

REPORT NO. 3843

**RISK ASSESSMENT OF EMERGING ORGANIC
CONTAMINANTS IN THE TREATED DISCHARGE
FROM THE NELSON NORTH WASTEWATER
TREATMENT PLANT**

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RISK ASSESSMENT OF EMERGING ORGANIC CONTAMINANTS IN THE TREATED DISCHARGE FROM THE NELSON NORTH WASTEWATER TREATMENT PLANT

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EXECUTIVE SUMMARY

Emerging organic contaminants (EOCs) are synthetic or naturally occurring chemicals or micro-organisms that are not commonly monitored but have the potential to enter the environment and cause adverse ecological and / or human health effects. Nelson City Council (NCC) contracted Cawthron Institute (Cawthron) and Northcott Research Consultants Limited (by subcontract) to analyse a suite of EOCs (chemicals only) in samples of treated wastewater from the Nelson North Wastewater Treatment Plant (NWWTP) and assess their ecological risks. This study was undertaken to inform an assessment of environmental effects of the discharge in support of an application for the renewal of the coastal permit (SAR 05-61-01-06), which authorises the discharge of treated wastewater into Tasman Bay / Te Tai-o-Aorere (hereafter Tasman Bay).

We measured EOCs in two samples of treated wastewater from NWWTP (Sample 1 – dry weather; Sample 2 – wet weather), compared the concentrations obtained with those detected in other WWTPs in Aotearoa New Zealand and identified EOCs whose concentrations in the discharge may pose a risk to Tasman Bay biota. A total of 45 of the 84 individual EOCs analysed were detected in at least one of the samples. These included alkyl phosphate flame retardants (7); phenolic antimicrobial chemicals (5); paraben preservatives (3); industrial alkylphenols, including the industrial mixture of technical nonylphenols (3); insect repellents (3); polycyclic and nitro-musk fragrances (5); acidic pharmaceuticals (7); plasticisers (9); and steroid hormones (3) (numbers in brackets identify classes of chemical compounds).

Of the 45 EOCs detected for which there were existing data for comparison, the concentration of 23 compounds exceeded the previous maximum concentrations recorded in New Zealand treated wastewater. The concentrations of the remaining 22 EOCs either fell below or were within the range of those previously measured in samples from other New Zealand plants using a broad range of treatment technologies. The concentrations of EOCs were generally higher in Sample 1 (41 of 45 EOCs) than in Sample 2. The concentrations of the industrial alkylphenols 4-tert-octylphenol and technical nonylphenol, the pharmaceutical acetaminophen and the plasticiser metabolite monomethyl phthalate were all higher in Sample 2 (wet weather flow).

Although the comparative database of samples from New Zealand plants is quite limited, the relatively high concentrations of several EOCs suggest that the NWWTP may not be as effective in reducing organic chemicals as other treatment plants in New Zealand. However, the efficacy of removal cannot be properly quantified without analysis of hydraulically linked influent/effluent samples.

Some EOCs were measured at concentrations up to two orders of magnitude higher than their respective predicted no-effect concentration (PNEC) values. Hence, a minimum of 100:1 dilution in the discharge-receiving environment is required to reduce the risk posed by these EOCs to marine biota. Based on hydrodynamic modelling for projected 2059 flow

scenarios, median and first percentile dilutions at the mixing zone boundary for the NWWTP discharge have been estimated to be $\geq 2,300:1$ and $280:1$, respectively(). This available dilution is sufficient to reduce receiving water concentrations of these chemicals to below their PNEC values. Consequently, while mindful of the low sample number, the ecological risk from the NWWTP discharge can be considered very low based on the available evidence.

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ABBREVIATIONS

BPA	Bisphenol A
EOCs	Emerging organic contaminants
GCMS	Gas chromatography mass spectrometry
MCPB	4-(4-chloro-2-methylphenoxy)butanoic acid
MDLs	Method detection limits
MS/MS	Tandem mass spectrometry
MSTFA	N-methyl-N-(trimethylsilyl)trifluoroacetamide
MTBSTFA	N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide
NC	Negligible concentration
NCC	Nelson City Council
NOEC	No observable-effect concentration
NWWTP	Nelson North Wastewater Treatment Plant
PNEC	Predicted no-effect concentration
ppt	Parts per trillion
SPE	Solid-phase extraction
TBDMSCI	t-butyldimethylsilyl chloride
TBEP	Tris(2-butoxyethyl)phosphate
TCPP	Tris(1-chloro-2-propyl)phosphate
TDCP	Tris[2-chloro-1-(chloromethyl)ethyl]phosphate
TNP	Technical nonylphenol
TPP	Triphenyl phosphate

GLOSSARY

Alkylphenols	Organic industrial chemicals used in the production of lubricating oil additives, laundry and dish detergents, emulsifiers and solubilisers.
Nitro- and polycyclic musk fragrances	Synthetic fragrance ingredients typically used in cosmetics, perfume, air fresheners, cleansing agents, detergents and soap. Musks are also used as food additives, and in cigarettes and fish baits.
Parabens	Group of preservative ingredients used in cosmetics, personal hygiene products, food products and pharmaceuticals.
Pharmaceuticals	Chemicals used in the diagnosis, treatment or prevention of disease and for restoring, correcting or modifying organic functions.
Phosphorus flame retardants	Broad and expanding class of additive or reactive building blocks used to improve the fire safety of flammable materials such as plastics, textiles, wood and paper.
Phthalate esters and plasticisers	Chemicals that improve the fluidity of plastics during processing and their flexibility at room temperature.
Steroids	Natural hormones.

1. INTRODUCTION

1.1. Background

Nelson City Council (NCC) currently holds several resource consents associated with the operation of the Nelson North Wastewater Treatment Plant (NWWTP), including a coastal permit (SAR 05-61-01-06) that authorises the discharge of treated wastewater to Tasman Bay / Te Tai-o-Aorere (hereafter Tasman Bay). This resource consent was granted in 2004 for a duration of 20 years and expires in December 2024. The NWWTP lies on the seaward, northwest corner of an area of low-lying land in the upper parts of Nelson Haven between Glen Road and Boulder Bank Drive (Figure 1).

The wastewater treatment process consists of removal of gross solids through the inlet works, pre-treatment of influent flows to reduce biochemical oxygen demand and total suspended solids, pond-based treatment and final polishing through the wetland system, prior to discharge into Tasman Bay. The outfall consists of a buried cement pipe approximately 350 m long, which emerges from the seabed at its offshore end as an 18 m-long multiport diffuser at a water depth of 11 m (Barter & Forrest 1998). Wastewater is discharged through these ports via gravity flows.

Nelson City Council contracted Cawthron Institute (Cawthron) and Northcott Research Consultants Ltd (by subcontract) to assess the likelihood of emerging contaminants being present in the wastewater from the NWWTP, to support the application and assessment of environmental effects for the renewal of the coastal permit.

Emerging contaminants can be defined as synthetic or naturally occurring chemicals or micro-organisms that are not commonly monitored but have the potential to enter the environment, thereby causing known or suspected adverse ecological and / or human health effects (Rosenfeld & Feng 2011). Since the scope of our assessment does not include micro-organisms (these are addressed in a separate report; Campos 2023 [forthcoming]) and many of the chemicals tested are organic, we use the term emerging organic contaminants (EOCs) in this report.



Figure 1. Location of the NWWTP discharge point (red circle) in Tasman Bay / Te Tai-o-Aorere (inset map shows Boulder Bank Drive and oxidation pond in more detail).

1.2. Scope of this report

According to the New Zealand Coastal Policy Statement 2010, in managing wastewater discharges to the coastal environment, consideration must be given to the nature of the contaminants discharged, the capacity of the receiving environment to assimilate the contaminants and avoidance of significant adverse effects on ecosystems and habitats, after reasonable mixing (Department of Conservation 2010). To address these requirements, we have structured our report as follows:

- **Section 2** presents a brief overview of the sources of EOCs and their effects on the marine environment.
- **Sections 3 and 4** describe sample collection and laboratory testing methods, and presents the results of EOC monitoring in NWWTP wastewater samples.
- **Section 5** compares the EOC concentrations detected in NWWTP samples with those detected in samples taken from other treatment plants in New Zealand.
- **Section 6** presents the results of a risk assessment of EOCs in NWWTP wastewater samples to the receiving environment of Tasman Bay.
- **Section 7** provides the conclusions from the study pertaining to ecological risk in the coastal receiving environment.

2. SOURCES AND EFFECTS OF EMERGING CONTAMINANTS ON THE MARINE ENVIRONMENT

Wastewater discharges contain a mixture of EOCs that can cause a range of ecological and / or human health effects. Examples of classes of EOCs commonly detected in domestic wastewater include pharmaceuticals, plasticisers, antimicrobials, corrosion inhibitors, flame retardants, surfactants, UV filters, steroid hormones, musk fragrances and perfluorinated alkyl substances (Stewart & Tremblay 2020). Many EOCs are used in a wide variety of products and applications, and are therefore ubiquitous contaminants within domestic and industrial wastewaters. Most EOCs are synthetic, although some can occur naturally. The list is long and there is no internationally agreed classification for these substances.

The environmental occurrence and fate of EOCs have been documented in thousands of publications over the last two decades, highlighting the increasing concern about the potential ecological and human health effects of these chemicals (Morin-Crini et al. 2022). The diverse chemical forms and modes of action of EOCs makes it very challenging to identify and characterise them. Detection and quantification of EOCs is time-consuming, requires specialist chemistry knowledge and equipment, and needs highly sensitive methods to detect these substances at trace levels. Furthermore, the regulation of EOCs remains a challenge due to significant data gaps in characterising their ecotoxicological effects. Baseline data on photo- and biotransformation, abiotic transformation, and sorption and desorption processes are still lacking for many EOCs (Pal et al. 2010).

Most wastewater treatment processes used in Aotearoa New Zealand and overseas are not very effective at removing EOCs. Consequently, these chemicals are often discharged along with treated wastewater into receiving environments in their original forms. Several monitoring studies have found substantial reductions in EOC concentrations as the distance from wastewater discharges increases (Bolong et al. 2009). However, the concentrations vary markedly both spatially and temporally at any given site, reflecting local catchment characteristics and human activity. Rivers and coastal marine environments act as a sink for these contaminants and are exposure routes for bioaccumulation and biomagnification of some EOCs by aquatic organisms (Bolong et al. 2009).

An important aspect to consider when assessing the environmental effects of EOCs is that these chemicals can interact with other contaminants and environmental stressors (Schwarzenbach et al. 2006). As a result, organisms (including humans) are exposed to complex mixtures of chemicals, often with increased potency, where the individual chemicals themselves may be present at concentrations too low to raise concern (Stewart et al. 2016).

3. METHODS

3.1. Sample collection

Two 24-hour composite samples of wastewater were taken from the designated final wastewater channel (post-wetland treatment) at NWWTP by Nelmac Ltd personnel (on behalf of NCC) and delivered by courier to Northcott Research Consultants Ltd at Plant and Food Research Ruakura in Hamilton. The details of these samples are provided in Table 1. Sample 1 was collected following a dry-weather period (no rain over the previous 3 days), while Sample 2 was collected following a wet-weather period (12.3 mm of cumulative rain recorded at Wakapuaka Fire Station over the previous 3 days; TDC 2022).

Table 1. Details of samples collected for testing of emerging organic contaminants.

Sample information	Sample 1: November 2021	Sample 2: March 2022
Start date (time)	04/11/2021 (0730 h)	22/03/2022 (1145 h)
End date (time)	05/11/2021 (0730 h)	23/03/2022 (1145 h)
Temperature (°C)	15.5	18.9
Dissolved oxygen (mg/L)	3.3	1.6
pH	7.86	7.12
Conductivity (µs/cm)	3,183	3,661
Salinity (ppt)	1.7	1.9

On arrival at the laboratory, the samples were acidified (pH = 2.0) by the addition of concentrated sulphuric acid and filtered through a glass microfibre filter (47 mm, Labservice), topped with diatomaceous earth filter-aid medium (Hyflo® Super-Cel®, Sigma-Aldrich) to remove particulate material. Two aliquots of the filtered wastewater were collected in pre-cleaned glass Schott bottles (2 L and 0.5 L aliquots) and stored overnight under refrigeration. The wastewater samples were visually observed to contain residues of algae, and this was confirmed by the layer of green algal residue retained during the filtration of the samples.

3.2. Laboratory testing

3.2.1. Sample extraction

The prepared samples were extracted for analysis the following morning. The 2 L acidified and filtered wastewater sample destined for the analysis of EOCs excluding pharmaceutical compounds was spiked with a solution of carbon-13-labelled analogues of target EOCs for use as surrogate recovery compounds. The corresponding 0.5 L

acidified and filtered wastewater sample destined for analysis of acidic pharmaceuticals was spiked with a surrogate recovery solution containing the acidic herbicides dichlorprop, flamprop and 4-(4-chloro-2-methylphenoxy) butanoic acid (MCPB), and the plant growth regulator naphthalene acetic acid.

Neutral and phenolic EOCs were extracted from the 2 L wastewater sample by solid-phase extraction (SPE) using Waters™ Oasis HLB cartridges, and acidic pharmaceuticals from the 0.5 L wastewater sample using Waters™ Oasis MCX cartridges. EOCs eluted from the Oasis HLB SPE cartridge were purified using Florisil® adsorption chromatography, followed by gel permeation chromatography to remove the large amount of residual fats and lipids that can be present in WWTP wastewater samples.

The purified EOC sample extract was split into two equal portions – one for analysis of neutral EOCs, and the other for polar EOCs requiring chemical derivatisation prior to analysis by gas chromatography mass spectrometry (GCMS).

Half of the EOC sample extract was exchanged into isooctane, and internal standards (deuterated polycyclic aromatic compounds) were added. The extract was transferred into GC vials for the analysis of non-polar EOCs (nitro- and polycyclic musk fragrances, phthalate esters, alkyl phosphate flame retardants and insect repellents).

3.2.2. Sample extract derivatisation

The second half of the EOC sample solvent extract was spiked with a solution of deuterated polar EOC internal standards and gently blown to dryness. The polar EOCs (steroid hormones, phenolic antimicrobials, paraben preservatives and industrial alkylphenols) were derivatised to their respective trimethylsilyl ethers using a catalytic mixture of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), ammonium iodide and mercaptoethanol.

An internal standard mixed solution containing deuterated (-d4) monocarboxylic phthalate acid esters and ibuprofen-d3 was added to the acidic pharmaceutical solvent extracts, which were carefully evaporated to dryness. The polar acidic analytes were derivatised to their respective tertiary-butyl dimethyl silyl esters by reaction with N-tert-butyl dimethyl-silyl-N-methyltrifluoroacetamide (MTBSTFA) with 1% t-butyl dimethylsilyl chloride (TBDMSCl).

3.2.3. Analysis of emerging organic contaminants

The analysis of the different classes of EOCs required the use of different GCMS instruments and instrumental analysis methods. Alkyl phosphate flame retardants, musk fragrances, insect repellents, industrial alkylphenols, paraben preservatives, phenolic antimicrobials and steroid hormones were analysed using an Agilent 6890N gas chromatograph coupled to a 5975-mass spectrometer operating in single-ion

monitoring mode. Quantitation of target EOCs was achieved by internal standard quantitation using Agilent Technologies, Inc. ChemStation MS software. Phthalate esters, monocarboxylate phthalate esters and pharmaceuticals were analysed using an Agilent 7000 series triple quadrupole GCMS operating in tandem mass spectrometry (MS/MS) mode. Quantitation of target EOCs was achieved by internal standard quantitation using Agilent MassHunter MS/MS software.

A total of 84 individual chemicals representing nine different classes of EOCs were analysed, including:

- alkyl phosphate flame retardants (11 compounds)
- industrial alkylphenols (7 compounds)
- insect repellents (3 compounds)
- nitro- and polycyclic musk fragrances (10 compounds)
- paraben preservatives (10 compounds)
- pharmaceuticals (10 compounds)
- phenolic antimicrobials (8 compounds)
- phthalate esters and plasticisers (13 compounds)
- steroid hormones (12 compounds).

4. RESULTS OF EMERGING ORGANIC CONTAMINANTS TESTING

4.1. Recovery and surrogate standard compounds

The mean recovery of individual carbon-13-labelled and acidic herbicide surrogate standards spiked into the sample prior to extraction, and the overall mean recovery of all surrogate compounds, are presented in Table 2. The surrogate standard compounds spiked into the 2 L and 0.5 L samples of wastewater for EOCs and pharmaceutical analyses were added at an equivalent concentration of 50 ng/L (ppt).

The recovery of the surrogate standards meets the acceptance requirements of quality assurance criteria of > 70% for all carbon-13-labelled and acidic herbicide surrogate chemicals. The mean recoveries of the carbon-13-labelled EOCs and acidic herbicide surrogate standards were 91% and 104%, respectively. The level of surrogate compound recovery obtained from the samples spiked at the concentration of 50 ppt validated the performance of the analytical methodology.

Table 2. Recovery of emerging organic contaminants and pharmaceutical surrogate standard chemicals spiked into the NWWTP discharge samples.

Recovery compound	Percentage recovery
EOC surrogate	
¹³ C-methylparaben	110
¹³ C-ortho-phenylphenol	71
¹³ C-butylparaben	101
¹³ C-triclosan	88
¹³ C-bisphenol A	97
¹³ C-estrone	88
¹³ C-17β-estradiol	79
Mean recovery	91%
Pharmaceutical surrogate	
Diclorprop	105
NAA	100
MCPB	105
Flamprop	105
Mean recovery	104%

4.2. Residues of emerging organic contaminants

The EOC concentrations detected in the NWWTP wastewater samples are summarised in Table 3. All the analysed EOCs, together with their respective method detection limits (MDLs), are listed in Appendix 1. A total of 45 of the 84 individual EOCs analysed were detected in at least one of the analysed wastewater samples, including the following classes of compounds:

- alkyl phosphate flame retardants (7)
- phenolic antimicrobial chemicals (5)
- paraben preservatives (3)
- industrial alkylphenols, including the industrial mixture of technical nonylphenols (3)
- insect repellents (3)
- polycyclic and nitro-musk fragrances (5)
- acidic pharmaceuticals (7)
- plasticisers (9)
- steroid hormones (3).

Table 3. Concentrations of emerging organic contaminants detected in the NWWTP wastewater samples. Sample 1 – dry weather; Sample 2 – wet weather; ND = not detected.

Emerging organic chemical	Concentration (ng/L)	
	Sample 1	Sample 2
Alkylphosphate flame retardants		
Tri-isobutyl phosphate	76.3	27.9
Tri-butyl phosphate	261	19.6
Tri-(2-chloroethyl)phosphate	84.7	33.9
Tris(1-chloro-2-propyl)phosphate	2,162	726
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	288	67.9
Triphenyl phosphate	35.6	13.7
Tris(2-butoxyethyl)phosphate	1,350	129
Phenolic antimicrobials		
Chloroxlenol	3,392	1,425
Chlorophene	63.5	23.9
Chlorphenesin	750	317
o-phenylphenol	23.4	14.4
Triclosan	56.7	51.5
Paraben preservatives		
Ethylparaben	206	ND
Methylparaben	649	8.07
Propylparaben	474	186

Emerging organic chemical	Concentration (ng/L)	
	Sample 1	Sample 2
Industrial alkylphenols		
4-tert-amylphenol	11.7	4.26
4-tert-octylphenol	26.4	39.6
Tech-NP-equivalents	3,267	5,498
Insect repellents		
Benzyl benzoate	17.6	ND
DEET	1,869	746
Picaridin	1,708	1,059
Musk fragrances		
Cashmeran (DPMI)	110	40.0
Celestolide (ADBI)	4.23	1.24
Galaxolide HHCB)	926	537
Musk ketone	68.7	11.0
Tonalide (AHTN)	50.6	23.8
Acidic pharmaceuticals		
Acetaminophen	78,008	86,184
Carbamazepine	347	283
Diclofenac	397	235
Ibuprofen	10,173	7,270
Ketoprofen	63.7	38.1
Naproxen	2,831	1,544
Salicylic acid	9,231	5,489
Plasticisers		
Benzyl butyl phthalate	119	17.9
Di-n-butyl phthalate	222	87.7
Diethyl phthalate	12,173	1,470
Diethylhexylphthalate	119	7.31
Dimethylphthalate	123	71.7
Monobutyl-PAE	427	346
Monoethylhexyl-PAE	2,695	1,136
MonomethylPAE	147	212
Bisphenol A	1,475	1,104
Steroid hormones		
Estrone	17.5	ND
Estriol	232	126
Androstenediol	33.9	ND

5. COMPARISON WITH RESULTS FROM OTHER TREATMENT PLANTS

Over the period 2013 to 2023, a database of measured concentrations of EOCs in samples of treated wastewater from New Zealand treatment plants has been accumulated (Northcott, unpublished data). This database includes measured concentrations of EOCs in 25 samples from 11 WWTPs. These 11 WWTPs represent a broad range of treatment processes, catchment populations, balance of domestic to industrial inputs and geographic distribution. The treatment processes include primary oxidation, activated sludge, biological trickling filters, enhanced biological phosphorus removal, membrane bioreactors, waste stabilisation ponds, ultraviolet disinfection and constructed wetlands. The volumes of wastewater treated at these plants ranged from 183,771 m³ to 9,149,256 m³ (average per annum), and the level of treatment included both secondary (three WWTPs) and tertiary treatment (eight WWTPs).

Table 4 presents the concentrations of EOCs in the dissolved phase of the 25 treated wastewater samples from these 11 WWTPs compared to those measured in the two NWWTP treated wastewater samples. The concentrations of the EOCs in the 25 treated wastewater samples are presented as minimum, mean and maximum concentrations.

The concentrations of EOCs measured in the two samples of treated wastewater from the Nelson WWTP were generally higher in the dry-weather sample from November 2021 (Sample 1) compared to that from the wet-weather sample from March 2022 (Sample 2). The concentrations of 41 of the 45 EOCs detected in both treated wastewater samples were higher in the November 2021 sample. The concentrations of the industrial alkylphenols 4-tert-octylphenol and technical nonylphenol, the pharmaceutical acetaminophen and the plasticiser metabolite monomethyl phthalate were higher in March 2022 (Sample 2) compared to November 2021 (Sample 1).

The relatively high concentrations of many of the detected EOCs in the wastewater samples from the Nelson WWTP (Table 4) suggest that the treatment plant is not removing EOCs as effectively as other WWTPs in New Zealand. However, it is important to note that the samples provided for analysis were treated wastewater (effluent) only and the brief was to analyse EOCs solely in the dissolved phase of the wastewater samples. In the absence of hydraulically linked influent samples combined with analysis of EOCs in both the dissolved and particulate phases of the samples, a mass balance for the EOCs cannot be calculated and the efficacy of Nelson WWTP to remove or reduce EOCs cannot be fully determined.

Table 4. Comparison of the concentrations of emerging organic contaminants detected in treated wastewater samples from the NWWTP with those in other New Zealand treatment plants, as reported by Northcott et al. (2013) and unpublished data collected by Northcott Research Consultants Ltd.

	Concentration in ng/L (ppt)				
	Minimum	Mean	Maximum	NWWTP (Sample 1)	NWWTP (Sample 2)
Alkylphosphate flame retardant					
Tri-isobutylphosphate	< 0.1	58.2	182	76.3	27.9
Tri-butylphosphate	21.9	117	643	261	19.6
Tri-(2-chloroethyl)phosphate	< 0.1	188	526	84.7	33.9
Tris(1-chloro-2-propyl)phosphate	< 0.1	1,580	4,038	2,162	726
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	32.0	250	602	288	67.9
Triphenyl phosphate	< 0.1	38.7	165	35.6	13.7
Tris(2-butoxyethyl)phosphate	< 0.1	918	5,710	1,350	129
Phenolic antimicrobials					
Chlorophene	< 0.10	5.34	15.8	63.5	23.9
Chlorophenesin	< 0.10	0.10	0.10	750	317
Chloroxlenol	< 0.05	63.4	361	3,393	1,425
o-phenylphenol	< 0.10	5.38	33.1	23.4	14.4
Triclosan	4.15	75.12	813	56.7	51.5
Paraben preservatives					
Ethylparaben	< 0.05	5.69	141	206	ND
Methylparaben	< 0.05	8.44	55.2	649	8.07
Propylparaben	< 0.05	0.80	7.4	474	186
Insect repellents					
Benzyl benzoate	< 1	2.4	18.8	17.6	ND
DEET	< 1	255	1,294	1,869	746
Picaridin	< 1	11.0	63.4	1,708	1,059
Musk fragrances					
Cashmeran (DPMI)	< 0.1	62.7	179	110	40.0
Celestolide (ADBI)	< 0.1	6.5	29.7	4.23	1.24
Galaxolide HHCB)	< 0.1	1,471	6,160	926	537
Musk ketone	< 0.1	21.8	61.5	68.7	11.0
Tonalide (AHTN)	< 0.1	58.9	141	50.6	23.8
Industrial alkylphenols					
4-tert-amylphenol	< 0.1	1.13	10.9	11.7	4.26
4-tert-octylphenol	< 0.1	3.96	26.5	26.4	39.6
Technical nonylphenols	9.1	208	655	3,267	5,498

	Concentration in ng/L (ppt)				
	Minimum	Mean	Maximum	NWWTP (Sample 1)	NWWTP (Sample 2)
Acidic pharmaceuticals					
Acetaminophen	< 0.10	13.5	164	78,008	86,184
Carbamazepine	120	479	1,009	347	283
Diclofenac	16.0	447	913	397	235
Ibuprofen	4.08	1,301	483	10,173	7,270
Ketoprofen	< 0.10	16.9	54.5	63.7	38.1
Naproxen	2.69	229	770	2,831	1,544
Salicylic acid	2.00	29.1	118	9,231	5,489
Plasticisers					
Benzylbutylphthalate	< 0.1	11.9	60.3	119	17.9
Di-n-butylphthalate	< 5.0	74.2	318	222	87.7
Diethylphthalate	< 5.0	131	817	12,173	1,470
Diethylhexylphthalate	< 0.1	1,045	11,306	119	7.31
Dimethylhexylphthalate	0.48	30.6	226	123	71.7
Monobutylphthalate	< 1.0	15.1	52.0	427	346
Monoethylhexylphthalate	2.6	269	1,596	2,695	1,136
Monomethylphthalate	1.20	13.7	65.7	147	212
Bisphenol A (BPA)	0.68	36.6	247	1,475	1,104
Steroid hormones					
Androstenediol	< 0.10	0.12	0.28	33.9	ND
Estriol	< 0.05	3.09	42	232	126
Estrone	< 0.02	32.9	214	17.5	ND

Notes: Cells highlighted in green represent values that are less than the minimum.

Cells highlighted in orange represent values that fall within the range.

Cells highlighted in red represent values that exceed the maximum.

ND = not detected.

Of the 45 EOCs detected in the treated wastewater samples from the Nelson WWTP, for which there are data to compare against, the concentrations of 24 EOCs in the dry-weather sample and 16 in the wet-weather sample exceeded the maximum measured in other New Zealand treatment plants. The concentrations of the remaining EOCs detected in the dry-weather sample from the Nelson WWTP (21 chemicals) fell within the range of concentrations previously measured in treated wastewater samples from other treatment plants. The remaining EOC concentrations detected in the wet-weather sample either fell within the range of previously measured concentrations (23 chemicals) or were below the previously measured concentrations. The concentration of ethylparaben in the dry-weather sample (206 ng/L) was higher than those found in the 11 WWTPs and slightly higher than that found in the Bell Island WWTP (141 ng/L) (Northcott & Tremblay 2017).

The physico-chemical properties of the analysed EOCs, many of which display varying degrees of hydrophobicity, will result in them partitioning and accumulating on particulate organic matter in the wastewater discharge. This includes algae that have cell walls composed of cellulose and hemicellulose comprising 50% carbon.

As previously mentioned, the NWWTP samples contained visible residues of algae that were concentrated on the filtration media. It is likely that the visible particulate matter in these samples contained amounts of EOCs associated with the algae that are not accounted for in this current assessment. Hence the dissolved phase concentrations likely under-represent the total loading of EOCs from the discharge. Nonetheless, it is important to acknowledge that this additional loading component will also be present at other WWTPs where particulate material is entrained in the discharge.

The concentrations of many EOCs were substantially higher than the range reported for other New Zealand WWTPs, particularly in Sample 1 (dry weather flow). For instance, the insect repellent picaridin, which is readily degraded and removed during wastewater treatment in New Zealand, was measured in Nelson treated wastewater at a concentration that was two orders of magnitude greater than the previous maximum recorded in New Zealand treated wastewater.

There are several caveats to interpreting the relatively elevated EOC concentrations in these samples with respect to plant performance:

- Absence of sample replication or an extended time series of sampling carries the potential that samples may be atypical of normal operation.
- Absence of influent samples hydraulically-linked to those of the discharge does not allow assessment of true reductions across the process.
- Only three of the eleven WWTPs in the comparative dataset were for a comparable (secondary) level of treatment.

While the collection and analysis of influent samples hydraulically-linked to those of the discharge would have allowed the calculation of removal efficacy, it is worth noting that there is little to set the catchment served by the NWWTP apart from those of other similar plants nationally. Therefore, there was no expectation that the influent would differ markedly, especially across the full range of chemicals for which such exceedances occurred. Hence the relatively elevated discharge concentrations in Table 4 remain noteworthy.

While the discharge concentrations suggest that, at the time of sampling, the treatment process at the NWWTP was not very effective in reducing / degrading several EOCs compared to other secondary treatment plants, it is understood that the plant's trickling

filter is not run continuously but used to handle higher loads only¹. This means that, for much of the time, following screening to separate grit and gross solids, the ponds and wetlands may serve as the sole mechanisms for EOC removal. This may be a factor in the higher concentrations compared to those of other secondary treatment plants.

To optimise the plant for removal of EOCs, further investigation could be undertaken to quantify reductions across individual stages of the treatment process. However, the limited nature of both the current NWWTP sample set and the national comparative dataset means that the need for such steps is not well defined; hence the focus should remain on the post-discharge environmental risk.

¹ The pre-treatment plant consists of a clarifier and trickling filter and can be used or bypassed depending on the needs of the facultative pond with respect to pond health (Stantec 2023).

6. RISKS OF EMERGING CONTAMINANTS FROM THE NELSON NORTH WWTP DISCHARGE TO TASMAN BAY

In this study, we assessed the risk of EOCs in the treated wastewater discharge from the NWWTP to the receiving environment of Tasman Bay by comparing the measured concentrations of the detected EOCs with the predicted no-effect concentrations (PNECs) reported in the literature. PNEC is an estimate of the concentration below which exposure to a substance is not expected to cause adverse effects. For those EOCs where a PNEC was not available, we considered the no observable-effect concentration (NOEC) instead. EOCs measured at concentrations equal or similar to their respective PNEC values represent a low risk to exposed biota in the receiving environment.

The results from the analyses, along with available PNEC values, are summarised in Table 5. Many of the PNEC values were obtained from the European Norman Network, which is the most comprehensive ecotoxicological database available (Norman Network 2022). For the PNECs that were not available for the marine environment, those derived for freshwater environments were used instead. However, it should be noted that these will inevitably tend to overestimate the risk to marine environments due to the less constrained wastewater dilution compared to freshwater systems. Another potentially mitigating factor for marine systems is that ionic interactions tend to decrease dissolved phase toxicity in seawater.

The concentrations of 10 EOCs detected in the treated wastewater samples of the NWWTP were of the same order of magnitude as their respective PNEC values. There were 11 occasions where published PNEC values were exceeded by measured concentrations in the NWWTP samples, involving 8 individual EOCs. Five EOCs were measured at concentrations two orders of magnitude higher than their (Norman Network 2022) PNEC values. These were BPA and estrone - which are recognised endocrine disrupters - and the pharmaceuticals carbamazepine, diclofenac and ibuprofen.

The chemical exposure risk of any wastewater discharge to the receiving environment is reduced as the wastewater is diluted in the receiving waters. It is accepted that a minimum 100:1 dilution ratio is required to reduce the risk of a chemical contaminant with a concentration that exceeds its respective PNEC by two orders of magnitude. The worst-case dilution ratio predicted by hydrodynamic modelling under existing median discharge flow rates was 3,200:1 at the mixing-zone boundary². Under predicted future (2059) flow scenarios, a worst-case dilution of 2,300:1 is predicted for median flow rates and 280:1 for the lowest 1% of flow rates (1%ile). These available dilutions under

² Estimates of present and future dilutions at the mixing-zone boundary, based on MetOcean modelling (MetOcean Solutions 2023), provided by Rob Lieffering, SLR, in an email to Ross Sneddon, 18 July 2023.

median discharge rates are more than an order of magnitude greater than that required to reduce the concentrations of EOCs below their corresponding PNEC values.

The assessment of risk based on the modelled available dilution is conservative, not only due to the assumption of worst-case conditions for dispersion, but because the buoyant freshwater plume is unlikely to have more than limited contact with the seabed within the immediate vicinity of the discharge. Biota in the water column are likely to experience only short duration exposures due to the high level of available dilution as water moves through the mixing zone.

However, notwithstanding its conservative aspects, another point to consider is that the present assessment is based on the risks posed by individual EOCs. In reality, these compounds occur as a mixture in the final treated wastewater, raising the possibility that ecotoxic effects may arise in the receiving environment due to the cumulative and / or synergistic toxicity of multiple chemicals. Because the EOCs concentrations measured in the NWWTP treated wastewater samples are relatively high compared to those in other New Zealand treatment plants, it may be advisable to determine the toxicity of the treated wastewater by means of a direct toxicity assessment if the elevated concentrations of the dry weather sample are shown to be characteristic of the discharge.

The treated wastewater samples analysed had a noticeable amount of particulate matter when viewed with the naked eye. This reduced the extraction efficiency of the method used, which includes a filtration step. Because a proportion of some EOCs would be associated with the residual particles on the filter, these have not been accounted for in the dissolved phase concentrations. EOCs include a wide range of solid-phase affinities, so the estimation of this additional fraction from the current data is not straightforward. While total recoverable concentrations would better reflect total EOC loading to the receiving environment, PNEC values are based on the dissolved phase, so the assessments of potential toxicity remain valid.

Table 5. Concentrations of emerging organic contaminants in NWWTP wastewater samples compared to limits recommended by worldwide agencies. PNEC = predicted no-effect concentration; NOEC = no observed effect concentration, indicated by an asterisk (*).

Emerging organic contaminant	Abbreviation	Nelson WWTP concentration (µg/L)	Above / below PNEC / NOEC	Order of magnitude	PNEC or NOEC* (µg/L)	Source
Tri-isobutylphosphate		0.076 / 0.028	Below	2	1.10	Norman Network (2022)
Tri-butylphosphate	TBP	0.261 / 0.020	Below	1–2	6.60	Norman Network (2022)
Tris(2-chloroethyl)phosphate	TCEP	0.085 / 0.034	Below	1	0.40	Norman Network (2022)
Tris(1-chloro-2-propyl)phosphate	TCPP	2.16 / 0.73	Below	3	1,700 (aquatic ecosystems)	ECCC & Health Canada (2020)
			Below	1–3	640 (inverts) 260 (algae) 64 (fish)	European Commission (2008a)
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	TDCP	0.288 / 0.068	Below	1–2	1.3 (aquatic ecosystems)	Environment Canada (2020)
				3–4	1 mg/L (seawater) 10 mg/L (freshwater)	European Commission (2008b)
			Equal / below		0.11 µg/L	Norman Network (2022)
Triphenylphosphate	TPP	0.036 / 0.014	Below	1	0.16 (aquatic organisms)	Verbruggen et al. (2005) (Netherlands)
					0.74 (surface waters)	Sorokin et al. (2008)
					0.074 (marine water)	
Tris(2-butoxyethyl)phosphate	TBEP	1.35 / 0.13	Below	1	4.48	Norman Network (2022)
Chlorophenesin		0.75 / 0.32	Equal / below		0.54	Norman Network (2022)
o-phenylphenol		0.023 / 0.014	Below		0.09	Norman Network (2022)
Triclosan	TCS	0.057 / 0.052	Equal		0.02	Norman Network (2022)

Emerging organic contaminant	Abbreviation	Nelson WWTP concentration (µg/L)	Above / below PNEC / NOEC	Order of magnitude	PNEC or NOEC* (µg/L)	Source
Methylparaben	TNP	0.65 / 0.081	Equal / below	1	0.50	Norman Network (2022)
Propylparaben		0.47 / 0.19	Below	1	1.23	Norman Network (2022)
4-tert-octylphenol		0.026 / 0.040	Equal		0.01	Norman Network (2022)
Technical nonylphenol		3.27 / 5.50	Above	1	0.20 (water)	WHO (2004) (Europe)
			Above	1	0.330	European Chemicals Bureau (2002)
Benzyl benzoate		0.018	Below	2	3.33	Norman Network (2022)
DEET		1.87 / 0.75	Below	3	407 (algae, daphnia zebrafish)	Sun et al. (2016)
				2	43 (aquatic organisms)	European Commission (2010)
				1–2	8.8	Norman Network (2022)
Picaridin		1.71 / 1.06	Below	1	31.4	Norman Network (2022)
					39 (marine copepods)	HERA (2004)
Galaxolide	HHCB	0.93 / 0.54	Below	3		European Commission (2008c)
			Below	2	6,800 (marine organisms)	
			Equal /below	1	0.70	Norman Network (2022)
Acetaminophen		78/86	Equal		13.4	Norman Network (2022)
Carbamazepine		0.35 / 0.28	Below	2	25	Li (2014)
			Above	2	0.005	Norman Network (2022)
Diclofenac		0.40 / 0.24	Below	2	9.8	Zhao et al. (2017)
			Above	2	0.005	Norman Network (2022)

Emerging organic contaminant	Abbreviation	Nelson WWTP concentration (µg/L)	Above / below PNEC / NOEC	Order of magnitude	PNEC or NOEC* (µg/L)	Source
Ibuprofen		10.2 / 7.3	Above	1–2	0.11	Norman Network (2022)
Ketoprofen		0.064 / 0.038	Below	1	0.22	Norman Network (2022)
Naproxen		2.8 / 1.5	Below	1	37	Li (2014)
			Above	1	0.18	Norman Network (2022)
Salicylic acid		9.2 / 5.5	Below	2	119	Ortiz de Garcia et al. (2014)
			Below	1	17.1	Norman Network (2022)
Benzyl butyl phthalate		0.12 / 0.018	Below	1	0.75	Norman Network (2022)
Di-n-butylphthalate	DnBPAE	0.22 / 0.088	Below	5–6	57,000	Staples et al. (2000)
			Equal/below	1	0.23	Norman Network (2022)
Diethylhexylphthalate		0.12 / 0.007	Below	1–3	1.3	Norman Network (2022)
Dimethylphthalate		0.12 / 0.072	Below	2–3	19.2	Norman Network (2022)
Bisphenol A	BPA	1.48 / 1.10	Equal		1.5	European Commission (2008d)
			Equal		1.6	AIST (2007)
			Above	1	0.175	Environment Canada & Health Canada (2008)
			Above	2	0.01	Norman Network (2022)
Estrone		0.018	Above	1	0.006	Caldwell et al. (2012)
			Above	2	0.00036	Norman Network (2022)
Estriol		0.023 / 0.013	Above	1	0.006	Norman Network (2022)
Androstenediol		0.034	Below	1	0.60	Norman Network (2022)

7. CONCLUSIONS

The concentrations of a number of EOCs measured in the treated wastewater samples from the NWWTP were higher than the range previously reported in New Zealand. This suggests that the effectiveness of the NWWTP in reducing / degrading these chemicals is limited relative to other plants, including some for which (like NWWTP) wastewater is treated only to secondary level.

As some EOCs were measured at concentrations two orders of magnitude higher than their respective PNEC values, a minimum 100:1 dilution of the discharged treated wastewater is required to reduce the risk they pose to marine biota in the vicinity of the discharge. Worst-case wastewater dilutions at the boundary of the mixing zone ($\geq 280:1$) exceed this dilution. Based on these results, the overall risk of adverse effects in the receiving environment can be considered very low.

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9. APPENDIX

Appendix 1. List of analysed emerging organic contaminants and their method detection limits (MDLs) in NWWTP treated wastewater samples (ND = not detected above the MDL).

Emerging organic chemical	Concentration (ng/L)		MDL (ng/L)
	Sample 1	Sample 2	
Alkylphosphate flame retardants			
Tri-isobutylphosphate	76.3	27.9	0.10
Tri-butylphosphate	261	19.6	0.10
Tris(2-chloroethyl)phosphate	84.7	33.9	0.10
Tris(1-chloro-2-propyl)phosphate	2,162	726	0.10
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	288	67.9	0.10
Tri-phenylphosphate	35.6	13.7	0.10
Tris(2-butoxyethyl)phosphate	1,350	129	0.10
Tris(2-ethylhexyl)phosphate	ND	ND	0.10
Tri-o-cresylphosphate	ND	ND	10
Tri-m-cresylphosphate	ND	ND	10
Tri-p-cresylphosphate	ND	ND	10
Phenolic antimicrobials			
Chloroxylenol	3,392	1,425	0.05
Chlorophene	63.5	23.9	0.10
Chlorophenesin	750	317	0.10
Dichlorophen	ND	ND	0.05
o-phenylphenol	23.4	14.4	0.10
Methyl triclosan	ND	ND	0.50
Triclosan	56.7	51.5	0.50
3,4,5,6- tetrabromo-o-cresol	ND	ND	0.50
Paraben preservatives			
Benzylparaben	ND	ND	0.05
Butylparaben	ND	ND	0.05
isobutyl-paraben	ND	ND	0.05
Ethylparaben	206	ND	0.05
Heptyl-paraben	ND	ND	0.05
Hexyl-paraben	ND	ND	0.05
Methyl paraben	649	8.07	0.05
Pentyl-paraben	ND	ND	0.05
Phenyl-paraben	ND	ND	0.05
Propylparaben	474	186	0.05
Isopropyl-paraben	ND	ND	0.05

Emerging organic chemical	Concentration (ng/L)		MDL (ng/L)
	Sample 1	Sample 2	
Industrial alkylphenols			
4n-amyphenol	ND	ND	0.10
4t-amyphenol	11.7	4.26	0.10
4t-Heptylphenol	ND	ND	0.10
4n-nonylphenol	ND	ND	0.10
4n-Octylphenol	ND	ND	0.10
4t-Octylphenol	26.4	39.6	0.10
Tech-NP	3,267	5,498	5.0
Insect repellents			
Benzylbenzoate	17.6	N.D.	1.0
DEET	1,869	746	1.0
Picaradin	1,708	1,059	1.0
Musk fragrances			
Cashmeran (DPMI)	110	40.0	1.0
Celestolide (ADBI)	4.23	1.24	1.0
Galaxolide (HHCB)	926	537	1.0
Musk ketone	68.7	11.0	1.0
Musk moskene	ND	ND	1.0
Musk tibetene	ND	ND	5.0
Musk xylene	ND	ND	1.0
Phantolide	ND	ND	1.0
Tonalide(AHTN)	50.6	23.8	1.0
Traseolide (ATII)	ND	ND	1.0
Acidic pharmaceuticals			
Acetaminophen	78,008	86,184	0.10
Aspirin	ND	ND	0.10
Carbamazepine	347	283	0.10
Clofibric acid	ND	ND	0.50
Diclofenac	397	235	0.10
Ibuprofen	10,173	7,270	0.10
Ketoprofen	63.7	38.1	0.10
Meclofenamic	ND	ND	0.50
Naproxen	2,831	1,544	0.10
Salicylic acid	9,231	5,489	2.0

Emerging organic chemical	Concentration (ng/L)		MDL (ng/L)
	Sample 1	Sample 2	
Plasticisers			
4-Bromophenyl phenyl ether	ND	ND	5.0
4-Chlorophenyl phenyl ether	ND	ND	1.0
Chloro-ethoxymethane	ND	ND	5.0
Benzylbutylphthalate	119	17.9	0.10
Di-n-butylphthalate	222	87.7	0.10
Diethylphthalate	12,173	1,470	5.0
Diethylhexylphthalate	119	7.31	0.10
Dimethylphthalate	123	71.7	25.0
Di-n-octylphthalate	ND	ND	5.0
monobutyl phthalate	427	346	1.0
monoethylhexyl phthalate	2,695	1,136	1.0
monomethylphthalate	147	212	1.0
Bisphenol A	1,475	1,104	0.50
Steroid hormones			
Estrone	17.5	ND	0.02
17α-estradiol	ND	ND	0.02
17β-estradiol	ND	ND	0.02
Estriol	232	126	0.05
Mestranol	ND	ND	0.02
17α-ethynylestradiol	ND	ND	0.02
Androstenediol	33.9	ND	0.1
19-Nortestosterone	ND	ND	1.0
Androstenedione	ND	ND	0.1
Testosterone	ND	ND	0.1
19-Norethindrone	ND	ND	1.0
Norgestrel	ND	ND	1.0