies an annual median nitrite-nitrate nitrogen (NNN) coastal water quality standard concentration for estuaries of <0.048 mg/L (Table 54). These will be discussed separately.

The maximum NO₃-N groundwater concentration (13.9 mg/L) exceeded the <u>lowest</u> value (0.01 mg/L) of the range of oNRP coastal water quality standard concentrations by 1,390x. If the <u>highest</u> value (0.06 mg/L) of the range of oNRP coastal water quality standard concentrations is used, the exceedance (RQ) is 232x.

Maximum NO₂-N and NO₃-N concentrations were added (to give nitrite-nitrate nitrogen: NNN) (14.14 mg/L) and compared with the pNRP coastal water quality standard concentration (<0.048 mg/L), resulting in an exceedance (RQ) of 295x. NO₂-N is a minor component of oxidised nitrogen species, with the maximum concentration (0.24 mg/L) being only 0.2% of the maximum NO₃-N concentration (13.9 mg/L). Therefore, the pNRP SWQG for nitrite-nitrate nitrogen (NNN) (0.048 mg/L) is effectively for NO₃-N. This is also close to the high end of the oNRP SWQG range (0.06 mg/L).

The maximum ammoniacal-nitrogen (NH $_4$ -N) concentration (0.88 mg/L) was 176x the oNRP SWQG and 38x the pNRP SWQG, respectively.

<u>PFAS</u>

Following on from an initial characterisation of PFAS contamination in soil, sediment, surface water and groundwater by Refining NZ in June 2016, a second round of groundwater sampling was completed by Tonkin & Taylor in June 2019. Groundwater samples were collected from three monitoring wells in the vicinity of the fire training area and a surface water/stormwater sample was collected from the drain to the west of the fire training area.

In summary results of relevance to the marine receiving environment (Table 55) are:

- Total PFHxS has no relevant guidelines to assess against.
- Maximum total PFOS concentration (0.07 μ g/L) was below interim ANZECC 80% (31 μ g/L) and 95% (0.13 μ g/L) marine guidelines. The detection limit for total PFOS (0.01 μ g/L) was not sufficient to assess against the ANZECC 99% marine guideline (0.00023 μ g/L).
- Maximum PFOS + PFHxS concentration (0.22 μ g/L) was ca. 10x below the recreational water guideline.
- Total PFOA concentration was well below all relevant criteria.

Table 55. PFAS concentration in wells P8a, P8b and P8c - 2016 and 2019 of relevance to marine receiving environment (modified from Tonkin & Taylor Ltd, 2019).

Analyte	Range of concentrations reported (µg/L)	ANZECC 2000 Guideline – 80% marine (µg/L)	ANZECC 2000 Guideline – 95% marine (µg/L) ¹	ANZECC 2000 Guideline – 99% marine (µg/L) ²	Recreational water guideline - (µg/L) ³
Total PFHxS	<0.01 - 0.18	-	-	-	-
Total PFOS	<0.01 - 0.07	31	0.13	0.00023	-
PFOS + PFHxS	0.035 - <u>0.22</u>	-	-	-	<u>2</u>
PFOA	<0.1 - 0.56	1,824	220	19	10

¹ For groundwater, 95% adopted for bioaccumulation for a highly disturbed system (i.e. increase level of protection from 80% to 95%).

² For marine surface water receptor (slightly to moderately disturbed system), 99% recommended based on bioaccumulation.

³ Australian Government National Health and Medical Research Council, 2019. *Guidance on Per and Polyfluoroalkyl substances (PFAS) in Recreational Water).*

- no guideline value available

Bold – exceeds 99% protection level.

<u>Underlined</u> – exceeds adopted drinking water value.

5.2.2 Groundwater dilution in receiving environment

Groundwater outflow from the Refinery was estimated by Tonkin & Taylor to be 458,525 m³/year, or 1,256 m³/day (Table 56). If the Refinery is estimated to occupy 3 km of the coastline, then the outflow will be 419 m³/day/km of coastline, or 0.419 m³/day/m of coastline. In contrast, the average discharge from the stormwater basin in 2018 was 6369 m³/day. Therefore, groundwater discharge from the Refinery (when considered as a diffuse discharge over 3 km) is orders of magnitude below the surface water discharge (when considered as a point source discharge). Although tidal flushing has not been modelled at the open-ocean sites, it is expected to be large, leading to high dilution of groundwater discharges.

Table 56. Estimation of groundwater flow from the refinery.

Attribute	Value	Unit
Groundwater Outflow (from Table 8-4 (T&T))	458,525	m³/year
Groundwater Outflow	1,256	m³/day
Refinery coastline (approximately)	3	km
Groundwater Outflow	419	m³/day/km coastline
Groundwater Outflow	4.19	m³/day/10m coastline
Groundwater Outflow	0.419	m³/day/m coastline
Groundwater Outflow	0.0171	m³/hour/m coastline

Attribute	Value	Unit
SWB discharge (2018 average)	6369	m³/day

¹ For perspective, this corresponds to 17 L/hour/m coastline or 283 mL/min/m coastline.

5.2.3 November 2019 groundwater and surface water sampling

Refining NZ undertook groundwater and surface water sampling along the beach side of the Refinery (at the open-ocean sites) (Figure 28). Nine groundwater sites on the beach (coloured green in Figure 28) and nine surface water sites 3–4 m immediately adjacent on the ocean side were collected at the same time. These sites were close to the NRC open-ocean site 100629 (Bream Bay). Dissolved metals (arsenic, cadmium, chromium, copper, lead, nickel and zinc) and nitrogen species (total nitrogen, total ammoniacal-nitrogen, nitrite-N, nitrate-N+nitrite-N [NNN] and total Kjeldahl nitrogen [TKN]) were measured.



Figure 28. Location of groundwater beach sampling sites (green squares) in November 2019. Red boxes correspond to groundwater wells within the Refinery. Corresponding surface water sites were located 3-4m immediately adjacent towards the ocean.

Dissolved metal/metalloid concentrations in groundwater beach samples (Table 57) and surface water beach samples (Table 58) were below applicable SWQG, with one exception. Dissolved zinc in 6 out of the 9 groundwater beach samples exceeded the SWQG (0.015 mg/L) by a maximum of 4.4x (Table 57). However, surface water zinc concentrations 3–4 m immediately adjacent on the ocean side were all below the detection limit (0.004 mg/L) and less than 30% of the SWQG. Perimeter groundwater wells within the Refinery, sampled in September 2019, had dissolved chromium, copper and zinc concentrations at 1.05x, 20x and 25x applicable SWQG, respectively (Table 53). This suggests that groundwater is being rapidly diluted as it moves from within the Refinery to groundwater beach sites and further to surface water.

Since 2015, the NRC open-ocean site 100629 (Bream Bay) has only been measured in September 2015; all metal/metalloid concentrations (total not dissolved) were below applicable SWQG (Table 18).

Analyte (dissolved)	Range of recorded concentrations	Maximum GW concentration ¹	SWQG	SWQG Source ²	Risk Quotient ³
Arsenic	<0.004 - 0.013	0.013	0.05	oNRP	0.3
Cadmium	<0.0002 - 0.0014	0.0014	0.002	oNRP	0.7
Chromium	<0.001 - 0.0021	0.0021	0.0044	ANZ	0.5
Copper	<0.001 - 0.0012	0.0012	0.0013	ANZ	0.9
Lead	<0.001 - <0.001	0.001	0.0044	ANZ	0.2
Nickel	<0.007 - <0.007	0.007	0.07	ANZ	0.1
Zinc	<0.004 - 0.066	0.066	0.015	ANZ	4.4

Table 57. <u>Dissolved metal/metalloid</u> concentrations (mg/L) in <u>groundwater</u> beach sampling sites in November 2019 and comparison with SWQG.

¹Less than detection limit italicised.

² See Table 3.
³ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

Table 58. <u>Dissolved metal/metalloid</u> concentrations (mg/L) in <u>surface water</u> beach sampling sites in November 2019 and comparison with SWQG.

Analyte (dissolved)	Range of recorded concentrations	Maximum SW concentration ¹	SWQG	SWQG Source ²	Risk Quotient ³
Arsenic	<0.004	0.004	0.05	oNRP	0.1
Cadmium	<0.0002 - 0.0007	0.0007	0.002	oNRP	0.4
Chromium (VI)	<0.001	0.001	0.0044	ANZ	0.2
Chromium	<0.001 - 0.0014	0.0014	0.0044	ANZ	
Copper	<0.001	0.001	0.0013	ANZ	0.8
Lead	<0.001	0.001	0.0044	ANZ	0.2
Nickel	<0.007	0.007	0.07	ANZ	0.1
Zinc	<0.004	0.004	0.015	ANZ	0.3

¹Less than detection limit italicised.

² See Table 3.

³ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

Nitrogen species concentrations in groundwater beach samples and surface water beach samples are presented in Table 59 and Table 60, respectively.

Table 59. Nitrogen species concentrations (mg/L) in <u>groundwater</u> beach sampling sites in November 2019 and comparison with SWQG.

Analyte	Range of recorded concentrations	Maximum GW concentration	SWQG	SWQG Source ¹	Risk Quotient ²
Nitrate (as N)	<0.001 - 0.026	0.026	0.01 - 0.06	oNRP	2.6
Nitrate (as N)	<0.001 - 0.026	0.026		pNRP	
Nitrite (as N)	<0.001 - 0.0165	0.0165	No value		
NNN ³	<0.001 - 0.042	0.042	<0.048	pNRP	0.9
Ammonia (as N)	<0.005 - 0.63	0.63	0.005	oNRP	126
Ammonia (as N)	<0.005 - 0.63	0.63	0.023	pNRP	27

¹ See Table 3.

²Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

³NNN = Nitrite-nitrate nitrogen.

Table 60. Nitrogen species concentrations (mg/L) in <u>surface water</u> beach sampling sites in November 2019 and comparison with SWQG.

Analyte	Range of recorded concentrations	Maximum SW concentration ¹	SWQG	SWQG Source ²	Risk Quotient ³
Nitrate (as N)	<0.001 - 0.0012	0.0012	0.01 - 0.06	oNRP	0.1
Nitrate (as N)	<0.001 - 0.0012	0.0012		pNRP	
Nitrite (as N)	<0.001 - <0.001	0.001	No value		
NNN ⁴	<0.001 - 0.0018	0.0018	<0.048	pNRP	0.04
Ammonia (as N)	0.01 - 0.04	0.04	0.005	oNRP	8.0
Ammonia (as N)	0.01 - 0.04	0.04	0.023	pNRP	1.7

¹Less than detection limit italicised.

² See Table 3.

³ Dilution required in receiving environment to satisfy SWQG. Exceedances bolded.

⁴NNN = Nitrite-nitrate nitrogen.

The maximum nitrate-nitrogen (NO₃-N) groundwater beach concentration (0.026 mg/L) exceeded the <u>lowest</u> value (0.01 mg/L) of the range of oNRP coastal water quality standard concentrations by 2.6x, however maximum surface water NO₃-N concentrations were 10% of the same standard (Table 59). For context, the maximum groundwater NO₃-N concentration at perimeter wells of the Refinery was 1,390x this standard.

High NO_3 -N concentrations in groundwater are likely to be from a mixture of historic contamination (the Refinery is predominantly hard surface now) and current catchment leaching. However, the extent of historic and current contamination is unknown.

Nitrite-nitrate nitrogen (NNN) also followed the same trend of concentration reduction, with maximum risk quotient of 295, 0.9, and 0.04 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively.

Ammoniacal-nitrogen (NH_4 -N) followed the same trend of concentration reduction with maximum risk quotients (assessed against the oNRP value of 0.005 mg/L) of 176, 126, and 8 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively. When assessed against the pNRP value of 0.023 mg/L, the maximum risk quotient was 38, 27, and 1.7 for Refinery perimeter groundwater, beach groundwater and beach surface water sites, respectively. However, these water quality limits are designed to assess effects from eutrophication and are usually based on annual median data (as is the case for pNRP and NH_4 -N). Although based on a single monitoring event (and not annual data), median risk quotients were

calculated for NH_4 -N in beach groundwater and beach surface water sites. Risk quotients were 10.2 and 2.2, respectively, for beach groundwater and beach surface water sites when assessed against the oNRP, and 4.6 and 1.0, respectively, for beach groundwater and beach surface water sites when assessed against the pNRP.

Since 2014, the NRC open-ocean site 100629 (Bream Bay) has been measured annually, with NH_{4^-} N concentrations ranging from 0.003 – 0.017 mg/L (Table 17 and Table 18). These values are comparable with sites within Whangarei Harbour (Table 17 and Table 18), but all are below the pNRP SWQG (0.023 mg/L).

The results of the groundwater perimeter sampling at the Refinery, along with the single beach sampling event in November 2019, show a clear reduction in concentrations of all toxicants as groundwater migrates from the Refinery to beach groundwater and into nearby surface water. There are minor localised effects at the beach groundwater sites for NH_4 -N, however this is based on a single monitoring event and effects were less than minor at beach surface water sites (when assessed against the pNRP) and there is no evidence that effects are seen at the NRC water quality site at Bream Bay.

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7. Common acronyms used in this report

AEE Assessment of Environmental Effects ANZ Australian and New Zealand Guidelines for Fresh and Marine Water Quality ANZECC Australian and New Zealand Environment and Conservation Council AOC Accidentally Oil Contaminated System ARI Average Recurrence Interval BCF Biochemical Oxygen Demand (5-day) BTEX Benzene, Toluene, Ethylbenzene and Xylene CASRN Chemical Abstracts Service Registry Number CCME Canadian Council of Ministers of the Environment CTU Colony Forming Unit COC Continuously Oil Contaminated System COD Chemical Oxygen Demand CPB Coccamido Propyl Betaine CSQG Coastal Sediment Quality Guideline CWQG Groundwater Quality Standard D Dissociation Coefficient DGWBE Diethylene Glycol Mono Butyl Ether DGV Default Guideline Value DIFA Di-isopropanolamine DL Detection Limit DO Dissolved Oxygen DRP Dissolved Reactive Phosphorus EC50 <	Acronym	Meaning
ANZ Australian and New Zealand Guidelines for Fresh and Marine Water Quality ANZECC Australian and New Zealand Environment and Conservation Council AOC Accidentally Oil Contaminated System ARI Average Recurrence Interval BCF Bioaccumulation Concentration Factor BOD-5 Biochemical Oxygen Demand (5-day) BTEX Benzene, Toluene, Ethylbenzene and Xylene CASRN Chemical Abstracts Service Registry Number CCME Canadian Council of Ministers of the Environment CFU Colony Forming Unit COC Continuously Oil Contaminated System COD Chemical Oxygen Demand CPB Cocoamido Propyl Betaine CSQG Coastal Vater Quality Guideline CWQS Coastal Water Quality Guideline CWQG Coundwater Quality Guideline CWQS Coastal Water Quality Standard D Dissociation Coefficient DGV Default Guideline Value DIPA Di-isopropanolamine DL Detection Limit DO Dissolved Reactive Phosphorus ECS0 Effects Concentration (for 50% of test species) <		
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NIWA National Institute of Water and Atmospheric Research NNN Nitrite-nitrate nitrogen NO2-N Nitrite-nitrogen	NDA	Non-Disclosure Agreement
NNN Nitrite-nitrate nitrogen NO2-N Nitrite-nitrogen	NH4-N	Ammoniacal-nitrogen
NO2-N Nitrite-nitrogen	NIWA	National Institute of Water and Atmospheric Research
	NNN	Nitrite-nitrate nitrogen
NO3-N Nitrate-nitrogen	NO2-N	Nitrite-nitrogen
	NO3-N	Nitrate-nitrogen
NOEC No-Observable Effects Concentration	NOEC	No-Observable Effects Concentration

Acronym	Meaning
NRC	Northland Regional Council
oNRP	operative Regional Plan for Northland
Р	Partition Coefficient
РАН	Polycyclic Aromatic Hydrocarbon
PFAS	Polyfluoroalkyl Substances
PFHxS	Perfluorohexane sulfonate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PNEC	Predicted No-Effects Concentration
pNRP	proposed Regional Plan for Northland
PPT	Parts Per Thousand
RQ	Risk Quotient
RSKSE	Relative Seasonal Kendall Sen Slope Estimator
SDS	Safety Data Sheet
SEL	Streamlined Environmental Ltd
SGV	Sediment Quality Guideline Value
SKSE	Seasonal Kendall Sen Slope Estimator
SWB	Stormwater Storage Basin
SWQG	Surface Water Quality Guideline
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbon
TPI	Tilted Plate Interceptor
TSS	Total Suspended Solids
USEPA	Unites States Environmental Protection Agency

8. Appendices

g/m3

Total Suspended Solids

1/5/14

1/4/15

Appendix 1: Water and sediment quality temporal trend graphs

Refining NZ SWB discharge water quality temporal trend graphs



Sen slope trend for pH (Lab)



1/2/17

Date

Sen slope trend for Total Suspended Solids

1/3/16

g/m3

1/1/18

1/12/18















Sen slope trend for Copper Total g/m3 5 g/m3 . • 4 • 3 . . • . 2 -----. . Copper Total 1 0 1/2/15 1/12/15 1/10/16 1/8/17 1/6/18 Date







Sen slope trend for Zinc Total g/m3



Receiving environment water quality temporal trend graphs for temperature

24 • • 22 20 100265 18 • 16 . • . • 14 12 1/4/15 1/5/14 1/3/16 1/2/17 1/1/18 1/12/18 Date



Sen slope trend for 100265








Receiving environment sediment temporal trend graphs



 30°







Sen slope trend for Lead (mg/kg)













Sen slope trend for Lead (mg/kg)









Sen slope trend for Chromium (mg/kg)



Sen slope trend for Lead (mg/kg)









Appendix 2: Receiving environment sediment toxicants as a percentage of SQG





Appendix 3: Process chemical risk assessment spreadsheets

BetzDearborn AE1115P

		BetzDearborn AE1115P						
Use		Floc	culant					
Supplier	GE Betz (a part of Suez)							
Area		Biological Treatment, D.	AF, bug tank, clarification					
Use (kg/day)			4.6					
		Chemical Information						
Ingredient(s)	Formulation	Isoparaffins petroleum hydrotreated HFP	Betz1	Betz2	Betz3			
Composition (%)	i of multion	22.400	30.000	0.040	0.700			
CAS #	_	64742-47-8	Restricted under NDA	Restricted under NDA	Restricted under NDA			
		Synonyms: ICP solvent, Hydrotreated light distillate						
Chemical formula/ structure		(petroleum). ICP solvent is equivalent to classical kerosene or xylene	Restricted under NDA	Restricted under NDA	Restricted under NDA			
Molecular weight		ca. 100	Restricted under NDA	Restricted under NDA	Restricted under NDA			
Ŭ		Physical and Chemical Properties						
Form	Liquid	,						
Water solubility	Miscible							
pH (as supplied)	7							
LogP ¹	Not available	3.14	-0.05	-0.78	Inorganic			
Log D (pH 5.5, pH 7.4) ¹	Not available	3.25	,-0.40,-2.20	-0.67	Inorganic			
	Not available	173.90	1.00					
BCF (pH 5.5, pH 7.4) ¹	Not available		1.00	1.00	Inorganic			
		Ecological Information						
		Chemwatch SDS						
Persistence (Water/Soil)	No data available for all ingredients	No data available for all ingredients						
Biodegradability	No data available for all ingredients	No data available for all ingredients						
Bioccumulation Potential	_	Low (BCF = 159)						
Aquatic Species (mg/L)								
		Chemwatch SDS						
Fish - 96h/LC ₅₀	Not available	>1; 4.1; 0.14						
Fish - 96h/NOEC	Not available	1						
Crustacea - 48h/EC ₅₀	Not available	>1; 4.5						
Crustacea - 720h/NOEC	Not available	0.024						
Algae - 96h/EC ₅₀	Not available	0.277						
Algae - 72h/EC ₅₀	Not available	>1						
		Sigma SDS						
Toxicity to fish		2.9	Not available	90	240			
Toxicity to daphnia and other aquatic invertebrates		1.4	Not available	160	102			
Toxicity to algae		No data						
		USEPA ECOTOX Database						
		No marine species data	93-218 (Water flea; 2 days)	Not checked as not toxic	Not checked as not toxic			
		See https://echa.europa.eu/registration-dossier/- /registered-dossier/15375/6/2/1 for other						
		ecotoxicological data						
		ECHA PNEC						
PNEC (Marine)		0.0048	No data	0.002	0.11			
Assessment Factor		50		1000	100			

Cortrol OS7780

	· · · · · · · · · · · · · · · · · · ·		С	ortrol OS7780					
Use				Water based disso	olved oxygen scavenger / metal passiva	tor			
Supplier		GE Betz (a part of Suez)							
Area					Western AOC Trench				
Use (kg/day)					13.7				
			Che	mical Information					
Ingredient(s)	Formulation	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 under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	
Chemical formula/ structure		OH	o o o	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	
Molecular weight		110.11	108.09	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA	
			Physical a	and Chemical Proper	ties				
Form	Liquid			-					
Water solubility	Miscible								
pH (as supplied)	7.5								
LogP ¹	Not available	0.64	0.26	No data	1.77	0.74	-0.16	Inorganic	
Log D (pH 5.5, pH 7.4) ¹	Not available	0.53	0.13	No data	1.41	,-2.49,-1.73	0.29	Inorganic	
BCF (pH 5.5, pH 7.4) ¹	Not available	1.48	1.00	No data	6.96/6.95	1.00	1.00	Inorganic	
			Ecol	ogical Information Chemwatch SDS					
Persistence (Water/Soil)		Low						Low	
Biodegradability									
Bioccumulation Potential		Low (BCF = 65)						LOW (LogKOW = -1.38)	
Aquatic Species (mg/L)				Chemwatch SDS				mg/L	
Fish - 96h/LC ₅₀		0.044							
Crustacea - 48h/EC ₅₀		0.061							
Algae - 96h/EC ₅₀		0.008							
Algae - 72h/BCF		0.05							
Algae - 72h/NOEC	-	0.002							
				Sigma SDS					
Toxicity to fish		0.04 - 0.1	0.04-0.125	5000	0.8	1780	31	45.4-125	
Toxicity to daphnia and other aquatic invertebrates		0.13	1-3.5	>100	4.4	165	57	40.4	
Toxicity to algae		0.335	0.080	>100		44	>100		
				EPA ECOTOX Database					
		0.35 (sw, fish, LC50)	0.22 (sw, diatom, pop changes)	Not checked as not toxic ECHA PNEC	0.062 (Pacific Oyster embryo LC50)	80 (fw fish)	22.4 (sw juvenile shrimp)		
PNEC (Marine)		0.000057	0.000086	0.01	0.000403	0.006230	No data	No data	
Assessment Factor		100	1,000	10,000	100	10,000			
			Oxidation of hydroquinone during process to 1,4- benzoquinone						

Cortrol OS5614

Cort	rol OS5614 (alterna	tive to OS7780)					
Use	Water	Water based dissolved oxygen scavenger / metal passivator					
Supplier		GE Betz (a part of Suez)					
Area		Western AOC Trench					
Use (kg/day)		13.7					
	Chemical Inform	nation					
Ingredient(s)	Formulation	Formulation Cort6 Co					
Composition (%)		11.9699	0.006				
CAS #		Restricted under NDA	Restricted under NDA				
Chemical formula/ structure		Restricted under NDA	Restricted under NDA				
Molecular weight		Restricted under NDA	Restricted under NDA				
	Physical and Chemical	l Properties					
Form	Liquid	1					
Water solubility	Miscible						
pH (as supplied)	9						
LogP ¹	Not available						
Log D (pH 5.5, pH 7.4) ¹	Not available						
BCF (pH 5.5, pH 7.4) ¹	Not available						
	Ecological Inform	nation					
	Suez SDS						
Persistence (Water/Soil)	Not available						
Biodegradability	Not available						
Bioccumulation Potential	Not available						
Aquatic Species (mg/L)							
	Suez SDS						
Fish - 96h/LC ₅₀	140						
Daphnia - 48h/NOEL	460						
	USEPA ECOTOX Dat	abase					
	ECHA PNEC						
PNEC (Marine)		0.00015					
Assessment Factor		10000					
		Decomposes to ammonia (NH4-N),					
	n	itrogen (N2), and carbon dioxide (CO2)					
		above 200 °C					

Embreak 2021

				1	Embreak 2021				
se					Cun 2521	Emulsion breaker			
pplier	Emussion or reacter GE Betz (a part of Suez)								
rea					n	eoiled water from TPIs/Process	Water		
se (kg/day)					b	128.7	water		
se (kg/ uay)				Cha	emical Information				
њ. ()									
ngredient(s)	Formulation	Emb1	Emb2	Nonylphenol (technical)	Naphthalene	Emb3	Emb4	Emb5	Solvent Naphtha, Petroleum, Heavy Aromatic
omposition (%)		0.0045	0.0405	1.1750	6.6650	5.9050	0.4050	0.1152	31.6823
AS #		Restricted under NDA	Restricted under NDA	84852-15-3	91-20-3	Restricted under NDA	Restricted under NDA	Restricted under NDA	64742-94-5
hemical formula/ structure		Restricted under NDA	Restricted under NDA	C ₉ H ₁₉ OH	Petroleum distallate	Restricted under NDA	Restricted under NDA	Restricted under NDA	Petroleum distallate
Aolecular weight		Restricted under NDA	Restricted under NDA	221.36		Restricted under NDA	Restricted under NDA	Restricted under NDA	
				Physical	and Chemical Pr	operties			
orm	Liquid			,		r · · · ·			
ater solubility	Miscible								
H (as supplied)	Not available								
ogp ¹	Not available			5.82				Not available	
og D (pH 5.5, pH 7.4) ¹	Not available	Petroleun	ı distallate	5.43	Petroleum distallate	Petroleum distallate	Petroleum distallate	Not available	Petroleum distallate
	Not available			>7800				Not available	
3CF (pH 5.5, pH 7.4) ¹	Not available							Not available	
				Ecol	logical Informati Chemwatch SDS	on			
ersistence (Water/Soil)				High					
iodegradability				0					
ioccumulation Potential				Low (BCF = 271)					
Aquatic Species (mg/L)									
					Chemwatch SDS				
ish - 96h/LC ₅₀				0.028	0.213				0.58
ish - 96h/EC ₂₀				0.075					
ish - 504h/BCF				0.081	10.2				
ish - 48h/NOEC					0.0001				
rustacea - 48h/EC ₅₀				0.104	1.6				0.76
rustacea - 96h/NOEC				0.001					
lgae - 96h/EC ₅₀				0.027					
lgae - 72h/EC ₅₀					ca.0.4				<1
lgae - 72h/NOEC									
lgae - 96h/NOEC									0.12
g,					Sigma SDS				
oxicity to fish				0.209				1.0	
oxicity to daphnia and other aquatic invertebrates				0.0844				12.2	
oxicity to algae				0.33				8 (NOEC)	
· · · · · · · · · · · · · · · · · · ·					ater Quality Guideline	· · · · · · · · · · · · · · · · · · ·		- ()	
				0.00033 (EU WFD)					
				0.001 (ANZECC)					
					EPA ECOTOX Databas	e			
		Not checked as petroleum distallate	Not checked as petroleum distallate	0.017 (sw, flounder larva, LC50)	Not checked as petroleum distallate	Not checked as petroleum distallate	Not checked as petroleum distallate	0.15 (sw, copepod egg, development)	No data
			<u> </u>		ECHA PNEC				
PNEC (Marine)		Not checked as petroleum distallate	Not checked as petroleum distallate	0.001	Not checked as petroleum distallate	Not checked as petroleum distallate	Not checked as petroleum distallate	0.001	Not checked as petroleum distallate

		Embreak	2021		· · · · · · · · · · · · · · · · · · ·	
		Emulsion bro				
		GE Betz (a part				
		Deoiled water from TPI				
		128.7				
		Chemical Info	ormation			
Ingredient(s)	Emb6	Light Aromatic Naphtha	Emb7	Emb8	Emb9	Emb10
Composition (%)	40.4700	4.8600	0.2350	3.1500	0.6750	4.4775
CAS #	Restricted under NDA	64742-95-6	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA
Chemical formula/ structure	Restricted under NDA	Petroleum distallate	Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA
Molecular weight	Restricted under NDA		Restricted under NDA	Restricted under NDA	Restricted under NDA	Restricted under NDA
		Physical and Chemi	ical Properties			
Form			-			
Water solubility						
pH (as supplied)						
LogP ¹	5.82		Not available			0.00
Log D (pH 5.5, pH 7.4) ¹	5.43	Petroleum distallate	Not available	Petroleum distallate	Petroleum distallate	0.82
BCF (pH 5.5, pH 7.4) ¹	>7800		Not available			2.49
		Ecological Infe	ormation			
		Chemwatch				
Persistence (Water/Soil)						
Biodegradability						
Bioccumulation Potential						
Aquatic Species (mg/L)						
1 1 0 0		Chemwatch	1 SDS			
Fish - 96h/LC ₅₀		4.1				
Fish - 96h/EC ₂₀						
Fish - 504h/BCF						
Fish - 48h/NOEC						
Crustacea - 48h/EC ₅₀		3.2				
Crustacea - 96h/NOEC						
Algae - 96h/EC ₅₀						
Algae - 72h/EC ₅₀		>1				
Algae - 72h/NOEC		1				
Algae - 96h/NOEC			25			
Torrisity to fish		Sigma SI	15			>10,000
Toxicity to fish Toxicity to daphnia and other aquatic invertebrates						>10,000
Toxicity to daphnia and other aquatic invertebrates						
,		Water Quality 0	Guideline			
		USEPA ECOTOX	Database			
		Not checked as petroleum distallate	0.15 (sw, copepod egg, development)	Not checked as petroleum distallat	Not checked as petroleum distallate	12.5 (sw, algae, mortality)
		ECHA PN	EC			
PNEC (Marine)		Not checked as petroleum distallate	See NP ethoxylate	Not checked as petroleum distallate	Not checked as petroleum distallate	No ecotox data
Assessment Factor						

Klaraid IC1172

Kla	raid IC1172					
Use	Water treatmen	t additive				
Supplier	GE Betz (a part of Suez)					
Area	Biological treatment, DAF, B					
Use (kg/day)	156.7	-				
	cal Information					
Ingredient(s)	Formulation	Aluminium Chlorohydrate				
Composition (%)		40.0000				
CAS #		12042-91-0				
Chemical formula/ structure						
Molecular weight		210.48				
Physical and	l Chemical Properties					
Form	Liquid					
Water solubility	Miscible					
pH (as supplied)	3.7					
LogP ¹	Not available	Inorganic				
Log D (pH 5.5, pH 7.4) ¹	Not available	Inorganic				
BCF (pH 5.5, pH 7.4) ¹	Not available	Inorganic				
Ecologi	ical Information					
	nemwatch SDS					
Persistence (Water/Soil)	No data available for all ingredients					
Biodegradability	No data available for all ingredients	Not biodegradable				
Bioccumulation Potential	No data available for all ingredients					
Aquatic Species (mg/L)						
cł	nemwatch SDS					
Fish - 96h/LC ₅₀		1				
Fish - 1440h/NOEC		0.013				
Crustacea - 48h/EC ₅₀		0.33				
Algae - 72h/EC ₅₀		0.075				
GEO Spec	ciality Chemicals SDS					
Toxicity to fish	265.5-776.4	100-500				
Toxicity to daphnia and other aquatic invertebrates	33.2-803.8					
Toxicity to algae	No information available					
Water Quality Guideline (ANZ	ECC, low reliability marine trigger val					
		0.0005				
USEPA	ECOTOX Database					
		0.8 (sw, lc50, shrimp embryo)				
	ECHA PNEC	Nr. doction (or				
PNEC (Marine)		No classification (see note)				
Assessment Factor						

Spectrus NX1100

		Spe	ctrus NX1100				
Use		1		Biocide			
Supplier	1			GE Betz (a part of Suez)			
Area				Deoiled water from TPIs			
Use (kg/day)				0.2			
		Chem	ical Information				
Ingredient(s)	Formulation	Bronopol	Magnesium nitrate	Isothiazolinones, mixed (Kathron 886)	Magnesium chloride	Spec1	Spec2
Composition (%)		5.5440	3.6800	2.5760	1.6560	0.9800	0.1903
CAS #		52-51-7	13446-18-9	55965-84-9	7786-30-3	Restricted under NDA	Restricted under NDA
Chemical formula/ structure			MgNO ₃	See 2 compounds to the right	MgCl ₂	Restricted under NDA	Restricted under NDA
Molecular weight		200.0	148.3		95.2	Restricted under NDA	Restricted under NDA
Ŭ			d Chemical Prop	erties			
Form	Liquid						
Water solubility	Miscible	280 g/l at 23 °C					
pH (as supplied)	3.0						
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
			gical Information				
			Chemwatch SDS	1			
Persistence (Water/Soil)							
Biodegradability		50 % - Partially biodegradable					
Bioccumulation Potential		Due to the distribution coefficient n-octanol/water, accumulation in organisms is not expected					
Aquatic Species (mg/L)							
		(Chemwatch SDS				
Fish - 96h/LC ₅₀		20	1-378	0.129	2-119.3		
Fish - 720h/NOEC			58				
Crustacea - 48h/EC ₅₀		0.78	490	0.007	140		
Crustacea - 48h/NOEC					1-479		
Algae - 72h/EC ₅₀		0.25		0.0063	>100		
Algae - 72h/NOEC		0.08					
Algae - 48h/NOEC			01 0F 0				
m 1 1 4 C 1		ac 2 44 a	Sigma SDS			10	2020
Toxicity to fish Toxicity to daphnia and other aquatic invertebrates		35.7-41.2 1.4-1.6	No data available No data available		2119 548	42	2820 344
Toxicity to daphnia and other aquatic invertebrates		0.37	No data available		>100	29	2700
Toxicity to algae		0.3/	ino uata avaliable		>900		2700
		DOW Aus	tralia SDS (Kathron 88	36)			
Acute toxicity to fish							
Acute toxicity to aquatic invertebrates							
Chronic toxicity to aquatic invertebrates							
Acute toxicity to algae/aquatic plants							
Toxicity to bacteria							
				PBT assessment			
			A ECOTOX Database				
		0.18 (sw, EC50, diatom)	FOUL DUEC		Not checked as not toxic	36 (sw, fish, LC50)	Not checked as not toxic
		A 677	ECHA PNEC	0.000			
PNEC (Marine)		0.001		0.003			
Assessment Factor		100		10			

Inhibitor AZ8104

		Inhibitor A	Z8104						
Use		Internal boiler treatment							
Supplier		GE Betz (a part of Suez)							
Area		Deoiled water from TPIs							
Use (kg/day)				5.5					
		Chemical Info	rmation						
Ingredient(s)	Formulation	Chlorotolyltriazole sodium salt	AZ1	Sodium Tolyltriazole	Sodium Hydroxide	AZ2			
Composition (%)	101111111111	13.1000	3.2500	1.4000	1.1400	5.8000			
CAS #		202420-04-0	Restricted under NDA	64665-57-2	1310-73-2	Restricted under NDA			
Chemical formula/ structure		CI N=N Na*	Restricted under NDA	Na*	NaOH	Restricted under NDA			
Molecular weight		215.61	Restricted under NDA	181.17	40.00	Restricted under NDA			
		Physical and Chemi	ical Properties						
Form	Liquid		_						
Water solubility	Miscible								
pH (as supplied)	12.7								
$LogP^1$	Not available	Not available	Not available	1.78	Inorganic	Inorganic			
Log D (pH 5.5, pH 7.4) ¹	Not available	Not available	Not available	1.78	Inorganic	Inorganic			
BCF (pH 5.5, pH 7.4) ¹	Not available	Not available	Not available	Not available	Inorganic	Inorganic			
		Ecological Inf Chemwatch							
Persistence (Water/Soil)	_								
Biodegradability	_								
Bioccumulation Potential									
Aquatic Species (mg/L)									
		Chemwatch	SDS						
Fish - 96h/LC ₅₀		20.6		55	125				
Fish - 96h/NOEC					56				
Crustacea - 48h/EC ₅₀		32.3		8.6	40.4				
Crustacea - 504h/NOEC		<1.1							
Crustacea - 504h/EC ₁₀				0.4					
Algae - 72h/EC ₅₀		6.8							
Algae - 72h/NOEC				10.0					
Algae - 96h/EC ₅₀					3180000				
		Sigma Sl							
Toxicity to fish		Not available	Not available	Not available					
Toxicity to daphnia and other aquatic invertebrates		Not available	Not available	Not available					
Toxicity to algae		Not available	Not available	Not available					
		USEPA ECOTOX							
		No data	Not applicable	No data	Not checked as low toxicity				
		ECHA PN	EL	0.008					
PNEC (Marine)		Data not provided by registrant		0.008					
Assessment Factor				50					

Embreak2050

			Embreak 2050						
Use		Emulsion breaker							
Supplier		GE Betz (a part of Suez)							
Area	Process Water ex desalters								
Use (kg/day)				5.2					
		Che	emical Information						
Ingredient(s)	Formulation	Emb11	Emb12	Diethylene Glycol Monobutyl Ether	Emb13				
Composition (%)		0.0250	0.0150	4.9500	32.0000				
CAS #		Restricted under NDA	Restricted under NDA	112-34-5	Restricted under NDA				
Chemical formula/ structure		Restricted under NDA	Restricted under NDA	CH ₃ CH ₂ CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OH	Restricted under NDA				
Molecular weight		Restricted under NDA	Restricted under NDA	162.23	Restricted under NDA				
		Physical	and Chemical Properties						
Form	Liquid								
Water solubility	Miscible								
pH (as supplied)	Not available								
LogP ¹	Not available	-1.51	0.80	0.44	No data				
Log D (pH 5.5, pH 7.4) ¹	Not available	-1.09	0.77	0.55	No data				
BCF (pH 5.5, pH 7.4) ¹	Not available	1.00	2.28	1.53	No data				
		Eco	logical Information						
			Chemwatch SDS						
Persistence (Water/Soil)				Low					
Biodegradability				Readily biodegradable					
Bioccumulation Potential				Low (BCF = 0.46)					
Aquatic Species (mg/L)									
			Chemwatch SDS						
Fish - 96h/LC ₅₀				1-300					
Crustacea - 48h/EC ₅₀				4-950					
Algae - 72h/EC ₅₀				1-101					
Algae - 96h/NOEC				>=100					
			Sigma SDS						
Toxicity to fish		>32,000	1,474	1300	10,000				
Toxicity to daphnia and other aquatic invertebrates		>10,000	1,550	>100					
Toxicity to algae		2,700	1,840	100					
Toxicity to bacteria		1,995		1170					
			SEPA ECOTOX Database						
		Not checked as non-toxic	Not checked as non-toxic	2,000 (sw, fish, LC50)	Not checked as non-toxic				
			ECHA PNEC						
PNEC (Marine)		1	0.88	0.11	No ecotox data				
Assessment Factor		100	100	10,000					

Steammate NA0808

	St	teammate NA08	08					
Use		Blend of neutralising amines						
Supplier		GE Betz (a part of Suez)						
Area		Western AOC Trench						
Use (kg/day)			16.1					
	C	hemical Information	on					
Ingredient(s)	Formulation	SM1	Monoethanolamine	3-dimethylaminopropylamine				
Composition (%)	1 01 11010101	0.2000	39.6000	19.9000				
CAS #	-	Restricted under NDA	141-43-5	109-55-7				
Chemical formula/ structure		Restricted under NDA	HO NH2	H ₃ C _N H ₃ C _N H ₂ H ₂				
Molecular weight	_	Restricted under NDA	61.1	102.2				
	Physics	and Chemical Pro		10212				
Form	Liquid		operties					
Water solubility	Miscible							
pH (as supplied)	12.7							
LogP ¹	12.7	-1.50	-1.31	-0.29				
	_							
Log D (pH 5.5, pH 7.4) ¹	_	,-4.13,-2.71	,-4.19,-3.41	,-4.31,-3.47				
BCF (pH 5.5, pH 7.4) ¹		1.00	1.00	1.00				
	Ec	cological Informati Chemwatch SDS	on					
Persistence (Water/Soil)			LOW	HIGH				
Biodegradability			Readily biodegradable (>70%, 28d)	Readily biodegradable (60-70%, ?d)				
Bioccumulation Potential			LOW (LogKOW = -1.31)	LOW (LogKOW = -0.4502)				
Aquatic Species (mg/L)								
		Chemwatch SDS						
Fish - 96h/LC ₅₀			2-70	100				
Crustacea - 48h/EC ₅₀			32.6	59.46				
Crustacea - 528h/NOEC				3.64				
Crustacea - 504h/NOEC			0.85					
Crustacea - 528h/EC ₁₀				5.65				
Algae - 72h/EC ₅₀			2.1					
		Sigma SDS						
Toxicity to fish		540	349	122				
Toxicity to daphnia and other aquatic invertebrates		55	65	59.46				
Toxicity to algae			2.8	56.2				
Toxicity to bacteria			110	No data				
		USEPA ECOTOX Databas						
		103 (sw, diatom, EC50)	>100 (sw, shrimp, LC50)	No data				
		ECHA PNEC						
PNEC (Marine)		0.002	0.009	0.007				
Assessment Factor		500	100	500				

Genguard GN8220

				Gei	nguard GN8220				
Use						oiler treatment			
Supplier	GE Betz (a part of Suez)								
Area						ater from TPIs			
Use (kg/day)						6.03			
ove (Ng/ aug)				Cher	nical Information				
Ingredient(s)	Formulation	Gen1	Maleic acid	Gen2	Phosphoric acid	Gen3	Gen4	Gen5	Gen6
Composition (%)	rormulation	9,3000	0.2790	0.1215	3.8983	0.2059	0.4325	5,4643	<0.1%
CAS #		Restricted under NDA	110-16-7	Restricted under NDA	7664-38-2	Restricted under NDA	Restricted under NDA	Restricted under NDA	Ingredients making up <0.1% of formulation
CA3 #		Restricted under NDA	110-10-7	Restricted under NDA	7004-38-2	Restricted under NDA	Restricted under NDA	Restricted under NDA	ingredients making up <0.1% of formulation
Chemical formula/ structure		Restricted under NDA	ощон орнорон	Restricted under NDA	H_3PO_4	Restricted under NDA	Restricted under NDA	Restricted under NDA	Ingredients making up <0.1% of formulation
Molecular weight		Restricted under NDA	116.1	Restricted under NDA	98.0	Restricted under NDA	Restricted under NDA	Restricted under NDA	Ingredients making up <0.1% of formulation
worken weight		Restricted under NDA	110.1		nd Chemical Properties	Restricted under NDA	Restricted under NDA	Reserved under NDA	ingreatents making up 40.1% of formulation
P	r taut d			r nysicai a	nu chemicai rioperties				
Form Water solubility	Liquid Miscible								
	2.1								
pH (as supplied)		N. 1.4							
LogP ¹	Not available	No data	-0.01	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
Log D (pH 5.5, pH 7.4) ¹	Not available	No data	,-3.42,-4.73	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
BCF (pH 5.5, pH 7.4) ¹	Not available	No data	1.00	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
					ogical Information				
Persistence (Water/Soil)									
Biodegradability			Readily biodegradable	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
Bioccumulation Potential			,	Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
Aquatic Species (mg/L)				Inorganic	Inorganic	Inorganic	Inorganic	Inorganic	
inquarie opecies (ing, 2)					Chemwatch SDS	0			
Fish - 96h/LC ₅₀			5		75				
Crustacea - 48h/EC ₅₀			5-600		>5.62				
Algae - 72h/EC ₅₀			17.2		15.3				
Algae - 72h/EC ₁₀					37.7				
Algae - 72h/NOEC			10		3.7				
Algae - 24h/BCF			0.05						
			0.05		Sigma SDS				
Toxicity to fish		>100	75	2,400	No data	No data	120	No data	
Toxicity to daphnia and other aquatic invertebrates		>1000	42.8	-,	No data	No data	2,564	No data	
Toxicity to algae			74.4		No data	No data	-,	No data	
				USE	PA ECOTOX Database				
		No data	3,48 (fw. nematode, LC50)		15-150 (sw, oyster larvae, mortality)	No data	Not checked as non-toxic	92 (fw, zebra mussel, LC50)	
			,,,,,		ECHA PNEC		in the second se	(,	
PNEC (Marine)		No ecotox data	0.01	0.005	No hazard identified	No data: aquatic toxicity unlikely	1.11	No hazard identified	
Assessment Factor			1000	20,000			1000		

GE Spectrus BD1501E

		GE Spectrus BD1501E							
Use		•	Biodispersant						
Supplier		GE Betz (a part of Suez)							
Area			Deoiled water from TPIs						
Use (kg/day)			0.05						
		Chemical Information							
Ingredient(s)	Formulation	Alcohols, C10, alkoxylated	GE1	GE2					
Composition (%)		14.0000	13.8873	<0.1%					
CAS #		166736-08-9	Restricted under NDA	Ingredients making up <0.1% of formulation					
Chemical formula/ structure		Polymerisation of isodecanol with propylene oxide. Will likely give a range of related polymers. CAS# search produced NZ EPA hit for Oxirane, 2-methyl-, polymer with oxirane, mono(2-propylheptyl) ether, which maybe used as a single component chemical under appropriate group standard	Restricted under NDA	Ingredients making up <0.1% of formulation					
Molecular weight		>1100	Restricted under NDA	Ingredients making up <0.1% of formulation					
		Physical and Chemical Prope	rties	с с.					
Form	Liquid	,							
Water solubility	Miscible								
pH (as supplied)	6.7								
LogP ¹	Not available	No data	No data						
Log D (pH 5.5, pH 7.4) ¹	Not available	No data	No data						
BCF (pH 5.5, pH 7.4) ¹	Not available	No data	No data						
ber (pii 5.5, pii 7.4)	riot uvulluoie	Ecological Information	no unu						
		Chemwatch SDS							
Persistence (Water/Soil)	Not available	No data							
Biodegradability	Not available	60-90%							
Bioccumulation Potential	Not available	No data							
Aquatic Species (mg/L)	iter uvullete								
inquatic species (ing/ E)		Chemwatch SDS							
Toxicity to any species		Not							
		Sigma SDS							
Toxicity to fish			>10,000						
		Valagro Erger SDS							
Toxicity to fish (Brachydanio rerio) - 96h LC_{50}		10-100							
Toxicity to invertebrates (Daphnia magna) - 48h EC ₅₀		10-100							
Toxicity to plants (Scenedesmus subspicatus) - 72h EC ₅₀		10-100							
		BETZDEARBORN IEC5E SDSs (incl. 0.1-19	6 NaOH)						
Toxicity to fish (fathead minnow) - LC_{50}		114.9							
Toxicity to fish (rainbow trout) - LC ₅₀		141.4							
Toxicity to crustacea (Daphnia magna) - LC ₅₀		162.5							
		USEPA ECOTOX Database							
		No ecotox data	12.5 (sw, algae, mortality)						
		ECHA PNEC							
PNEC (Marine)		No ecotox data	0.00125						
Assessment Factor			10,000						

Optisperse ADJ5150

Use Ingredient(s) Area Ingredient(s) Composition (%) Formul CAS # Chemical formula/ structure Molecular weight Pl Form Liqu Water solubility Comp pH (as supplied) 14. LogP ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava BCF (pH 5.5, pH 7.4) ¹ Not ava	25.0000 1310-73-2 NaOH 40.00 hysical and Chemica aid	ADJ1 0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	ADJ2 <0.1 Ingredients making up <0.1% of formulation Ingredients making up <0.1% of formulation
Area Ingredient(s) Use (kg/day) Formula Ingredient(s) Formula Composition (%) Implementation CAS # Implementation Chemical formula/ structure Implementation Molecular weight Implementation Form Liqu Water solubility Comp pH (as supplied) 14. Log P ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	lation Sodium Hydr 25.0000 1310-73-2 NaOH 40.00 hysical and Chemica	GE Betz (a part of Suez Western AOC Trench 0.05 nation oxide ADJ1 0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	ADJ2 <0.1 Ingredients making up <0.1% of formulation
Use (kg/day) Use (kg/day) Ingredient(s) Composition (%) CAS # Chemical formula/ structure Molecular weight Form Use Solubility PH (as supplied) Liqu Comp PH (as supplied) 14. Log D ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	lation Sodium Hydr 25.0000 1310-73-2 NaOH 40.00 hysical and Chemica	0.05 nation oxide ADJ1 0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	<0.1 Ingredients making up <0.1% of formulation
Ingredient(s) Formula Composition (%) Formula/structure CAS # PI Chemical formula/structure Itique Molecular weight PI Form Lique Water solubility Comp pH (as supplied) 14. Logp ¹ Not avaa Log D (pH 5.5, pH 7.4) ¹ Not avaa	lation Sodium Hydr 25.0000 1310-73-2 NaOH 40.00 hysical and Chemica	Anation poxide ADJ1 0.5000 0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	<0.1 Ingredients making up <0.1% of formulation
Composition (%) CAS # Chemical formula/ structure Molecular weight Form Explanation Water solubility pH (as supplied) LogP ¹ Log D (pH 5.5, pH 7.4) ¹	lation Sodium Hydr 25.0000 1310-73-2 NaOH 40.00 hysical and Chemica	ADJ1 0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	<0.1 Ingredients making up <0.1% of formulation
Composition (%) CAS # Chemical formula/ structure Molecular weight Form Explanation Water solubility pH (as supplied) LogP ¹ Log D (pH 5.5, pH 7.4) ¹	25.0000 1310-73-2 NaOH 40.00 hysical and Chemica aid	0.5000 2 Restricted under NDA Restricted under NDA Restricted under NDA	<0.1 Ingredients making up <0.1% of formulation
CAS # Chemical formula/ structure Molecular weight Form Liqu Water solubility pH (as supplied) Log P ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	1310-73-2 NaOH 40.00 hysical and Chemica aid	2 Restricted under NDA Restricted under NDA Restricted under NDA	Ingredients making up <0.1% of formulation
Chemical formula/ structure Pl Molecular weight Pl Form Liqu Water solubility Comp pH (as supplied) 14. LogP ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	NaOH 40.00 hysical and Chemica	Restricted under NDA Restricted under NDA	
Molecular weight Pl Form Liqu Water solubility Comp pH (as supplied) 14. Log P ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	40.00 hysical and Chemica uid	Restricted under NDA	Ingredients making up <0.1% of formulation
Form Liqu Water solubility Comp pH (as supplied) 14. Log P ¹ Not ava Log D (pH 5.5, pH 7.4) ¹ Not ava	hysical and Chemica		
FormLiquWater solubilityComppH (as supplied)14.LogP1Not avaLog D (pH 5.5, pH 7.4)1Not ava	uid	al Properties	Ingredients making up <0.1% of formulation
FormLiquWater solubilityComppH (as supplied)14.LogP1Not avaLog D (pH 5.5, pH 7.4)1Not ava	uid	in roperties	
Water solubility Composition pH (as supplied) 14. Log P ¹ Not available Log D (pH 5.5, pH 7.4) ¹ Not available			
Log P1Not availableLog D (pH 5.5, pH 7.4)1Not available			
Log D (pH 5.5, pH 7.4) ¹ Not ava	.0		
	ailable Inorganio	r Inorganic salt	
BCF $(pH 5.5, pH 7.4)^1$ Not ava	ailable Inorganio	Inorganic salt	
100 (pr. 5,5) pr. / 11/	ailable Inorganio	r Inorganic salt	
	Ecological Infor Chemwatch SI		
Persistence (Water/Soil)	Low		
Biodegradability			
Bioccumulation Potential	LOW (LogKOW	= -1.38)	
Aquatic Species (mg/L)	mg/L		
	Chemwatch SI	DS	
Fish - 96h/LC ₅₀	125		
Fish - 96h/NOEC	56		
Crustacea - 48h/EC ₅₀	40.4		
Algae - 96h/EC ₅₀	3180000		
	Sigma SDS		
Toxicity to fish	45.4-125		
Toxicity to daphnia and other aquatic invertebrates	40.4		
Toxicity to algae		(1	
	USEPA ECOTOX Da		
	196 (sw, fish, ECHA PNEC	LC50)	
PNEC (Marine)	0.004		
Assessment Factor	0.004		

Optisperse HP2650

	•	Optisperse HP2650	·									
Use			nternal boiler treatment									
Supplier			GE Betz (a part of Suez)									
Area			Western AOC Trench									
Use (kg/day)			2.3									
		Chemical Information										
Ingredient(s)	Formulation	Sodium Hydroxide	HP1	HP2								
Composition (%)		3.0000	5.0000	0.0685 (total)								
CAS #		1310-73-2	Restricted under NDA	Ingredients making up <0.1% of formulation								
Chemical formula/ structure		NaOH	Restricted under NDA	Ingredients making up <0.1% of formulation								
Molecular weight		40.00	Restricted under NDA	Ingredients making up <0.1% of formulation								
	Physi	ical and Chemical Propert	ties									
Form	Liquid											
Water solubility	Complete											
pH (as supplied)	>13											
LogP ¹	Not available	Inorganic	Inorganic	Inorganic								
Log D (pH 5.5, pH 7.4) ¹	Not available	Inorganic	Inorganic	Inorganic								
BCF (pH 5.5, pH 7.4) ¹	Not available	Inorganic	Inorganic	Inorganic								
Ecological Information												
		Chemwatch SDS										
Persistence (Water/Soil)		Low										
Biodegradability												
Bioccumulation Potential		LOW (LogKOW = -1.38)										
Aquatic Species (mg/L)		mg/L										
		Chemwatch SDS										
Fish - 96h/LC ₅₀		125										
Fish - 96h/NOEC		56										
Crustacea - 48h/EC ₅₀		40.4										
Algae - 96h/EC ₅₀		3180000										
		Sigma SDS										
Toxicity to fish		45.4-125	No data									
Toxicity to daphnia and other aquatic invertebrates		40.4	No data									
Toxicity to algae			No data									
		USEPA ECOTOX Database										
		196 (sw, fish, LC50)	500 (sw, trout, mortality)									
		ECHA PNEC										
PNEC (Marine)		0.004	No ecotox data									
Assessment Factor		10,000										

Crystalfloc Cationic Emulsions

	Crystalflo	c Cationic Emulsions		
Use		Processing aid for indust	trial applications	
Supplier		Ixom Operat		
Area		Into S 3901 Above		
Use (kg/day)		20		
	Cher	mical Information		
- 1 ()			6 I I I II I I	
Ingredient(s)	Formulation	branched tridecyl alcohol, ethoxylated	fatty alcohol alkoxylate	Adipic acid
Composition (%)		0-<5%	0-<5%	0-<2%
CAS #		Not available	Not available	124-04-9
Chemical formula/ structure		Not available	Not available	но
Molecular weight	-	Not available	Not available	146.14
	Physical a	nd Chemical Properties		
Form	Liquid	in enemient reperies		
Water solubility	Miscible			
pH (as supplied)	4-6			
	4-0			0.00
LogP ¹	-			0.08
Log D (pH 5.5, pH 7.4) ¹				,-1.50,-4.48
BCF (pH 5.5, pH 7.4) ¹				1.00
	Ecolo	ogical Information Chemwatch SDS		
Persistence (Water/Soil)				
Biodegradability				
Bioccumulation Potential				
Aquatic Species (mg/L)				
• • •		Chemwatch SDS		
Fish - 96h/LC ₅₀	10-100 (Ixom SDS)			97
Crustacea - 48h/EC ₅₀	10-100 (Ixom SDS)			85.7
Crustacea - 840h/NOEC				
Crustacea - 504h/NOEC	-			6.3
Algae - 72h/EC ₅₀	-			
Algae - 72h/EC ₁₀				14.0
Algae - 96h/EC ₅₀	_			
Aigae - 9011/ EL 50		Sigma SDS		26.6
Tarisita ta Cale		Sigilia SUS		07
Toxicity to fish				97
Toxicity to daphnia and other aquatic invertebrates				46
Toxicity to algae				59
Toxicity to bacteria		TA ROTOR D. C.L.		92-7911
	USE	EPA ECOTOX Database		1 - (
				97 (LC50, fw, fish, juveline)
		ECHA PNEC		
PNEC (Marine)				0.013
Assessment Factor				500

DIPA

D	i-Isopropanolamine - Liquid (DIPA)						
Use	Base for fatty acid soaps used in polishes, textiles, cutting oils, and insecticide emulsions						
Supplier	Ixom Operations						
Area	Western AOC Trench						
Use (kg/day)	420						
	Chemical Information						
Ingredient(s)	Bis(2-hydroxypropyl)amine (DIPA)						
Composition (%)	>=99%						
CAS #	110-97-4						
Chemical formula/ structure	$H_{3C} \xrightarrow{OH} N \xrightarrow{OH} CH_{3}$						
Molecular weight	133.19						
	Physical and Chemical Properties						
Form	Liquid						
Water solubility	Miscible						
pH (as supplied) Not available							
LogP ¹	-0.81						
Log D (pH 5.5, pH 7.4) ¹	,-3.70,-2.48						
BCF (pH 5.5, pH 7.4) ¹	1.00						
	Ecological Information Chemwatch SDS						
Persistence (Water/Soil)	Low						
Biodegradability							
Bioccumulation Potential	Low (LogKOW = -0.82)						
Aquatic Species (mg/L)							
	Chemwatch SDS						
Fish - 96h/LC ₅₀	1-466						
Crustacea - 48h/EC ₅₀	277.7						
Algae - 72h/EC ₅₀	74						
Algae - 72h/NOEC	125						
	Sigma SDS						
Toxicity to fish	1100						
	USEPA ECOTOX Database						
	410 (fw, frog, LC50)						
	ECHA PNEC						
PNEC (Marine)	0.028						
Assessment Factor	10,000						

ADIP-X

AD	IP-X (Activate	d Amietol M12-201)		
Use		Acid gas rer	noval solvent	
Supplier		Not s	upplied	
Area		Western A	AOC Trench	
Use (kg/day)		1	03	
	Chemical	Information		
Ingredient(s)	Formulation	methyldiethanolamine	piperazine	Caustic Soda(46%-50%) Liquid
Composition (%)		80%	13%	7%
CAS #		105-59-9	110-85-0	1310-73-2
Chemical formula/ structure		СН ₃ НО И ОН	H Z J H	NaOH
Molecular weight		119.16	86.14	40.00
0	Physical and Ch	emical Properties		
Form	Liquid	in the period		
Water solubility	Complete			
pH (as supplied)	Not available			
LogP ¹	Not available	-0.72	-1.17	Inorganic
Log D (pH 5.5, pH 7.4) ¹	Not available	,-3.39,-1.79	,-4.18,-3.15	0
				Inorganic
BCF (pH 5.5, pH 7.4) ¹	Not available	1.00	1.00	Inorganic
	•	Information watch SDS		
Persistence (Water/Soil)		Low	Low	Low
Biodegradability		7% - not biodegradable		
Bioccumulation Potential		LOW (LogKOW = -1.5024)	LOW (BCF = 3.9)	LOW (LogKOW = -1.38)
Aquatic Species (mg/L)		mg/L	mg/L	mg/L
	Chemy	watch SDS		
Fish - 96h/LC ₅₀		>1	>1-800	898
Fish - 96h/NOEC		1		
Crustacea - 48h/EC ₅₀		230	21	
Algae - 96h/EC ₅₀		20	54	8769
Algae - 96h/EC ₂₀		7.4		
Algae - 72h/NOEC			>1	
	Sig	ma SDS		
Toxicity to fish		1466	>1800	45.4-125
Toxicity to daphnia and other aquatic invertebrates		233	21	40.4
Toxicity to algae		>100	>1000	
	USEPA ECO	TOX Database		
		No data	No data	196 (sw, fish, LC50)
	ECH	A PNEC		
PNEC (Marine)		0.004	0.125	
Assessment Factor		10,000	100	

CC Eliminator

	C	hemical Information		
Ingredient(s)	Formulation	Lauramine Oxide	alcohols C12-16 ethoxylated	Caustic Soda(46%-50%) Liquid
Composition (%)		25-30%	0-5%	balance
CAS #		1643-20-5	68551-12-2	1310-73-2
Chemical formula/ structure		H ₃ C H ₃ C	Not available	NaOH
Molecular weight	_	229.4		40.00
0	Physica	l and Chemical Properties		
Form	Liquid	1		
Water solubility	Complete			
pH (as supplied)	Not available			
LogP ¹	Not available	3.27	No data	Inorganic
Log D (pH 5.5, pH 7.4) ¹	Not available	3.42/3.50	No data	Inorganic
BCF (pH 5.5, pH 7.4) ¹	Not available	225.9/269.4	No data	Inorganic
· · · · · · · · · · · · · · · · · ·	Ec	cological Information Chemwatch SDS		, C
Persistence (Water/Soil)			Low	Low
Biodegradability		Readily biodegradable (Sigma SDS)		
Bioccumulation Potential		LOW (see BCF above)	LOW (BCF = 3.9)	LOW (LogKOW = -1.38)
Aquatic Species (mg/L)				
		Chemwatch SDS		
Fish - 96h/LC ₅₀			>1-800	898
Fish - 96h/NOEC				
Crustacea - 48h/EC ₅₀			21	
Algae - 96h/EC ₅₀			54	8769
Algae - 96h/EC ₂₀				
Algae - 72h/NOEC			>1	
		Sigma SDS		
Toxicity to fish		0.495-31.8	ND	45.4-125
Toxicity to daphnia and other aquatic invertebrates		3.9	ND	40.4
Toxicity to algae		0.015-0.2	ND	
		USEPA ECOTOX Database		
		No data	No data	196 (sw, fish, LC50)
		ECHA PNEC		
PNEC (Marine)		0.003	0.001	
Assessment Factor		20	1,000	

CC414P

		CC414	P (event based us	e only, during a shut	tdown)			
Use				Removal of benzene, hydrog		1		
Supplier					Concepts			
Area					ter from TPIs			
Use (kg/day)					only, during a shutdown)			
			Chemical	Information				
				mormation	Durandana Chural a Dutal			
Ingredient(s)	Formulation	d-Limonene	Dodecylbenzenesulfonic Acid	Methoxypropoxypropanol	Propylene Glycol n-Butyl Ether	Diethanolamine	Nonylphenol Ethoxylate	Tetrasodium EDTA
Composition (%)		5-15%	5-15%	5-10%	5-10%	0-5%	0-5%	0-5%
CAS #		5989-27-5	27176-87-0	34590-94-8	5131-66-8	111-42-2	9016-45-9	64-02-8
Chemical formula/ structure		H ₂ C _S ^{4,1} CH ₃	C12H25C6H4SO3H	СНЗОСЗН6ОСЗН6ОН	СН3(СН2)30С3Н6ОН	HN(CH2CH2OH)2	C ₉ H ₁₉ OH	
Molecular weight		136.2	326.5	148.2	132.2	105.1	680.0	416.2
			Physical and C	hemical Properties				
Form	Liquid							
Water solubility	Appreciable							
pH (as supplied)	8-8.5							
LogP ¹		4.45	Not available	-0.46	1.14	-1.50	Not available	Not available
Log D (pH 5.5, pH 7.4) ¹		4.40	Not available	0.05	1.04	,-4.13,-2.71	Not available	Not available
• • • •		1307	Not available	1.00	3.62	1.00	Not available	Not available
BCF (pH 5.5, pH 7.4) ¹		1307			5.02	1.00	NOT available	NOL available
			0	l Information				
			Chem	watch SDS				
Persistence (Water/Soil)	Not determined							
Biodegradability		eadily biodegradable (Sigma SDS	Not available	eadily biodegradable (Sigma SDS		eadily biodegradable (Sigma SDS	5)	Not available
Bioccumulation Potential	Not determined	Not available	Not available	Not available	Not available	Not available		Not available
Aquatic Species (mg/L)								
			Chem	watch SDS				
Fish - 96h/LC ₅₀								
Fish - 96h/NOEC								
Crustacea - 48h/EC ₅₀								
Algae - 96h/EC ₅₀								
Algae - 96h/EC ₂₀								
Algae - 72h/NOEC								
			Sig	gma SDS				
Toxicity to fish		0.72		>1,000		540 (NOEC)	1.0	
Toxicity to daphnia and other aquatic invertebrates		0.36		1919		<4.2	12.2	
Toxicity to algae				>969		55	8 (NOEC)	
				OTOX Database				
		Freshwater data only	0.1 (sw, invertebrate, reproduction)	Freshwater data only	Freshwater data only	103 (sw, diatom, EC50)	0.15 (sw, copepod egg, development)	Freshwater data only
			ECI	HA PNEC				
PNEC (Marine)		0.0014	1.0	1.9	0.0525	0.002	0.001	0.22
Assessment Factor		100	10	1000	10000	500	5	100

SolbergDoD3155 (Fire training)

		Solberg DoD31	55			
Use			Fire fighting f	oam		
Supplier			Solberg Asia Paci			
Area		Fire	Training Ground - Dischar			
Use (kg/day)			242.4 (per event - typical			
		Chemical Informat	tion			
Ingredient(s)	Formulation	Diethylene glycol mono butyl ether	Sol1	Alcohol sulphate C12-C14, triethanolamine salt	Cocoamido propyl betaine	Sol2
Composition (%)		8.6000	1.6500	3.4000	1.1200	2.0900
CAS #		112-34-5	Restricted under NDA	90583-18-9	61789-40-0	Restricted under NDA
Chemical formula/ structure		CH ₃ CH ₂ CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₂ CH ₂ OH	Restricted under NDA			Restricted under NDA
Molecular weight		162.23	Restricted under NDA			Restricted under NDA
		Physical and Chemical P	roperties			
Form	Liquid					
Water solubility	Miscible					
pH (as supplied)	7-8.5					
LogP ¹		0.44	No data	No data	0.32	No data
Log D (pH 5.5, pH 7.4) ¹		0.55	No data	No data	0.93	No data
BCF (pH 5.5, pH 7.4) ¹		1.53	No data	No data	4.18	No data
		Ecological Informa	tion			
		Chemwatch SDS				
Persistence (Water/Soil)		Low				
Biodegradability	Readily biodegradable	Readily biodegradable				
Bioccumulation Potential	Slightly or not bioaccumulative (components)	Low (BCF = 0.46)				
Aquatic Species (mg/L)						
		Chemwatch SDS				
Fish - 96h/LC ₅₀	22 (rainbow trout)	1-300		No data	1	
Fish - 96h/NOEC						
Fish - 672h/NOEC					0.16	
Crustacea - 48h/EC ₅₀	69 (Daphnia)	4-950		No data	6.4	
Crustacea - 504h/NOEC					1	
Crustacea - 504h/EC ₁₀						
Algae - 72h/EC ₅₀		1-101		No data		
Algae - 72h/NOEC						
Algae - 96h/EC ₅₀		01			0.55	
Taniaita ta fak		Sigma SDS				
Toxicity to fish Toxicity to daphnia and other aquatic invertebrates						
Toxicity to daphnia and other aquatic invertebrates						
TOALLY TO aight		USEPA ECOTOX Databa	ase			
		2,000 (sw, fish, LC50)	0.075 (NOEC, fw clam)	No data	No data	No data
		ECHA PNEC				
PNEC (Marine)		0.11	No data	0.001	0.00032/0.002 (intermittent)	No data
Assessment Factor		10,000		100	500	

Appendix 4: Process chemical risk assessment mass balance calculations

RQ1

Formulation	Use (kg/day)	Worst case all ends up in SW (mg/L)	Volume of SW basin (L)	Lowest ecological guideline for most toxic component (mg/L)	Guideline note	Guideline source	Toxic component	Toxic component % of formulation	Adjusted ecological guideline (mg/L)	RQ1	Partition correction undertaken?	Reason
						Every-day u	ise					
BetzDearborn AE1115P	4.6	0.92	5,000,000	0.002	PNEC (Marine)	1	Betz2	0.04%	5.00	0.2	No	Lower than lowest ecological guideline
BetzDearborn AE1115P	4.6	0.92	5,000,000	0.00048	PNEC (Marine) based on 720h/NOEC crustacea + 2 other long term (AF50)	1	Isoparaffins petroleum hydrotreated HFP	22%	0.00	85.9	No	Does not come into contact with hydrocarbon
Cortrol OS7780	13.7	2.74	5,000,000	0.000057	PNEC (Marine)	1	Hydroquinone	2.5%	0.002	1202	No	Hydroquinone oxidised to 1,4- benzoquinone during process
Cortrol OS7780	13.7	2.74	5,000,000	0.000086	PNEC (Marine) NOEC fish (AF1000)	2	1,4-Benzoquinone	2.5%	0.00344	797	No	Does not come into contact with hydrocarbon
Cortrol OS7780	13.7	2.74	5,000,000	0.01	PNEC (Marine)	1	Cort1	0.024%	41.7	0.1	No	Lower than lowest ecological guideline
Cortrol OS7780	13.7	2.74	5,000,000	0.000403	PNEC (Marine)	1	Cort2	0.008%	5.0375	0.5	No	Lower than lowest ecological guideline
Cortrol OS7780	13.7	2.74	5,000,000	0.00623	PNEC (Marine)	1	Cort3	0.010%	62.3	0.04	No	Lower than lowest ecological guideline
Embreak 2021	128.7	25.74	5,000,000	0.001	PNEC (Marine)	1	Nonylphenol (technical)	1.175%	0.085	302	Yes	Greater than lowest ecological guideline
Embreak 2021	128.7	25.74	5,000,000	0.001	PNEC (Marine)	2	Emb5	0.115%	1	30	Yes	Greater than lowest ecological guideline

Formulation	Use (kg/day)	Worst case all ends up in SW (mg/L)	Volume of SW basin (L)	Lowest ecological guideline for most toxic component (mg/L)	Guideline note	Guideline source	Toxic component	Toxic component % of formulation	Adjusted ecological guideline (mg/L)	RQ1	Partition correction undertaken?	Reason
Embreak 2021	128.7	25.74	5,000,000	0.001	PNEC (Marine)	2	Emb7	0.235%	0	60	Yes	Greater than lowest ecological guideline
Embreak 2021	128.7	25.74	5,000,000	0.001	Water Quality Guideline	4	Emb6	40.000%	0.003	1029 6	Yes	Greater than lowest ecological guideline
Embreak 2021	128.7	25.74	5,000,000	12.5	Mortality (saltwater, algae)	2	Emb10	4.478%	279.174	0.1	No	Lower than lowest ecological guideline
Klaraid IC1172	156.7	31.34	5,000,000	No classification	PNEC (Marine)	1	Aluminium Chlorohydrate	40%	Not applicable	Not appli cable	No	See ECHA summary ref7
Spectrus NX1100	0.2	0.04	5,000,000	0.001	PNEC (Marine)	1	Bronopol	5.544%	0.018	2.2	Yes	Greater than lowest ecological guideline
Spectrus NX1100	0.2	0.04	5,000,000	0.003	PNEC (Marine)	1	Isothiazolinones, mixed (Kathron 886)	2.576%	0.116	0.3	Yes	Greater than lowest ecological guideline
Inhibitor AZ8104	5.5	1.10	5,000,000	0.008	PNEC (Marine)	1	Sodium Tolyltriazole	1.4%	0.57	1.9	Yes	Greater than lowest ecological guideline
Crystalfloc Cationic Emulsions	20.0	4.00	5,000,000	0.013	PNEC (Marine)	1	Adipic acid	2.0%	0.65	6.2	Yes	Greater than lowest ecological guideline
Embreak 2050	5.2	1.04	5,000,000	0.1	PNEC (Marine)	1	Diethylene Glycol Monobutyl Ether	4.95%	2.2	0.5	No	Lower than lowest ecological guideline
Steammate NA0880	16.1	3.22	5,000,000	0.009	PNEC (Marine)	1	Monoethanolami ne	39.6%	0.02	142	Yes	Greater than lowest ecological guideline
Steammate NA0880	16.1	3.22	5,000,000	0.007	PNEC (Marine)	1	3- Dimethylaminopr opylamine	19.9%	0.04	92	Yes	Greater than lowest ecological guideline
Steammate NA0880	16.1	3.22	5,000,000	0.002	PNEC (Marine)	1	SM1	0.2%	1.00	3.2	Yes	Greater than lowest ecological guideline
Genguard GN8220	6.0	1.21	5,000,000	0.005	PNEC (Marine)	1	Gen2	3.9%	0.1	9.4	Yes	Greater than lowest ecological guideline

Formulation	Use (kg/day)	Worst case all ends up in SW (mg/L)	Volume of SW basin (L)	Lowest ecological guideline for most toxic component (mg/L)	Guideline note	Guideline source	Toxic component	Toxic component % of formulation	Adjusted ecological guideline (mg/L)	RQ1	Partition correction undertaken?	Reason
Genguard GN8220	6.0	1.21	5,000,000	0.01	PNEC (Marine)	2	Maleic acid	3.9%	0.3	4.7	Yes	Greater than lowest ecological guideline
Spectrus BD1501E	0.05	0.01	5,000,000	0.001	PNEC (Marine) based on AF 10,000 applied	1	GE1	14%	0.01	1.1	Yes	Greater than lowest ecological guideline
Optispearse ADJ5150	0.05	0.01	5,000,000	0.00404	Crustacea - 48h/EC50	1	Sodium hydroxide	25%	0	0.6	No	Lower than lowest ecological guideline
Optispearse HP2650	2.3	0.46	5,000,000	0.00404	Crustacea - 48h/EC50	1	Sodium hydroxide	3%	0	3.4	No	Inorganic
			,			Spill even	t		,			
ADIP-X	103.0	9.73	10,589,00 0	0.004	PNEC (Marine)	1	Methyldiethanola mine	80%	0.01	1945	No	Does not come into contact with hydrocarbon
ADIP-X	103.0	9.73	10,589,00 0	0.125	PNEC (Marine)	1	Piperazine	13%	1.0	10	No	Does not come into contact with hydrocarbon
DIPA	420.0	39.66	10,589,00 0	0.028	PNEC (Marine)	1	Bis(2- hydroxypropyl)a mine	100%	0.03	1417	Yes	Greater than lowest ecological guideline
						Plant Shutdo	own					
CC Eliminator	222.7	44.54	5,000,000	0.003	PNEC (Marine)	1	Lauramine Oxide	30%	0.01	4454	Yes	Greater than lowest ecological guideline
CC Eliminator	222.7	44.54	5,000,000	0.0	PNEC (Marine) based on Algae - NOEC (AF1000)	1	alcohols C12-16 ethoxylated	5%	0.0	2227	Yes	Greater than lowest ecological guideline
CC 414P	15.1	3.02	5,000,000	0.0014	PNEC (Marine)	1	d-Limonene	15%	0.009	324	Yes	Greater than lowest ecological guideline
CC 414P	15.1	3.02	5,000,000	0.002	PNEC (Marine)	1	Diethanolamine	5%	0.04	76	Yes	Greater than lowest ecological guideline

¹ Europe ECHA Registered Substances - Ecotoxicological Information - Aquatic Toxicity. ² USEPA Ecotox database ³ ANZECC (2000) Trigger Value

RQ2

Formulation	Toxic Component	RQ1	logP	Р	logD	D	RQ2	% oil	% water
		Encore							
_ 1 1		-	/-day use		1				I
Embreak 2021	Nonylphenol (technical)	302	5.82	660693			0.0005	99.9998%	0.0002%
Embreak 2021	Nonylphenol (technical)	302			5.43	269153	0.001	99.9996%	0.0004%
Embreak 2021	Emb5	29.7	5.8	660693			0.00004	99.9998%	0.0002%
Embreak 2021	Emb7	60.5	5.8	660693			0.00009	99.9998%	0.0002%
Embreak 2021	Emb6	10296	6	660693			0.02	99.9998%	0.0002%
Spectrus NX1100	Bronopol	2.22	1.72	52.48			0.04	98.13%	1.87%
Spectrus NX1100	Bronopol	2.22			1.34	21.88	0.1	95.63%	4.37%
Steammate NA0880	Monoethanolamine	141.7	-1.31	0.05			135	4.67%	95.33%
Steammate NA0880	Monoethanolamine	141.7			-3.41	0.0004	142	0.04%	99.96%
Steammate NA0880	3-Dimethylaminopropylamine	91.5	-0.29	0.51			61	33.90%	66.10%
Steammate NA0880	3-Dimethylaminopropylamine	91.5			-3.47	0.0003	92	0.03%	99.97%
Steammate NA0880	SM1	3.2	-1.50	0.03			3.1	3.07%	96.93%
Steammate NA0880	SM1	3.2			-2.71	0.0019	3.2	0.19%	99.81%
Inhibitor AZ8104	Sodium Tolyltriazole	1.93	1.78	60.26			0.03	98.37%	1.63%
Genguard GN8220	Gen2	9.4	Inorganic				9.4	0.00%	100%
Genguard GN8220	Maleic acid	4.7	-0.01	0.98			2.4	49.42%	50.58%
Genguard GN8220	Maleic acid	4.7			-4.73	0.00002	4.7	0.002%	99.998%
Crystalfloc Cationic Emulsions	Adipic acid	6.2	0.08	1.20			2.8	54.59%	45.41%
Crystalfloc Cationic Emulsions	Adipic acid	6.2			-4.48	0.00003	6.2	0.003%	99.997%
		Spi	ll event						
DIPA	Bis(2-hydroxypropyl)amine	1417	-0.81	0.15			1227	13.41%	86.59%
DIPA	Bis(2-hydroxypropyl)amine	1417			-2.48	0.00331	1412	0.330%	99.670%
		Plant	Shutdown						

Formulation	Toxic Component	RQ1	logP	Р	logD	D	RQ2	% oil	% water
CC Eliminator	Lauramine Oxide	4454	3.27	1862			2.4	99.95%	0.05%
CC Eliminator	Lauramine Oxide	4454			3.50	3162	1.4	99.97%	0.03%
CC Eliminator	alcohols C12-16 ethoxylated	2227	4.94	87096			0.03	100.00%	0.00%
CC Eliminator	alcohols C12-16 ethoxylated	2227			4.03	10715	0.21	99.99%	0.01%
CC 414P	d-Limonene	324	4.45	28184			0.01	99.996%	0.004%
CC 414P	d-Limonene	324			4.40	25119	0.01	99.996%	0.004%
CC 414P	Diethanolamine	76	-1.5	0.03			73	3.1%	96.9%
CC 414P	Diethanolamine	76			-2.71	0	75	0.2%	99.8%

RQ3

Formulation	Toxic Component	Highest RQ2	Highest RQ3	Modelling Scenario						
Every-day use										
BetzDearborn	Isoparaffins	86	0.5	Worst-case extreme event - 24hr post discharge						
Cortrol OS7780	1,4-Benzoquinone	797	4.6	Worst-case extreme event - 24hr post discharge						
Crystalfloc Cationic Emulsions	Adipic acid	6.2	0.04	Worst-case extreme event - 24hr post discharge						
Steammate NA0880	MEA	142	0.8	Worst-case extreme event - 24hr post discharge						
Genguard GN8220	Sodium phosphate	9.4	0.05	Worst-case extreme event - 24hr post discharge						
Optispearse HP2650	Sodium hydroxide	3.4	0.02	Worst-case extreme event - 24hr post discharge						
Spill event										
ADIP-X	MDA	1945	11	Worst-case extreme event - 24hr post discharge						
DIPA	DIPA	1412	8	Worst-case extreme event - 24hr post discharge						
Plant Shutdown										
CC Eliminator	Lauramine Oxide	2.4	0.01	Worst-case extreme event - 24hr post discharge						
Formulation Toxic Component		Highest RQ2 Highest RQ3		Modelling Scenario						
-----------------------------	-----	-------------------------	-----	--						
CC 414P Diethanolamine		75	0.4	Worst-case extreme event - 24hr post discharge						
Solberg CPB		106	0.6	Worst-case extreme event - 24hr post discharge						
Solberg	СРВ	14.8	0.1	Worst-case extreme event - 24hr post discharge						

Solberg Fire Training (RQ1 to RQ3 and BCF)

Formulation	Use (kg)	Volume of Retention basin and SW basin (L)	Worst case all ends up in SW (mg/L)	Lowest Ecological guideline for most toxic component (mg/L)	Guideline note	Guideline Source	Toxic Component	Toxic component % of formulation	Adjusted ecological guideline (Column E/%) (mg/L)	RQ1	Partition correction undertaken?	Reason	RQ2	Highest RQ3	BCF
SolbergDoD3155	242.4	12,800,000	18.94	0.002	PNEC (Marine) - intermittent discharge	1	СРВ	1.12%	0.18	106	No	Not applicable	106	0.6	4.18
SolbergDoD3155	242.4	12,800,000	18.94	0.110	PNEC (Marine)	1	DGMBE	8.6%	1.28	15	Yes	Not applicable	15	0.1	4.18

¹Europe ECHA Registered Substances - Ecotoxicological Information - Aquatic Toxicity.

Appendix 5: Hydrodynamic modelling report (MetOcean Solutions, 2020)



Waste Water Dispersion Modelling

Report prepared for Refining New Zealand (RNZ)

7th July 2020



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1. Introduction

Refining New Zealand (RNZ) commissioned MetOcean Solutions to undertake a dispersion modelling study of Whangarei Harbour (Figure 1.1) to study the potential environmental impact of waste water outfalls.

RNZ wastewater is primarily made up of two streams:

- 1. Process water, and
- 2. Ship de-ballast water /ship tank wash water.

The Water Effluent Treatment Unit (WETU) receives wastewater from continuous process flow streams, first flush stormwater and intermittent process streams, and is designed to collect and treat all effluent water streams before final disposal. Treated effluents, along with the treated ship deballast and ship tank water, pass through the Retention Basin and then to the Stormwater Storage Basin. Combined treated wastewater, groundwater and stormwater flows and discharges to the lower Whangarei Harbour via a submarine diffuser attached to the Refinery jetty.

Surface runoff is collected from the process area and other sites around the Refinery via a stormwater system of closed drains and open canals. Stormwater from process areas is treated in a series of holding basins before being transferred to the Stormwater Storage Basin. The stormwater is combined with the Treated wastewater and discharged to the lower Whangarei Harbour via a submarine diffuser attached to the Refinery jetty.

In addition to the resource consents related to the discharge via the harbour diffuser, RNZ hold, and are looking to renew, consents for the discharge from the stormwater basin diffuser bypass (stormwater outfall) and the stormwater basin overflow spillway.

Additionally, the numerical modelling considers two cases: an existing case base on the actual bathymetry of the harbour as well as a possible future scenario including consented work. The latter combines an additional proposed berth known as Berth 4 (Figure 1.2) and the proposed deepened channel (Figure 1.3).

This report is structured as follows. A list of measured data used to calibrate/validate the model is described in Section 2. Methods applied, including numerical model definitions are presented in Section 3. Model validation and results are presented in Section 4 and a concise summary is provided in Section 5. References cited are given in Section 6.



Figure 1.1 Maps of Whangarei Harbour (top) and its entrance (bottom) with the locations used in the present study for the establishment of the numerical models and the description of the effect of the channel deepening on the coastal dynamics.



Figure 1.2 Satellite image showing the Northport Berth 4 reclaim area included in the hydrodynamic model bathymetry.





Figure 1.3Bathymetry map (upper plot) and depth differences (lower plot) between the Option 4.2 channel design and
the existing channel configuration. Positive amplitudes indicate a deepening of the channel.

2. Field measurement

The first dataset is focusing on tidal elevation in the upper harbour. Water level was measured at four locations (Figure 2.1) in the harbour during May 2016. At those locations, RBRs solo pressure sensors were recording water pressure continuously at 2 Hz (i.e. 0.5-sec interval).

The second dataset used in this report is a moving vessel Acoustic Doppler Current Profilers (ADCP) survey in the entrance region. ADCP moving vessel deployments have the benefit of providing 3-dimensional velocity data over different sections of the navigation channel thereby allowing a spatial time-dependent validation of the tidal models. Note however that velocity data provided by ADCP moving vessel deployments are slightly degraded by various factors such as Doppler noise, large sampling volume and beam divergence over rapidly changing bathymetry. Nonetheless, it was the preferred method to provide a spatial validation source in the complex tidal flows of the entrance. The ADCP moving vessel deployment was undertaken over three different zones (A, B and C) illustrated in Figure 2.1 from 19 - 21 May 2015. Current velocities were measured during 13 hours through each area to capture the peak ebb and flood tidal stages.

The third dataset consisted in two ADCP's. Those data were acquired by Cawthron between March and June 2016 focusing mainly on the Outer harbour. One upward facing ADCP were deployed in Bream Bay (Figure 2.2) between March and April 2016 in 44 m water depth. The second ADCP were deployed near Ruakaka beach between April and June 2016 in 9 m water depth. Both ADPC's measured current velocity profile as well as near-seabed temperature and sea level elevation.



A summary of the instrument configuration for the whole campaign is presented in Table 2.1.

Figure 2.1 Locations of current velocity measurements (Zone A in green, B, in red and C in orange) and water level measurements (K17, P10, W2 and Parua) used to calibrate and validate the SCHISM (and Delft3D) tidal model within Whangarei Harbour and Bream Bay.





Figure 2.2 Location of the four ADCP deployments in Bream Bay between January and July 2016. The geographic coordinates of each position is presented in Table 2.1. Also shown are the proposed disposal grounds 3.2 and 1.2.

Table 2.1	Summary of all the measured data used in the model validation
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Site	Instrument	Latitude (WGS84)	Longitude (WGS84)	Depth (m)	Start (dd/mm/yyy y)	End (dd/mm/yyy y)	Bin size	Sampling period
P1	RDI Sentinel V	-46.7567	168.0668	37	03/12/2018	16/01/2019	1 m	5 min
P2	RDI	-46.7703	168.0614	32	02/12/2018	03/01/2019	1m	30min
Р3	RDI Workhorse	-46.7884	168.0538	25	03/12/2018	16/01/2019	1 m	60 min

3. Methodology

3.1 Hydrodynamic model

3.1.1 Model description

The 2D and 3D baroclinic hydrodynamics of the harbour were modelled using the open-sourced hydrodynamic model SCHISM ¹². The benefit of using open-source science models is the full transparency of the code and numerical schemes, and the ability for other researchers to replicate and enhance any previous modelling efforts for a given environment.

SCHISM is a prognostic finite-element unstructured-grid model designed to simulate 3D baroclinic, 3D barotropic or 2D barotropic circulation. The barotropic mode equations employ a semi-implicit finite-element Eulerian-Lagrangian algorithm to solve the shallow-water equations, forced by relevant physical processes (atmospheric, oceanic and fluvial forcing). A detailed description of the SCHISM model formulation, governing equations and numerics, can be found in Zhang and Baptista (2008).

The SCHISM model is physically realistic, in that well-understood laws of motion and mass conservation are implemented. Therefore, water mass is generally conserved within the model, although it can be added or removed at open boundaries (e.g. through tidal motion at the ocean boundaries) and water is redistributed by incorporating aspects of the real-world systems (e.g. bathymetric information, forcing by tides and wind). The model transports water and other constituents (e.g. salt, temperature, turbulence) through the use of quadrilateral and triangular volumes (connected 3-D polyhedrons).

The finite-element triangular grid structure used by SCHISM has resolution and scale benefits over other regular or curvilinear based hydrodynamic models. SCHISM is computationally efficient in the way it resolves the shape and complex bathymetry associated with estuaries, and the governing equations are similar to other open-source models such as Delft3D and Regional Ocean Modelling System (ROMS). SCHISM has been used extensively within the scientific community³,⁴ where it forms the backbone of operational systems used to nowcast and forecast estuarine water levels, storm surges, velocities, water temperature and salinity⁵.

3.1.2 Model domain

Model bathymetries were derived from a combination of relevant ENC (Electronic Navigation Charts), LIDAR, and survey data (single-beam and multi-beam surveys). All data were converted to a common horizontal projection (NZTM), and reduced to a common vertical datum.



¹ http://ccrm.vims.edu/schism/

² http://www.ccrm.vims.edu/w/index.php/Main_Page#SCHISM_WIKI

³ http://www.stccmop.org/knowledge_transfer/software/selfe/publications

⁴ http://ccrm.vims.edu/schism/schism_pubs.html

⁵ https://tidesandcurrents.noaa.gov/ofs/creofs/creofs_info.html

The model resolution was optimised to ensure replication of the salient hydrodynamic processes. The resolution in the middle of Bream Bay was approximately 300 m and reduced to 5 m near the coast. The triangular elements of the model domain mesh and associated bathymetries are presented in Figure 3.1.



Figure 3.1 Model depth and mesh of the Whangarei Harbour and surrounds. Depths are given in metres below Mean Sea Level (MSL) The mesh covers the offshore region, including the ebb tidal delta, while salient bathymetric features are represented inside the harbour.



3.1.3 Vertical discretisation

The vertical discretisation of the water column consisted of a Localised Sigma Coordinate system with Shaved Cell (LSC²), a type of terrain-following layers described in Zhang et al. (2014).

For this study, the model was configured with increase vertical resolution near the surface and near bottom (Figure 3.2). The vertical grid is constituted of sigma layer terrain-following coordinate with 12 layers in the shallow regions (<6 m) and up to 25 layers in the deep area of Bream Bay. Vertical section showings both the sigma layers and the water depths along transect are presented in Figure 3.2.

Some of the shallow water areas such as the inter-tidal area in the Inner Harbour near Portland were set up to run in 2D in order to make the model computationally efficient.



Figure 3.2 Map of the model domain showing the number of vertical levels used in the model (left). The cross section represented by the red line is shown on the right panel. Depths are relative to Mean Sea Level (MSL).

3.1.4 Vertical mixing/ turbulence closure

Vertical mixing was modelled using a *GLS* model (Kantha and Clayson, 1994) with a stability function with minimum and maximum diffusivities set to 1×10^{-6} and 1×10^{-2} , respectively, following model validation and calibration. These values were adjusted as part of the model validation and calibration process.

The constant surface mixing length was held to the recommended default value of 0.1 (i.e. 10% of the uppermost sigma layer). However, variations of the mixing length were also examined during the validating and calibration process.

Frictional stress at the seabed was approximated with a quadratic drag law, with the drag coefficient (*CD*) determined using a bottom roughness of 0.001 m. Detailed explanations of the determination of the drag coefficient are given in Zhang and Baptista (2008).

3.2 Model boundary condition

3.2.1 Hydrodynamic forcing

Tidal boundary conditions for the SCHISM model were derived from constituents defined from a 1-year ROMS model domain of Whangarei with approximately 0.35 km resolution. The tidal velocities were interpolated in 3D assuming a logarithmic profile.

The open-boundary residual velocities, water elevations, salinity and temperature were prescribed from a ROMS model with similar resolution at 3-hour interval.

3.2.2 Temperature forcing

Within SCHISM temperature nudging is available by means of analysis nudging (Newtonian relaxation). The nudging allows the model state to be reconciled with observations in four dimensions. For this project, sea surface temperatures within the SCHISM model domain was nudged using available satellite data from the 0.05-deg resolution Operational Sea Surface Temperature and Sea Ice Analysis (OSTIA) with the nudging weighted to the order of 1-day. Fluvial discharges are relatively constant with respect to temperature and were held constant for the modelling.

3.2.3 Atmospheric forcing

MetOcean Solutions maintains an up-to-date atmospheric hindcast reanalysis from 1979 to 2019 at 12 km resolution for the entire New Zealand and approximately 4 km over the Hauraki Gulf (including Whangarei). This atmospheric hindcast was produced using the Weather and Research Forecasting (WRF) model forced with boundary conditions from the global Climate Forecast System Reanalysis (CFSR) product (with spatial resolutions of 0.31° from 1979–2010 and 0.20° beyond 2011).

The improvement in resolution from CFSR to WRF adds accuracy and variability to the atmospheric fields that force the SCHISM model, especially over coastal margins where topography is known to substantially change the large-scale wind patterns and local responses. WRF variables such as winds, atmospheric pressure, relative humidity, surface temperature, long and short wave radiation, and precipitation rate were used at hourly intervals to provide air-sea fluxes to force SCHISM model.

3.2.4 River forcing

River discharge data at or near the boundary of the salient rivers discharging into Whangarei Harbour were sourced from NRC (i.e. Otaika Creek, Raumanga Stream and the Hataea River, all of which are gauged, e.g. Figure 3.3.).



Figure 3.3 Fluvial discharges (in m³.s⁻¹) into the Whangarei Harbour from the Hatea River

3.3 Near-field model

Near-field modelling of the initial turbulent mixing was undertaken using CORMIX⁶, which is a USEPAsupported mixing zone model and decision support system for environmental impact assessment of regulatory mixing zones resulting from continuous point source discharges. The system emphasizes the role of boundary interaction to predict steady-state mixing behaviour and plume geometry.

CORMIX was used to define the near-field plume characteristics (plume extent, initial dilution) under a range of representative conditions (water depth, current velocities, discharge characteristics, diffuser configurations) for input into the far-field model.

An example of the plume shape and location is presented in Figure 3.4

⁶ http://www.cormix.info/



Figure 3.4 Aerial photography representing different plume shapes from the diffuser outfall. The location Shapes are calculated by CORMIX and are inferred by current speed and direction.

3.4 Far-field trajectory models

During this study, two different types of particle were modelled using Eulerian and Lagrangian methods. A passive tracer was modelled in order to represent any contaminant discharge without sinking velocities. On the other hand, particles representing any sediment discharge were attributed a sinking velocity based on the sediment grain size. Furthermore, a re-suspension criteria was used so particle settling on the sea-bed would be put back into the simulation if the critical shear stress is above the value of 0.2 N.m⁻² based on Van Rijn, (2016)

3.4.1 Lagrangian modelling

A Lagrangian model developed by MetOcean Solutions was used to simulate the trajectories of particles in a flow field. Here, the particles represent the pollutants or contaminants found in the discharged wastewaters.

The model consists in trajectory scheme applied to the existing 3D Eulerian current field (\tilde{u}, \tilde{v}) solving for the motion of discrete particles.

$$\frac{dx_p}{dt} = \tilde{u}(x, y, z, t) + u_t$$

$$\frac{dy_p}{dt} = \tilde{v}(x, y, z, t) + v_t$$

$$\frac{dz_p}{dt} = -w_s + w_t$$
(3.1 a,b,c)

where (x_p, y_p, z_p) are the particle coordinates, (u_t, v_t, w_t) are the diffusion components representing turbulent motions and w_s is the particle settling velocity.

In the horizontal plane, the model uses an Ordinary Differential Equations (ODE) solver, including a 4th order Runge-Kutta method, to calculate the trajectory of a given particle (x_p, y_p) in the time-varying current field.

In the vertical plane, particle motion is controlled only by the vertical diffusion component w_t as defined in equation 3.1c. Time-varying gridded sea surface elevation fields were included in the simulations to reproduce the ebbing and flooding phases, and associated wetting/drying of intertidal areas.

Time-varying gridded horizontal and vertical diffusion calculated by the SCHISM model were also included in the simulation.

Finally, in the present model implementation, any particle reaching the shoreline, the seabed or sea surface was allowed to become re-suspended due to ambient currents (i.e. non-sticky boundaries).

3.4.1.1 Lagrangian concentration computation

The combined particles clouds for each of the sediment classes and passive contaminant were postprocessed using kernel density estimator (KDE). In the kernel density approach, individual particles are assumed to represent the centre of mass of a "cloud"; the density profile of the cloud is described by the kernel function, while the spreading of the particle's equivalent mass is defined by the bandwidths associated with a given particle or receptor (Bellasio, R., et al., 2017; Vitali et al., 2006). These two components are then used to derive a particle density field, also referred to as a probability density function (PDF). A probability density function (PDF) quantifies the spatial distribution of the suspended or settled particles, and the sum of each PDF equals to one. Quantitative estimates of the probable depositional thickness can be obtained by multiplying the probability densities for each size fraction or contaminant load (here set to a maximum of 1) and each depth by their respective fraction of the discharge volumes:

$$D(x, y) = \sum d \sum i k_i V_d P D F_{d,i}(x, y)$$

where D(x,y) is the depositional thickness at the grid node location (x,y) in the cast of discharged sediment, or concentration in the case of passive particles, Vd is the discharge volume for release depth d, ki is the volume fraction of size fraction i or concentration and PDFd, i(x,y) is the probability density at location (x,y)for the respective size fraction or passive tracer and release depth.

Due to the interpolation process, care should be taken when evaluating KDE derived values for concentration/dilution near locations where elevated particle counts (either as passive tracers or sediment) can occur, specifically in areas adjacent to shallow water where;



- 1. the resident times of particles can be relatively long due to comparatively quiescent conditions resulting in higher concentrations when averaged over time,
- 2. the process of converting to depth averaged concentrations within a KDE framework can elevate apparent concentrations in shallower water, and
- 3. small fluctuations within the intertidal shallow areas may pool, with contaminant levels maintained at elevated levels due to the inability of the areas to effectively flush.

As such, locations close to shore should be considered 'worst-case' with respect to lower dilutions than would be expected.

3.4.2 Eulerian modelling

Eulerian tracer is a concentration field that obeys a classical advection-diffusion equation driven with currents of the hydrodynamic model (Meier and Höglund, 2013). (Deleersnijder et al., 2001) presented a detailed description of Eulerian tracer theory applied to the age distribution of seawater. Sources, sinks and initial and boundary conditions are specified for the tracer under consideration.

A detailed description of Eulerian tracer technique to obtain dilution is presented in (Zhang et al., 2010). These authors investigated the time scales associated with the spreading of the Hudson River source waters across the inner shelf of New York Bight. Differing from the common Lagrangian approach, which is characterised by the release of many tracers and extracting time-scale information from their differential transport, Eulerian tracer technique is computationally much cheaper (Zhang et al., 2010). It is a very useful technique for studying spatial patterns of circulation and mixing and the associated time scales (Hall and Haine, 2002; Zhang et al., 2010), and is appropriate for this study given the relatively high model resolution of the receiving environment.

The sediment release were done using module SED3D. It is fully integrated to SCHISM model and adapted from the Community Sediment Transport Model (Warner et al., 2010). The model is capable of reproducing bedload transport and suspended load for mud-like and sand-like sediment type.

3.5 Discharge conditions

From Marsden Point, three discharge locations were considered in this report (Figure 3.5). For every discharge a mix of sediment and pollutant was released (Table 3.1):

• The existing diffuser:

Release from the diffuser outfall is treated as constant throughout the year during dry weather where the bypass/spill way is not active. Contaminants and sediments are released at a constant rate with a flow of 1274 m³.s⁻¹. According to the sediment sampling, two grain sizes were modelled from this outfall: silt and sand class with associated falling velocities (see Table 3.1). This outfall is modelled using the Lagrangian approach.

• The diffuser bypass:

At this location, a release only occurs during times of high rainfall exceeding the capacity of the diffuser outlet. Contaminants and sediments are release at a constant rate with a flow of $1580 \text{ m}^3.\text{s}^-$



¹. According to the sediment sampling, only one grain size is modelled from this outfall: a silt class with associated falling velocities (see Table 3.1). This outfall is modelled using the Eulerian approach.

• The overflow spillway:

The release from this location is related to extreme rainfall event and only occurs on short time on top of the stormwater outfall. The flow out of the spillway is directly link to the rainfall. Similarly to the stormwater outfall, only one grain size (silt) is modelled out of this location. This outfall is modelled using the Eulerian approach.

The release of pollutants into an oceanic or estuarine environment through an outfall is a process that is generally either continuous over time or at defined tidal stages, as for Whangarei Harbour. These discharges are often subject to significant fluctuations in released quantities. The outcome of such releases is inherently non-deterministic and is governed, in part, by random variables such as currents, turbulences, wastewater network use and precipitation, it is therefore difficult to accurately predict when such events will occur.

However, the probability of future estuarine conditions can be assessed from the historical conditions, thereby allowing estimations of the general geographical dispersion expected. In the present study, the approach consists in running year-long simulations within two contrasting historical contexts (La Niña /El Niño episodes, June 2010 - June 2011, and June 2015 - June 2016, respectively), actual events and extreme events.

• year-long simulations:

During El Niño conditions, New Zealand typically experiences stronger or more frequent westerly winds during summer. This leads to a greater risk of drier-than-normal conditions in east coast areas and more rain than normal in the west. In winter, colder southerly winds tend to prevail, while in spring and autumn, south-westerlies tend to be stronger or more frequent, bringing a mix of the summer and winter effects.

During La Niña conditions, more north–easterly winds are typical, which tend to bring more moist, rainy conditions to the north–east of the North Island, and reduced rainfall to the South and South–West of the South Island.

By considering both La Niña /El Niño episodes, a robust probabilistic estimate of the plume dispersion and dilution patterns can be determined and thus provide guidance on expected concentration levels associated with the Whangarei discharge outfall.

El Niño and La Niña events are modelled in June 2010-June 2011, and June 2015-June 2016, respectively. During those simulations only the existing diffuser is modelled (Table 3.2).

• Actual events:

In this case, RNZ has provided 13 historical events over the last 3 years where high rainfall events required the diffuser bypass to be operated (and in one case the spillway to be opened). During those events, outfall from the diffuser is continuous in time and the stormwater overflow is opened and

closed during specific times. For all the 13 modelled events only one of them includes the spillway overflow (event on 26/03/2017, Table 3.2).

• Extreme events:

In order to capture every possible scenario, different spillway overflows were simulated based on various tidal states (low tide or high tide), wind speeds (4, 8 and 15 m.s⁻¹) and wind directions (North-East or South-East). Those simulations are simulated along with a 100-year average recurrence interval (ARI) event. Fluvial discharges for the salient rivers and streams entering the harbour are also considered. During this event, the three outfalls (diffuser, diffuser bypass and spillway) are discharging wastewater (Table 3.2).

Table 3.1Summary of the type of wastewater and sediment release for each of the outfall.

Location/discharge		Falling velocity [mm/s]	Fraction [%]	Size [mm]
	Contaminant	0	100	-
spillway/bypass	Silt	0.5	100	0.02777
	Sand	-	-	-
	Pollutant	0	100	-
Diffuser outfall	Silt	3.1	58.23	0.06
	Sand	218.1	41.77	1.5

Table 3.2Summary of outfall location for each of the cases modelled

Case/Location	Existing diffuser	Diffuser bypass	Overflow spillway		
Year-long simulation	On	Off	Off		
Actual event	On	On	On/Off		
Extreme event	On	On	On		

Summary of all parameters used for each of the event modelled. Table 3.3

Eve Disch		Diffuser event [NZST]	Diffuser bypass event [NZST]	Spillway event [NZST]	Outfall temp [deg]	Outfall salinity [PSU]	Diffuser sediment discharge [mg/L]	Diffuser bypass Sediment discharge [mg/L]	Spillway sediment discharge [mg/L]	Diffuser bypass contaminant discharge [mg/L]	Spillway contaminant discharge [mg/L]
Actual event		10/08/16	10/08/16	-	17.3272	4.6365	72	72	0	1	1
		08/03/17	08/03/17	-	23.8809	3.9323	14	14	0	1	1
		26/03/17	26/03/17	26/03/17	23.8809	3.9323	24	24	24	1	1
		04/04/17	04/04/17	-	20.8158	4.7133	11	11	0	1	1
		12/04/17	12/04/17	-	20.8158	4.7133	8	8	0	1	1
	vent	02/06/17	02/06/17	-	17.6013	7.03	33	33	0	1	1
	la le	04/01/18	04/01/18	-	25.6252	3.5742	20	20	0	1	1
	Acti	12/03/18	12/03/18	-	23.8809	3.9323	7	7	0	1	1
		28/04/18	28/04/18	-	20.8158	4.7133	5	5	0	1	1
		20/06/18	20/06/18	-	17.6013	7.03	13	13	0	1	1
		15/07/18	15/07/18	-	15.8018	2.5818	28	28	0	1	1
		24/12/18	24/12/18	-	23.3944	3.2387	10	10	0	1	1
		29/12/18	29/12/18	-	23.3944	3.2387	5	5	0	1	1
e events	High tide	26/03/17	26/03/17	27/03/17	23.8809	3.9323	24	24	24	1	1
Extreme	Low tide	26/03/17	26/03/17	27/03/17	23.8809	3.9323	24	24	24	1	1
Year-	long events	01/05/10	-	-	variable	variable	24	0	0	0	0
Year- long events		01/05/15	-	-	variable	variable	24	0	0	0	0





Figure 3.5 Aerial photo of Marsden Point showing the location of the three outfalls considered in this study



4. Results

4.1 Hydrodynamic model calibration and validation

4.1.1 Elevation

Measured sea level data from inside and outside Whangarei harbour (see Figure 2.1 and Figure 2.2) are given in Figure 4.1 and Figure 4.2, respectively and show a typical spring/neap tidal signal.

Comparisons show that the model successfully reproduces the propagation of the tidal wave through Whangarei harbour, with good agreement between both amplitudes and phases.





Figure 4.1 Comparison of modelled (red) and measured (blue) tidal elevation inside the harbour at K17, P10, W2 and Parua Bay in May 2015.









4.1.2 Velocities

The direct comparison of the near-surface speeds and direction for the two sites are presented in Figure 4.3 and Figure 4.4, respectively. Comparison of the near-bottom speeds and directions are shown in Figure 4.5 and Figure 4.6, respectively.

The comparisons between measured and modelled near-surface tidal currents at the two ADCP sites are shown in Figure 4.7 and Figure 4.8. Time series of the eastward and northward residual current velocities at three levels of the water column for the two sites are presented from Figure 4.9 to Figure 4.12.

Results at near-surface, mid-depth and near-bottom from the moving vessel ADCP near Marsden Point are presented in Figure 4.13.

In general, the measured and modelled velocities are in agreement. The model reproduces the circulation in Bream Bay and near Marsden Point.

Separation of the total velocity into tidal (Figure 4.7 and Figure 4.8) and residual (Figure 4.9 to Figure 4.12) components indicates that the model generally reproduces the phase and amplitude of tidal flows. The comparison of the residual component of the velocity shows a good near-bottom validation. However, the model does not fully reproduce some of the events in the near-surface layer since this layer is easily influenced by the local wind variations which are only partially captured in the atmospheric model. Irrespective, given the environs is tidally dominated and residuals are comparatively small the impact of not capturing some of the fluctuations in the near-surface layer is considered minor.





Figure 4.3 Measured (blue) and modelled (red) near-surface current speeds at two ADCP sites in Bream Bay from March 2016 to May 2016.





Figure 4.4 Measured (blue) and modelled (red) near-surface current directions at two ADCP sites in Bream Bay from March 2016 to May 2016.




Figure 4.5 Measured (blue) and modelled (red) near-bottom current speeds at two ADCP sites in Bream Bay from March 2016 to May 2016.



Figure 4.6 Measured (blue) and modelled (red) near-bottom current directions at ADCP2 (top) and ADCP3 (bottom) in Bream Bay from March 2016 to May 2016.





Figure 4.7 Measured (blue) and modelled (red) surface tidal speed at ADCP2 (top) and ADCP3 (bottom) from March 2016 to May 2016.





Figure 4.8 Measured (blue) and modelled (red) surface tidal direction at ADCP2 (top) ADCP3 (bottom) from April 2016 to May 2016.





Figure 4.9 Measured (blue) and modelled (red) East-West residual current velocities at ADCP2 for three level of the water column in March 2016 to April 2016.





Figure 4.10 Measured (red) and modelled (blue) North-South residual current velocities at ADCP2 for three level of the water column in March 2016 to April 2016.





Figure 4.11 Measured (blue) and modelled (red) East-West residual current velocities at ADCP3 for three level of the water column in April 2016 to May 2016.





Figure 4.12 Measured (blue) and modelled (red) North-South residual current velocities at ADCP3 for three level of the water column in April 2016 to May 2016.



near-surface



Mid-depth



near-bottom



Figure 4.13 Aerial photography from Marsden point representing vector of current velocity from the Moving-vessel ADCP (blue) and the hindcast data (red).



4.1.3 Temperature

Time series of near-bottom temperature at ADCP2 and ADCP3 are presented in Figure 4.14. The daily temperature variation is well represented in the model time series as well as the seasonal drop in temperature occurring in May 2016.





Figure 4.14 Comparison of near-bottom temperature measured (blue) against modelled (red) at ADCP2 (top) and ADCP3 (bottom) during March 2016 to May 2016.



4.2 Hydrodynamic at release location

Time-series of depth-average total current speed and direction at the approximate centre of the existing diffuser outfall is given in Figure 4.15 and Figure 4.16 for La Niña and El Niño periods, respectively.

Depth-average total current roses at the approximate centre of the existing diffuser outfall location are shown in Figure 4.17 and Figure 4.18 for the two simulation periods considered, i.e. 2010-2011(La Niña) and 2015-2016 (El Niño), respectively.

As expected, total current directions are bi-directional and, at the discharge site, are aligned with the thalweg of the channel, with maximum velocities in the order of \sim 1.0 m.s⁻¹ consistent with published navigation charts.





Figure 4.15 Depth-average total elevation (top), current speed (middle) and current direction (bottom) timeseries with the existing bathymetry (blue) and the reclaim/dredged bathymetry(red) for El Niño period from August 2015 to February 2016 at the diffuser location.





Figure 4.16 Depth-average total elevation (top), current speed (middle) and current direction (bottom) timeseries with the existing bathymetry (blue) and the reclaim/dredged bathymetry(red) for La Niña period from August 2010 to February 2011 at the diffuser location.





Figure 4.17 Depth averaged total current rose for the 2015-2016 periods (El Niño) with the existing bathymetry (left) and with the dredged/reclaim bathymetry (right).



Figure 4.18 Depth-averaged total current rose for the 2010-2011 periods (La Niña) with the existing bathymetry (left) and with the dredged/reclaim bathymetry (right).

4.3 Near-field modelling

The plume dilution at the boundary of the near-field, the near-field location and plume extents were defined using the USEPA-supported mixing zone model CORMIX.

The discharged plume consists of water that, once discharged at the port diffuser, will form a plume rising to the surface due to buoyancy gradients with respect to the ambient seawater.

CORMIX was run for a range of different discharge rates and ambient current velocities. Results are shown in Table 4.1 and Table 4.2 for the wastewater and sediment plume, respectively.

Ambient current velocity (m/s)	Dilution at the edge of the near-field	Centre of Near field plume at boundary (m)		Plume dimension (m)	
		Х	Y	Half width	Thickness
<0.05	158.4	98.44	167.3	124.39	0.28
0.1	94.8	138.05	78.44	61.55	0.41
0.2	25.5	5.77	11.33	2.4	2.4
0.4	64.5	14.61	8.57	5.34	5.34
0.6	107.5	27.41	7.43	5.63	5.63
0.8	149.4	44.13	6.6	5.75	5.75
>0.9	169.6	53.82	6.26	5.78	5.78

 Table 4.1
 Wastewater plume location and dimension, calculated by CORMIX, under different current speed.

 Table 4.2
 Sediment plume location and dimension, calculated by CORMIX, under different current speed

Ambient current velocity (m/s)	Dilution at the edge of the near-field	Near field location (m)		Plume dimension (m)	
		Х	Y	Half width	Thickness
<0.05	586	101	184	42	14
0.1	662.3	139.13	123.76	25.87	14
0.2	934	308	89.29	18.95	14
0.4	77.2	11.39	11.87	5.85	5.85
0.6	131.2	20.13	10.63	6.22	6.22
0.8	197.2	35.99	10.05	6.16	6.16
>0.9	233.1	47.8	9.88	6.77	6.77

4.4 Far field dispersion

Results from the Lagrangian and Eulerian methods were both post-processed to calculate a depth-average dilution and a concentration. This depth-average concentration was then divided by the water depth in order to obtain a unit in m³.

4.4.1 Release via existing diffuser

The outputs of the annual (El Niño/ La Niña) simulations of wastewater discharges were combined and postprocessed to produce average dilution for the entire period. The mean annual dilution over Whangarei harbour entrance is shown in Figure 4.19 and a zoom over Marsden Point is presented in Figure 4.21.



Figure 4.19 Average dilution over the year during El Niño (top) and La Niña (bottom) event using the existing (left) and reclaim (right) bathymetries. Note: the MM1 boundaries are defined using a Green outline and should not be confused with dilutions.



Figure 4.20 Marsden Point average dilution over the year during El Niño (top) and La Niña (bottom) event using the existing (left) and reclaim (right) bathymetries.

4.4.2 Actual events

The outputs of the actual events of wastewater discharges were combined and post-processed to produce mean dilution and concentration for 24h and 48h after the release started. As an example, the average dilution and sediment concentration for the event of 2016 (Table 3.3) from 0h to 24h after release is presented in Figure 4.21 and Figure 4.22. The average dilution from 24h to 48h after the start of the release are shown in Figure 4.23 and Figure 4.24.



Figure 4.21 Average dilution (top) and sediment concentration (bottom) for the first 24h after the release during the event of using the existing (left) and reclaim (right) bathymetries.



Figure 4.22Marsden point average dilution (top) and sediment concentration (bottom) for the first 24h after the release during
the event of using the existing (left) and reclaim (right) bathymetries.



Figure 4.23 Average dilution (top) and sediment concentration (bottom) for the next 24h after the release during the event of using the existing (left) and reclaim (right) bathymetries.



Figure 4.24 Marsden point average dilution (top) and sediment concentration (bottom) for the next 24h after the release during the event of using the existing (left) and reclaim (right) bathymetries.

4.4.3 Extreme events

The outputs of the extreme events of wastewater discharges were combined and post-processed to produce mean dilution and concentration for 24h and 48h after the release started. As an example, the first 24h average dilution and sediment concentration during a release from the spillway at high tide with a North-Easterlies wind of 15 m.s⁻¹ (Table 3.3) is illustrated in Figure 4.25 and Figure 4.26. The average dilution and sediment concentration between 24h to 48h after the start of the release are shown in Figure 4.27 and Figure 4.28.



Figure 4.25 Average dilution (top) and sediment concentration (bottom) for the first 24h after the high tide release during an extreme event with a North-Easterlies wind of 15 m.s⁻¹ using the existing (left) and reclaim (right) bathymetries.



Figure 4.26 Marsden point average dilution (top) and sediment concentration (bottom) for the first 24h after the high tide release during an extreme event with a North-Easterlies wind of 15 m.s⁻¹ using the existing (left) and reclaim (right) bathymetries.





Figure 4.27 Average dilution (top) and sediment concentration (bottom) for the next 24h after the high tide release during an extreme event with a North-Easterlies wind of 15 m.s⁻¹ using the existing (left) and reclaim (right) bathymetries.





Figure 4.28 Marsden point average dilution (top) and sediment concentration (bottom) for the next 24h after the high tide release during an extreme event with a North-Easterlies wind of 15 m.s⁻¹ using the existing (left) and reclaim (right) bathymetries.



4.5 Site specific concentration time series

Time series of both absolute dilution and sediment concentrations were extracted at several sites within the model domain (Figure 4.29).

In the present application, some of the sites of interest are in shallow waters, and can even be dry at times. The division by the water depth can therefore result in pollutant dilution spikes during periods of low water levels. Therefore, dilution at the shallowest sites such as P6 or P1 should be interpreted carefully.

As an example, time series of water elevation, depth averaged dilution and sediment concentration at C2 for the event of 2016 are shown in Figure 4.30. Time series for the extreme event under North-Easterlies wind at 15 m.s⁻¹ are shown in Figure 4.31.

As an example, time series of water elevation, surface and bottom dilution and sediment concentration at C1 for the event of 2016 are shown in Figure 4.32. Time series for the extreme event under North-Easterlies wind at 15 m.s⁻¹ are shown in Figure 4.33.

As an example, time series of water elevation, surface and bottom dilution and sediment concentration at C1 for the event of 2016 are shown in Figure 4.34. Time series for the extreme event under North-Easterlies wind at 15 m.s⁻¹ are shown in Figure 4.35.

Due to the interpolation process, care should be taken when evaluating KDE derived values (see Section 3.4.1.1) for concentration/dilution near locations where elevated particle counts (either as passive tracers or sediment) can occur, specifically in areas adjacent to shallow water where;

- 1. the resident times of particles can be relatively long due to comparatively quiescent conditions resulting in higher concentrations when averaged over time,
- 2. the process of converting to depth averaged concentrations within a KDE framework can elevate apparent concentrations in shallower water, and
- 3. small fluctuations within the intertidal shallow areas may pool, with contaminant levels maintained at elevated levels due to the inability of the areas to effectively flush.

As such, locations close to shore should be considered 'worst-case' with respect to lower dilutions than would be expected.





Figure 4.29 Position of control sites where concentrations were extracted.



Figure 4.30 Time series of water elevation (grey), depth averaged dilution (top) and sediment concentration (bottom) at site C2 during the event of 2016 with the existing (red) and reclaim (blue) bathymetries.



Figure 4.31 Time series of water elevation (grey), depth averaged dilution (top) and sediment concentration (bottom) at site C2 during an extreme event with the existing (red) and reclaim (blue) bathymetries.



Figure 4.32Time series of water elevation (grey), surface and bottom dilution (top) and sediment concentration (bottom) at site
C1 during the event of 2016 with the existing (red) and reclaim (blue) bathymetries.



Figure 4.33Time series of water elevation (grey), surface and bottom dilution (top) and sediment concentration (bottom) at site
C1 during an extreme event with the existing (red) and reclaim (blue) bathymetries.



Figure 4.34 Time series of water elevation (grey), surface and bottom dilution (top) and sediment concentration (bottom) at site C2 during the event of 2016 with the existing (red) and reclaim (blue) bathymetries.



Figure 4.35Time series of water elevation (grey), surface and bottom dilution (top) and sediment concentration (bottom) at site
C2 during an extreme event with the existing (red) and reclaim (blue) bathymetries.

5. Summary

This study described the pollutant dispersion and dilution and sediment concentration patterns associated with the wastewaters discharged at Marden Point, within Whangarei harbour, New Zealand. The following are the key points:

- In order to quantify the hydrodynamics of Whangarei harbour, a 3D high resolution finite element model of the environs was established, including salient fluvial inputs.
- The hydrodynamic model was calibrated and validated using measured current velocity and water level data collected inside and outside the Harbour as well as adjacent to the release locations.
- At the diffuser locations the total (residual + tidal) current directions are bi-directional and are aligned with the thalweg of the channel, with velocities in the order of ~0.5/0.75 m.s⁻¹. Under extreme conditions (i.e. during large flood events), total current velocities can approach 1.0 m.s⁻¹ near the discharge site.
- Near-field modelling of the initial turbulent mixing of the discharged waters was undertaken using the USEPA-supported mixing zone model CORMIX; providing the initial dilution rates and the near-field plume dimensions under a range of different discharge characteristics and ambient current velocities.
- The dispersion modelling, showing the expected dilution and sediment concentration, consisted in simulating three cases: (1) A realistic wastewater discharge over two different year-long simulations within contrasting ambient forcing contexts of El Niño and La Niña episodes; (2) Actual events based on real-world events; (3) Extreme events with 100 years return period flow associated with different winds scenarios.
- Annual time-series of pollutant dilution and concentration were extracted at a number of control sites for further analysis.

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Appendix 6: Memo to NRC on mixing zone



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17 June 2020

Riaan Elliot Environmental Affairs Manager Refining NZ

Dear Riaan

Response to NIWA review of Streamlined Environmental Ltd report: mixing zone size

- (1) This memo addresses an issue raised in a memo provided by Dr Bell (NIWA) dated 23/03/20 following his external review of my report titled "Water quality assessment at Marsden Point oil refinery to inform resource consent renewal applications" (Stewart (2019)).
- (2) This memo addresses the issue of mixing zone size.

Dr Bell's review

- (3) I understand that the purpose of Dr Bell's review was specifically to review the dispersion modelling relied upon in my assessment in Stewart (2019).
- (4) In his review, Dr Bell states that in his opinion "[t]he overall findings, i.e. that a few compounds or contaminants require some further in-situ dilution in more adverse discharge events, probably wouldn't change, but there are some issues with the way the dilutions have been calculated and applied as inputs within the far-field model."

- (5) Dr Bell cites three main issues. Brett Beamsley (MetOcean Solutions) is addressing the first two issues in a separate memo. In this memo I address the third issue, which Dr Bell states is:
 - "3. What is reasonable mixing? or what are the mixing lengths required for contaminants for RQ [Risk Quotient] to reduce to <1 with in-situ mixing?

It appears the rectangular mixing zone has already been prescribed by a former consenting process, which appears to be ~750 m in length (scaled from the latitude/longitude positions) for the main outfall. In the reports (Streamlined and Appendix 5) there is no discussion around what is reasonable mixing (Policy 23, NZCPS), based on what the mixing lengths are to achieve RQ<1 for each of the outlets/outfalls operating at the time of an adverse discharge event. Policy 23 requires the smallest mixing zone necessary to achieve the required water quality in the receiving environment. These aspects have not been clearly appraised from the modelling and analysis. Again, as discussed above, a desk exercise to calculate the minimum initial dilution versus distance from source around slack-tide periods would have been a useful way to triage any particular contaminants of concern and the extent of the mixing length to achieve the required water quality threshold. In the case of NH_{4^-} N, I agree it doesn't present as a water quality issue (e.g. algal blooms) if the threshold is only exceeded episodically during some adverse events."

My response to Dr Bell's review: the mixing zone used/proposed is appropriate

Planning framework: mixing zones

- (6) Several applicable planning documents contain provisions that are relevant to the concept of mixing zones, including the issue of mixing zone size. I set out in full in **Appendix One** relevant provisions from the New Zealand Coastal Policy Statement 2010 ("NZCPS"), the Operative Regional Coastal Plan for Northland ("Operative Regional Plan"), and the Proposed Regional Plan for Northland ("Proposed Regional Plan"). In summary, the planning framework provides the following with respect to mixing zone size:
 - (a) The NZCPS defines "mixing zone" as "the area within which 'reasonable mixing' of contaminants from discharges occurs in receiving waters and within which the relevant water quality standards do not apply".
 - (b) The Proposed Regional Plan definition of "zone of reasonable mixing" sates that for the purposes of activities that require resource consents the zone of reasonable mixing will be determined "consistent with" the zone of reasonable mixing applying to permitted discharges (being 20m from the point of discharge) "unless the nature and scale of the discharge requires that a case-by-case basis determination is

more appropriate, in which case the extent of departure from the zone... will be determined in accordance with Policy D.4.4 Zone of reasonable mixing."

- (c) The NZCPS (Policy 23)¹ and the Proposed Regional Plan (Policy D.4.4(1)) provide that mixing zones used shall be the smallest size necessary to achieve the required water quality in the receiving environment.
- (7) In addition to the provisions identified above which apply to mixing zones generally, the Operative Regional Plan maps and the Proposed Regional Plan maps² both also specifically identify the mixing zone applying to Refining NZ's coastal discharges (as identified in the resource consent currently authorising those discharges).
- (8) The NZCPS (Policy 23) and the Operative and Proposed Regional Plans also contain a suite of provisions regarding the *effects* of coastal discharges within and outside mixing zones (see **Appendix One**); and both the Operative Regional Plan and the Proposed regional Plan contain coastal a range of water quality standards.

A bespoke mixing zone is necessary and appropriate for the refinery

(9) In my opinion, Refining NZ's coastal discharges clearly justify a bespoke mixing zone, as opposed to an arbitrary default mixing zone size such as the "20m from the point of discharge" identified in the Proposed Regional Plan. As outlined in detail in Stewart (2019) and De Luca (2019), the nature and scale of the discharges mean that a departure from the Proposed Regional Plan's default is appropriate. A significant body of data/evidence is available – and has been presented in support of the re-consenting proposal – to justify a larger bespoke mixing zone area for Refining NZ's coastal discharges.

The current mixing zone for the refinery

² See the Operative Regional Plan and Proposed Regional Plan maps. These were included as Figure 1 and Figure 2 respectively in Stewart (2019). I understand that while the Decisions version of the Proposed Regional plan identified the mixing zone in the wrong position (slightly), this has recently been corrected by way of Environment Court consent order.



¹ In his review, Dr Bell refers to Policy 23 of the NZCPS which provides that the smallest mixing zone necessary to achieve the required water quality in the receiving environment shall be used. I note that this is not consistent with the Operative Regional Plan (which pre-dates the NZCPS), which does not specify or set out detailed provisions on mixing zone size (but which does show the mixing zone currently applying the Refining NZ discharge under the existing resource consent - see paragraph (11) of this memo). As identified above, Policy 23 of the NZCPS is, however, consistent with the Proposed Regional Plan, specifically Policy D.4.4. Notwithstanding the different approaches to mixing zones within the applicable plans, I acknowledge the requirement that the mixing zone size should be the smallest to achieve the required water quality in the receiving environment.

(10) The resource consent that currently authorises Refining NZ's coastal discharges specifies a mixing zone with a length of ~750m, a width of ~200m, and a surface area of ~150,000 m^{2} .³

The mixing zone proposed for the re-consenting proposal (and used for assessment to date)

(11) The mixing zone that is proposed to apply to Refining NZ's coastal discharges associated with the re-consenting proposal is the same mixing zone that is identified under Refining NZ's current resource consent, which is also the mixing zone identified in the planning maps for both the Operative Regional Plan and the Proposed Regional Plan. The water quality assessment undertaken for the re-consenting proposal (Stewart (2019)) assesses effects on water quality outside that mixing zone. The method used for the assessment calculated concentrations of stormwater basin contaminants at specific sites (including the four corners of the current mixing zone) after dilution in the receiving environment.

Analysis of, and justification for, the mixing zone proposed/used

- (12) In terms of the mixing zone size applying to Refining NZ's coastal discharges, I consider that there are three options: (a) maintain the mixing zone at the current size (i.e. the *status quo*); (b) reduce the size of the mixing zone; or (c) increase the size of the mixing zone.
- (13) Based on my water quality assessment (Stewart (2019)) and Dr De Luca's marine ecology assessment (De Luca (2019)), in my opinion the mixing zone proposed/used (being the *status quo* of maintaining the mixing zone at the current size) is appropriate. Reasons include:
 - (a) The mixing zone proposed/used is the smallest extent necessary to achieve the required water quality in the receiving environment.⁴
 - (b) Within the proposed mixing zone, effects on the life-supporting capacity of water will be minimised and are appropriate (being minor at worst).⁵ In particular, the mixing zone contaminant concentrations and levels of dissolved oxygen will not cause acute toxicity effects on aquatic ecosystems.⁶

³ Refer Resource Consent AUT.008319.01.04. A map showing the location of the mixing zone is provided in Stewart (2019) (see Figure 13).

⁴ NZCPS Policy 23(e) and Proposed Regional Plan Policy D.4.4(1).

⁵ NZCPS Policy 23(f).

⁶ Proposed Regional Plan Policy D.4.4(2).

- (c) After reasonable mixing, significant adverse effects on ecosystems and habitats will be avoided;⁷ and overall water quality will be maintained.⁸
- (14) The above conclusions have been arrived at following comprehensive assessment, including with respect to the sensitivity of the receiving environment; the nature and concentration of the contaminants to be discharged (and associated risks); and the capacity of the receiving environment to assimilate contaminants.⁹
- (15) Below I outline the analysis underpinning the above conclusions.
- (16) As stated in paragraph 11, the method used for the assessment calculated concentrations of stormwater basin contaminants at specific sites (including the four corners of the current mixing zone) after dilution in the receiving environment. The hydrodynamic modelling undertaken for the re-consenting proposal (MetOcean Solutions, 2019) includes all tidal flows, including slack-tide periods (the time when dilution will be limited due to low tidal flows).
- (17) Calculated concentrations of stormwater basin contaminants at specific sites were assessed against surface water quality guidelines (SWQG),¹⁰ which were a combination of coastal water quality standards from both the Operative and Proposed Regional Plans, the Australian and New Zealand (ANZ) Guidelines for Fresh and Marine Water Quality 95% marine default guideline values (DGV), and water quality indices from Auckland Council.¹¹ Generally, the most restrictive SWQG values were used for the assessment.
- (18) The water quality assessment (Stewart, 2019) used practical normal-case¹² and worst-case¹³ scenarios to assess frequency and scale of adverse effects of the Refinery stormwater basin discharge on water quality outside the current mixing zone. As addressed in detail in Stewart (2019) and subsequent assessment:

- median dilution at each site;
- median SWB contaminant concentrations;
- up to 24 hours after discharge.

- lowest practical dilution at each site;
- maximum SWB contaminant concentrations;
- up to 24 hours after discharge.

⁷ NZCPS Policy 23(d).

⁸ Proposed Regional Plan Policy D.4.1(1).

⁹ NZCPS Policy 23(1)(a)-(c).

¹⁰ Stewart (2019) used the term surface water quality guidelines (SWQG) instead of surface water quality standards as some metrics used for assessment are guidelines and not standards.

¹¹ Refer Table 3 in Stewart (2019).

¹² A practical normal-case scenario for annual, actual and extreme modelled events was used, consisting of:

¹³ A practical worst-case scenario for annual, actual and extreme modelled events was used, consisting of:

- (a) Under the normal-case scenario, negligible effects on water quality were exhibited for all contaminants assessed.
- (b) Under the worst-case scenario, a few contaminants may exhibit no more than minor <u>and</u> transitory effects on water quality: ammoniacal nitrogen (NH₄-N); faecal coliforms (FC); the every-day process formulations Cortrol OS7780, Steammate NA0880, and BetzDearborn; the Refinery shutdown process chemical CC414P; and fire training foam Solberg DoD3155.
- (19) Whole effluent toxicity testing of the stormwater basin discharge showed that for 11 out of 12 tests a low dilution was required (1-8 times) within the current mixing zone in order to avoid adverse effects on the test organism. One test showed that a 256 times dilution was required to completely avoid effects on blue mussel larval development in that single instance (De Luca, 2019). This is 4-fold higher than the minimum dilution modelled under worst-case scenario (63 times, at Marsden Bank), suggesting the possibility for short-term adverse effects on blue mussel larval development at this site.
- (20) Dr Bell states in his review that "a desk exercise to calculate the minimum initial dilution versus distance from source around slack-tide periods would have been a useful way to triage any particular contaminants of concern and the extent of the mixing length to achieve the required water quality threshold." Based on the comprehensive analysis undertaken, including modelling of all tidal flows (including slack tides), I do not agree with Dr Bell that it would be useful or necessary to carry out a further desktop exercise around slack-tide periods to define the extent of the mixing length to achieve the required water quality threshold. Instead, I am of the opinion that there is sufficient scientific evidence, using a weight of evidence approach, to conclude that the current mixing zone is appropriate in the context of the panning framework. This includes the required water quality in the receiving environment.
- (21) Reducing the size of the mixing zone will likely increase the frequency and magnitude of exceedances of the applicable water quality standards/guidelines at the mixing zone boundary (particularly as described by the worst-case scenarios). Therefore, I do not consider it is feasible or appropriate to materially reduce the size of the proposed mixing zone, because to do so will mean that the required water quality standards/guidelines are not achieved outside of the mixing zone.¹⁴

¹⁴ See NZCPS Policy 23(e) and Proposed Regional Plan Policy D.4.4(1).

- (22) Increasing the size of the mixing zone will likely reduce the frequency and magnitude of exceedances of the applicable water quality standards/guidelines at the mixing zone boundary (particularly as described by the worst-case scenarios). However, the effects associated with such exceedances are considered to be no more than minor <u>and</u> transitory by the water quality assessment (Stewart, 2019) and less than minor by the ecological assessment (De Luca, 2019).
- (23) As the planning documents state that the mixing zone should be the smallest to achieve the required water quality in the receiving environment, the proposed mixing zone satisfies this. I do not consider there is a strong argument to increase the size of the current mixing zone.

Summary

- (24) In my opinion, scientific evidence demonstrates that the current (and proposed) mixing zone size is the correct size to achieve the required water quality in the receiving environment and is otherwise appropriate.
- (25) Based on my assessment and Dr De Luca's assessment, in summary I consider:
 - (a) The proposed mixing zone satisfies the planning framework directive that the mixing zone be the smallest extent necessary to achieve the required water quality in the receiving environment.
 - (b) Within the proposed mixing zone, effects on the life supporting capacity of water will be minimised and are appropriate (being minor at worst). In particular, the mixing zone contaminant concentrations and levels of dissolved oxygen will not cause acute toxicity effects on aquatic ecosystems.
 - (c) After reasonable mixing, significant adverse effects on ecosystems and habitats will be avoided; and overall water quality will be maintained.
- (26) Therefore, in my opinion the proposed mixing zone, satisfies the relevant water quality provisions of the applicable planning documents. As a result, I do not consider there is any compelling justification to change the size of the proposed mixing zone.

Yours sincerely

Dr Mike Stewart

Director/Environmental Chemistry Specialist



References

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- Stewart, M., 2019. Water quality assessment at Marsden Point oil refinery to inform resource consent renewal applications. Report # RNZ1801-FINAL CONSULTATION DRAFT-Dec2019, Streamlined Environmental, Hamilton, 234 pp. (Stewart (2019))



Appendix One - relevant planning provisions

NZCPS

The **definition** of "Mixing Zone" is:

The area within which 'reasonable mixing' of contaminants from discharges occurs in receiving waters and within which the relevant water quality standards do not apply.

Policy 23

- 1) In managing discharges to water in the coastal environment, have particular regard to:
 - *a*) *the sensitivity of the receiving environment;*
 - b) the nature of the contaminants to be discharged, the particular concentration of contaminants needed to achieve the required water quality in the receiving environment, and the risks if that concentration of contaminants is exceeded; and
 - c) the capacity of the receiving environment to assimilate the contaminants; and:
 - d) avoid significant adverse effects on ecosystems and habitats after reasonable mixing;
 - e) use the smallest mixing zone necessary to achieve the required water quality in the receiving environment; and
 - *f*) *minimise adverse effects on the life-supporting capacity of water within a mixing zone.*

Operative Northland Regional Plan

32 Assessment criteria

32.2.3 Discharges to coastal waters

32.2.3.5. Whether the level of treatment proposed will ensure that, after reasonable mixing, the water quality standards applicable to the receiving waters are met.

32.2.3.7. Whether provision has been made to aid the mixing of the discharged waters with the receiving waters.

31. Rules

31.4 Marine 2 (Conservation) Management Area

31.4.13 (c) General Performance Standards

Discharges to water shall, after reasonable mixing, comply with the relevant receiving water quality standards and shall not contain any contaminants which could cause:

- *i.* the production of conspicuous oil or grease films, scums or foams, or floatable or suspended materials.
- *ii.* any conspicuous change in the colour or visual clarity of the receiving waters.

- *iii.* any emission of objectionable odour.
- iv. accumulation of debris on the foreshore or seabed underlying or adjacent to the discharge point.
- v. any significant adverse effects on aquatic life or public health.

31.7 Marine 5 (Port Facilities) Management Area

31.7.12 (c) General Performance Standards

Discharges to water shall, after reasonable mixing, comply with the relevant receiving water quality standards and shall not contain any contaminants which could cause:

- *i.* the production of conspicuous oil or grease films, scums or foams, or floatable or suspended materials.
- *ii.* any conspicuous change in the colour or visual clarity of the receiving waters.
- iii. any emission of objectionable odour.
- iv. accumulation of debris on the foreshore or seabed underlying or adjacent to the discharge point.
- v. any significant adverse effects on aquatic life or public health.

Proposed Northland Regional Plan (Appeals Version - 29 July 2019)

The "zone of reasonable mixing" definition for coastal water is:

For the purpose of a discharge of a contaminant permitted by a rule in this Plan:

- ...
- (2) in relation to a lake, wetland or coastal water, a distance 20 metres from the point of discharge.
- (3) For the purpose of activities that require resource consent, the zone of reasonable mixing will be determined consistent with... above unless the nature or scale of the discharge requires that a case by-case basis determination is more appropriate, in which case the extent of departure from the zone defined above will be determined in accordance with Policy D.4.4 Zone of reasonable mixing.

D.4.4 Zone of reasonable mixing

When determining what constitutes the zone of reasonable mixing for a discharge of a contaminant into water, or onto or into land in circumstances which may result in that contaminant (or any other contaminant emanating as a result of a natural process from that contaminant) entering water, have regard to:

- 1) using the smallest zone necessary to achieve the required water quality in the receiving waters as determined under Policy D.4.1, and
- 2) ensuring that within the mixing zone contaminant concentrations and levels of dissolved oxygen will not cause acute toxicity effects on aquatic ecosystems.

D.4.1 Maintaining overall water quality¹⁵

When considering an application for a resource consent to discharge a contaminant into water:

- 1) have regard to the need to maintain the overall quality of water including the receiving water's physical, chemical and biological attributes and associated water quality dependent values, and
- 2) have regard to the coastal sediment quality guidelines in H.3 Water quality standards and guidelines, and
- 3) generally not grant a proposal if it will, or is likely to, exceed or further exceed a water quality standard in H.3 Water quality standards and guidelines.

¹⁵Appeal to Environment Court by i) Minister of Conservation ENV-2019-AKL-000122; ii) Mangawhai Harbour Restoration Society ENV-2019-AKL-000110; iii) NIWA ENV-2019-AKL-000108.