

**ANALYSIS OF SELECTED EMERGING ORGANIC CONTAMINANTS IN MBR
TREATED EFFLUENT AND AT TWO SITES WITHIN AND OUTSIDE THE
DISCHARGE POINT MIXING ZONE WITHIN LAKE ROTORUA**

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EXECUTIVE SUMMARY

Urban waste water is one of the major sources of Emerging Organic Chemicals (EOCs) entering freshwater and marine ecosystems in New Zealand. Despite being a major source very little data is available on the concentration of EOCs entering and being discharged from WWTPs into the environment in New Zealand.

Rotorua Lakes Council (RLC) contracted Northcott Research Consultants Limited (NRC Ltd) to determine the level of risk to aquatic organisms from emerging organic contaminants (EOCs) in the proposed WWTP discharge. This involved analysing EOCs in three 24-hour composite samples of MBR effluent from the RLC Waste Water Treatment Plant (WWTP), and two grab samples of lake water from Lake Rotorua, one from within and beyond the WWTP discharge point mixing zone. The ratio of discharge water and lake water was combined with dilution factors obtained from computer modelling to calculate the predicted concentration of EOCs beyond the mixing zone in Puarenga Bay Lake Rotorua following the WWTP upgrade and change in discharge location. The predicted concentration of EOCs in Lake Rotorua water was subsequently compared against available no-effect concentration values to determine the risk EOCs represent to aquatic organisms.

A total of seventy-eight individual EOCs from nine different classes of EOCs were analysed of which forty-one were detected in MBR permeate samples and twenty-eight in the two lake water samples. The concentration of EOCs in MBR permeate was similar to that in treated effluent from other waste water treatment plants in NZ. The presence of EOCs in the two samples of Lake Rotorua water demonstrates there are sources of these chemicals into Lake Rotorua other than the discharge of treated effluent from the RLC WWTP.

The predicted concentration of EOCs in lake water in Puarenga Bay Lake Rotorua beyond the mixing zone of the proposed discharge location was determined by adopting the mean concentration of EOCs measured in the MBR permeate samples as the concentration in discharge water following the proposed upgrade, the background concentration of EOCs in lake water at site 4, weighting based on the modelled ratio of discharge water and lake water at site 4, and excluding the enhanced degradation and loss of EOCs that will occur within the low pH and elevated temperature conditions prevalent in the discharge point mixing zone. The predicted concentrations of all twelve EOCs for which Predicted No Effect Concentration (PNEC) values were available, were below their respective PNEC concentrations beyond the mixing zone for the proposed discharge point in Lake Rotorua.

Of the seventy-eight EOCs that were analysed thirty-seven were not detected in the WWTP discharge water, there will be no change in the concentration beyond the zone of reasonable mixing for twelve EOCs and the concentration of twenty-one EOCs was below that considered a risk to aquatic organisms, and therefore present no risk to aquatic organisms.

Overall, EOCs entering Lake Rotorua in treated effluent discharged from the RLC WWTP following the proposed upgrade and change in discharge location, represents no discernible risk to aquatic organisms.

This study represents one of the most comprehensive to date on the potential impact of EOCs in WWTP effluent entering the New Zealand environment.

The proposed upgrade for RLC WWTP will result in all effluent being subject to ultrafiltration at 0.04 microns, or 40 nanometers. Ultrafiltration through pores of this size will remove all microplastics and a significant proportion of nano-sized plastic and other nano-sized residues from the treated effluent. The introduction of ultrafiltration at 0.04 microns for the treatment of effluent will result in RLC WWTP achieving the most efficient and highest level of reduction of microplastics and nanoplastics in wastewater effluent in New Zealand.

INTRODUCTION

Emerging organic contaminants (EOCs) include a vast number of chemicals used in industrial and domestic cleaning products, paints, inks and surface treatments, kitchen and laundry detergents, personal care products, cosmetics, pharmaceuticals and medicines. Products and medicines containing EOCs are used daily by human population and enter domestic waste water from bathing, laundry and toileting activities.

Urban waste water is one of the major source of EOCs to the environment in New Zealand which are largely discharged into freshwater or marine ecosystems. Despite being a major source very little data is available on the concentration of EOCs entering and being discharged from WWTPs into the environment in New Zealand.

RLC is proposing to upgrade the Rotorua City WWTP and change the discharge location (Mott MacDonald, 2017). Northcott Research Consultants Limited (NRC Ltd) was contracted by Rotorua Lakes Council (RLC) to determine the level of risk to aquatic organisms from emerging organic contaminants (EOCs) in the proposed WWTP discharge. NRC Ltd recommended seventy-eight emerging organic contaminants (EOCs) to be analysed. Three 24-hour composite samples of MBR effluent from the RLC Waste Water Treatment Plant, and two grab samples of lake water from Lake Rotorua, one from within and one from outside the WWTP discharge point mixing zone were analysed.

A total of seventy-eight individual Emerging Organic Chemicals (EOCs) representing nine different classes of EOCs were recommended for analysis. These included:

- Alkylphosphate flame retardants (11 compounds)
- Industrial alkylphenols (7 compounds)
- Insect repellents (3 compounds)
- Nitro- and polycyclic musk fragrances (11 compounds)
- Paraben preservatives (5 compounds)
- Pharmaceuticals (10 compounds)
- Phenolic antimicrobials (6 compounds)
- Phthalate esters and plasticisers (13 compounds)
- Steroid hormones (12 compounds)

This report describes:

- a description of the storage and preparation of MBR effluent and Lake Rotorua samples for analysis
- A description of the various methodologies employed in the analysis of EOCs in the samples
- a summary of the quality assurance data and outcomes
- tabulated results of residues of EOCs measured in the analysed samples
- a statistical summary of the concentration of EOCs detected in the three consecutive 24-hour composite samples of MBR effluent
- a comparison of the concentration of EOCs measured in RLC WWTP MBR permeate with the concentration measured in effluent discharged from other WWTPs in New Zealand

- a comparison of the mean concentration of EOCs detected in the three consecutive 24-hour composite samples of MBR effluent with that measured in Lake Rotorua water samples from Sites 4 and 5 beyond and within the discharge point mixing zone
- a comparison of the concentration of EOCs detected in the 24-hour composite samples of MBR effluent and predicted concentrations in Lake Rotorua water samples beyond the zone of reasonable mixing with available no-observable effect concentrations (NOECs) and predicted no-effect concentration (PNECs), and calculation of their respective risk quotients
- a discussion of the risk the residual EOCs in MBR effluent discharged from the RLC WWTP into Lake Rotorua represent to aquatic organisms
- recommend a reduced number of “priority EOCs” for future testing in the WWTP discharge for future Resource Consent monitoring

METHODOLOGY

SAMPLE DESCRIPTION AND STORAGE

The measured concentration of EOCs in the lake samples represents their background concentration prior to the WWTP upgrade and change in discharge location. EOCs detected in the current MBR-permeate represent those that will be in the WWTP discharge following the proposed upgrade to full MBR. The predicted concentration of EOCs in the lake following the proposed WWTP upgrade and change in discharge location will be determined based on the relative portion of discharge water and lake water at the lake sites following the upgrade.

24-hour composite samples of MBR effluent were sampled by staff of the RLC WWTP over three consecutive 24-hour periods from 22/11/2016 to 25/11/2016. The 24-hour composite samples collection period was initiated at 1300hrs on one day and terminated at 1300hrs the following day. The 24-hour composite samples of MBR effluent were transferred into pre-cleaned 4L amber glass bottles at the RLC WWTP, transferred into cooler bins containing ice packs, and couriered the same day to NRC Ltd at Plant and Food Research Ruakura, Hamilton.

The two samples of water from Lake Rotorua were sampled by Dr Chris Dado of Waikato University on 25/11/2016. One sample was obtained from Site 5 within the discharge point mixing zone and the other from Site 4 outside the discharge point mixing zone (Refer to figure 1). The Lake water samples were collected in two pre-cleaned 4L amber glass bottles, transferred to cooler bins containing ice-packs, and delivered to NRC Ltd on the same day by Dr Chris Dado.

Upon receipt by NRC Ltd the pH of the MBR effluent and Lake Rotorua samples was adjusted to <2.5 by the addition of concentrated sulphuric acid and they were immediately transferred into a walk-in chiller and stored overnight at 4°C.

SAMPLE EXTRACTION, PURIFICATION AND DERIVATISATION

Sample preparation

The morning after they were received by NRC Ltd the samples were removed from overnight storage at 4°C and the pH measured to confirm it remained <2.5. The aqueous samples were filtered through a glass microfiber filter (47 mm, Labservice) topped with diatomaceous earth filter aid media (Hyflo SuperCel) to remove particulate material. The sample filtrate was collected in pre-cleaned 2L Glass Schott bottles.

The filtered MBR permeate and lake water samples were spiked with a solution of deuterated and carbon-13 labelled analogues of target EOCs, the acidic herbicides Dichlorprop and MCPB, and the plant growth regulator naphthalene acetic acid, at a concentration of 25 parts per trillion (ng/L) to assess the recovery from each analysed sample.

Sample extraction and purification

Emerging organic contaminants (EOCs) in the filtered liquid effluent samples (dissolved phase) were extracted by passing through an Oasis HLB 1 g 20 mL SPE cartridge. The acidic pharmaceuticals were eluted from the Oasis SPE cartridge as the first fraction with a mixed solvent of acetone and bicarbonate buffer (pH 10). The SPE cartridge was rinsed with a solution of 20% acetone in purified water and dried under vacuum for 5 minutes. EOCs were eluted from the SPE cartridge as a second fraction with a mixed solvent of dichloromethane and methanol solvent and purified by a combination of florisil adsorption chromatography, followed by gel permeation chromatography, to remove pigments and residual fats and lipids that were present in the sample extracts.

The purified EOC sample extract was split into two equal portions- one for analysis of non-polar semi-volatile EOCs and the other for polar EOCs requiring chemical derivatisation for analysis by gas chromatography mass-spectrometry (GCMS). The portions of split sample extract were transferred into vials, capped and sealed and stored under refrigeration for analysis.

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

The raw pharmaceutical solvent extracts were concentrated under a stream of nitrogen gas to remove acetone. The remaining bicarbonate solution was acidified and the pharmaceuticals extracted into diethyl ether.

Sample extract derivatisation

A solution of deuterated polar internal standards was added to the second half of the EOC sample extracts and 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 pharmaceutical diethyl ether solvent extracts which were evaporated to dryness and converted to their respective tertiary-butyl dimethyl silyl esters by reaction with N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) with 1% t-butyldimethylsilyl chloride (TBDMSCL).

INSTRUMENTAL ANALYSIS OF EOCs

The analysis of the different classes of EOCs required the use of different GCMS instruments and instrumental analysis methods. Alkylphosphate 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 Chemstation MS software. Phthalate esters, monocarboxylate phthalate esters and acidic pharmaceuticals were analysed using an Agilent 7000 series triple quadrupole GCMS operating in MS/MS mode. Quantitation of target EOCs was achieved by internal standard quantitation using Agilent Mass Hunter MS/MS software.

QUALITY ASSURANCE PROCEDURES

A Quality Assurance (QA) blank SPE cartridge was included within each batch of extracted samples to account for background contaminants present in the laboratory and/or sourced from laboratory personal. As previously mentioned each individual sample was spiked with a solution of deuterated and carbon-13 labelled analogues of target EOCs at a concentration of 25 parts per trillion (ng/L) to monitor and assess the recovery from each analysed sample. A Milli-Q water blank and a Milli-Q water sample spiked with selected EOCs were included as QA samples in the final batch of extracted MBR permeate and lake water samples to assess recovery of selected target analytes.

Comparative standards, comprising the same volume of each individual QA spike solution incorporated into each batch of extracted samples, were prepared by dispensing aliquots of the individual QA spike solutions into labelled vials at the same time they were added to each batch of samples. The percentage recovery of surrogate and target compound spikes was determined by directly comparing the concentration of analytes measured in QA and sediment samples against that measured in the corresponding comparative standard(s).

Method detection limits (MDLs) for the eighty-one individual EOCs were calculated using a signal-to-noise ratio of 3:1 and by assessment of the mean concentration of EOCs detected in the QA blank samples. The higher of these two values was adopted as the MDL for each individual compound. The method detection limits (MDL) obtained for each of the eighty-one individual analysed EOCs in MBR permeate and Lake Rotorua water are listed in Appendix One.

RESULTS

QUALITY ASSURANCE OUTCOMES

The results obtained from quality assurance procedures met or exceeded accepted standards for laboratories undertaking trace analysis of organic contaminants and pesticides, confirming that the procedures used are robust.

The recovery of isotopic labelled surrogate spike standards fell within the accepted range of 70% to 130 % for all isotopic labelled surrogate recovery standards (Table 1), with an overall mean recovery of 86% at a relatively low spiked concentration of 25 parts per trillion (25 ng/L).

The 95% confidence intervals for the mean recovery of isotope labelled and surrogate standards incorporates the percentage recovery of each surrogate standard obtained from samples of the MBR permeate, water from Lake Rotorua, and the QA Milli-Q water blank and spiked samples. The acceptable mean recovery obtained for each surrogate compound combined with the relatively small confidence intervals further demonstrates the robustness of the analytical method.

Table 1. Recovery of surrogate standards spiked into MBR permeate and Lake water samples

Recovery compound	95% confidence interval for mean % recovery ^A
¹³ C-methylparaben	77 ± 7
¹³ C-butylparaben	74 ± 8
¹³ C-4-n-nonylphenol	83 ± 9
¹³ C-ortho-phenylphenol	92 ± 9
¹³ C-triclosan	100 ± 5
¹³ C-bisphenol-A	92 ± 7
¹³ C-17β-estradiol	91 ± 6
DEET-d ₇	79 ± 8
Musk Xylene-d ₁₅	86 ± 6
Tonalide-d ₃	88 ± 4
Dichlorprop ^B	93 ± 6
MCPB ^B	87 ± 4
NAA ^{BC}	99 ± 8
Mean recovery	88

^A N=10; ^B surrogate for acidic pharmaceuticals; ^C naphthalene acetic acid

A total of eleven EOCs were consistently detected in the QA solid-phase extraction cartridge blank samples. The mass of these eleven EOCs (in nanograms) was divided by four (equivalent to 4Ls of extracted sample) to calculate the equivalent concentration the background EOCs contribute to each extracted sample of MBR permeate or lake water (refer to Table two). The MDLs for these compounds were calculated as twice the equivalent background concentration and are displayed in Appendix One.

Table 2. Equivalent concentration of EOCs originating from background sources

Compound	Concentration (ng/L)
Aspirin	10
Benzylbenzoate	0.45
Bisphenol-A	0.48
Butylbenzyl Phthalate	0.50
Diethyl Phthalate	7.5
Diethylhexyl Phthalate	12.5
Di-n-butyl Phthalate	10
Dimethyl Phthalate	0.50
Ethyl-Paraben	5.0
Galaxolide	1.25
TPP	0.20

The percentage recovery of EOCs spiked into the Quality Assurance Mill-Q water spike recovery sample also fell within the accepted range of 70% to 130 % (Table 3). The corresponding 95% confidence intervals calculated for the mean recovery of EOCs within the different classes demonstrates both a high and consistent recovery of the wide range of analysed EOCs was obtained by the analytical method, confirming the robustness of the method.

Table 3. Percentage recovery of classes of EOCs from Quality Assurance spike sample

Class of EOCs	Range	95% confidence interval for mean % recovery
Antimicrobials, Alkylphenols and parabens	71 -108	86 ± 5
Alkylphosphate flame retardants	74 -107	89 ± 6
Musk fragrances	77 -106	87 ± 6
Acidic pharmaceuticals	76 -113	97 ± 8
Steroid hormones	76 -103	89 ± 7

CONCENTRATION OF EOCs IN MBR PERMEATE

The concentration of EOCs measured in MBR permeate from the current process are assumed to represent the level EOCs in the WWTP discharge following the proposed upgrade to a full-MBR process.

The full set of results reporting the concentration of EOCs in the three consecutive 24-hour composite samples of MBR permeate are presented in Appendix Two.

A total of forty-one EOCs were detected in the MBR permeate samples and 37 EOCs were not detected. Not all of the analysed compounds within each class of EOC were detected in all samples, and some were not detected in any samples.

The following presentation of the concentration of EOCs in MBR permeate only includes those that were detected in the samples of MBR permeate.

The concentration of EOCs in the three 24-hour composite MBR samples were considered as triplicate samples. The corresponding minimum, maximum and mean concentration of EOCs detected in the MBR permeate samples are presented to demonstrate the variability. The mean concentration of EOCs in the MBR permeate samples is calculated to enable comparison with the range of concentration measured in treated and discharged effluent from other WWTPs in New Zealand, and for comparison with concentrations that are known to pose a risk to aquatic organisms.

Alkylphosphate flame retardants

A total of eleven individual APFRs were analysed in the MBR permeate but only five of these were detected (Table 4). The concentration of the five APFRs detected was reasonably consistent in the three samples with the exception of Tri-butylphosphate (TBP) and Tris-(2-butoxyethyl) phosphate (TBEP) which varied twofold and threefold respectively. This variation in the concentration of TBP and TBEP reflects variability in their concentration in influent entering WWTPs arising from the secondary use of TBP a plasticiser and additive in some oil based lubricants, and TBEP as a plasticiser and viscosity regulator in various types of polymers.

Table 4. Concentration of alkylphosphate flame retardants detected in MBR permeate samples.

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
TiBP	44.5	47.3	46.1
TBP	87.1	167	135
TDCP	267	322	287
TPP	28.5	29.6	29.1
TBEP	819	2707	1529

The profile of APFRs in MBR permeate was dominated by TBEP and Tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP) and TBP which were present at the highest concentrations in the MBR permeate, varying from 87 to 2700 ng/L (ppt).

Phenolic antimicrobials, parabens and alkylphenols

Five of the six analysed phenolic antimicrobial chemicals were detected in the MBR permeate samples (Appendix Two). Tetrabromocresol was not detected. The profile of phenolic antimicrobial chemicals is dominated by triclosan and its bacterially methylated metabolite, methyl-triclosan (Table 5). The principal sources of triclosan entering WWTPs in New Zealand are residues of antimicrobial active plaque controlling toothpaste, antimicrobial soaps, and antimicrobial products used in medical facilities. Triclosan is subsequently metabolised by microorganisms during wastewater treatment to produce methyl-triclosan.

No residues of the five paraben preservatives were detected (Appendix Two), and only two of the seven analysed alkylphenols, 4-n-nonylphenol (4n-NP) and technical-nonylphenol (Tech-NP), were detected. The dominate alkylphenol in MBR permeate was Tech NP which was an order of

magnitude greater in concentration than 4n-NP (Table 5). Tech NP is the oxidation and microbial degradation product of parent non-ionic nonylphenol ethoxylate surfactants which are used in detergents, paints, pesticides, personal care products, and plastics. Tech NPs are also used in their own right as antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers, and solubilisers. Tech NP is a common contaminant in WWTP influent, effluent and sewage sludges.

Table 5. Concentration of phenolic antimicrobials and industrial alkylphenols detected in MBR permeate samples

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
<u>Phenolic Antimicrobials</u>			
Chlorophene	8.57	11.6	10.3
Chloroxyleneol	2.91	4.63	3.53
o-phenylphenol	2.51	33.1	29
Methyl triclosan	61.5	71.3	66.2
Triclosan	90.9	112	98.6
<u>Industrial Alkylphenols</u>			
4-n-nonylphenol	12.3	26.5	18.5
Tech-NP-equivalents	484	655	541

Insect repellents

No residues of the insect repellents DEET, Picaradin and Benzylbenzoate were detected in any of the MBR permeate samples, indicating these EOCs were either generally absent in the influent entering the RLC WWTP, or they were effectively removed from the waste water stream by MBR treatment.

Polycyclic and Nitro-musk fragrances

Only five of the eleven analysed musk fragrances were detected in the MBR permeate samples (Appendix 2 and Table 6), four of these being polycyclic musks and one single nitromusk. No residues of the polycyclic musks cashmeran and traseolide, or the nitro-musks musk ambrette, mosken, tibetene and xylene were detected. The five detected musk fragrances were present in all three samples at a similar concentrations.

The concentration of the five detected musk fragrances is dominated by the polycyclic musk galaxolide followed by tonalide with lesser contributions of two other polycyclic musks, cashmeran and celestolide (Table 6). Musk ketone was the only nitro-musk detected. The dominance of the polycyclic musks galaxolide and tonalide reflects their preferential use in personal care products compared to nitro-musk chemicals which have been progressively phased out and replaced by polycyclic musks. Galaxolide clearly dominates the profile of musk chemicals, reflecting the greater use of this particular musk fragrance in personal care products compared to all other polycyclic musk chemicals.

Table 6. Concentration of Polycyclic and Nitro-musk fragrances detected in MBR permeate samples

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
Celestolide (ADBI)	28.2	29.7	28.7
Galaxolide (HHCB)	330	354	341
Musk ketone	58.3	61.5	59.5
Phantolide	1.38	1.8	1.62
Tonalide(AHTN)	134	141	137

Acidic pharmaceuticals

Eight out of the ten analysed acidic pharmaceuticals were detected in the MBR permeate samples. No residues of aspirin and meclofenamic acid were detected and clofibric acid was present at a consistent low concentration around 1 ng/L (ppt). The concentration of the eight pharmaceutical compounds detected was reasonably consistent between the three samples.

The pharmaceuticals carbamazepine and diclofenac were present at the highest concentrations (Appendix 2 and Table 7), ranging from 300 to 400 ng/L (ppt). The concentration of the remaining five pharmaceutical compounds was reasonably low, varying between 9 to 39 ng/L (ppt).

Table 7. Concentration of acidic pharmaceuticals detected in MBR permeate samples

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
Acetaminophen	12.5	13.0	12.7
Carbamazepine	361	408	383
Clofibric acid	0.96	1.09	1.03
Diclofenac	290	328	304
Ibuprofen	30.8	34.4	32.3
Ketoprofen	32.1	38.9	34.6
Naproxen	9.24	11.5	10.5
Salicylic acid	33.3	38.0	35.2

Phthalate esters and plasticisers

The phthalate esters 4-bromophenyl phenyl ether, chloro-ethoxymethane and Di-n-octylphthalate were not detected in any of the MBR permeate samples (Appendix 2 and Table 8). The phthalate esters butylbenzyl phthalate and dimethyl phthalate were detected at very low concentrations, below 2.0 and 1.0 ng/L (ppt) respectively. The profile of phthalate esters in was dominated by diethylphthalate, diethylhexyl phthalate, and di-n-butyl phthalate (Table 8). This is reflected by the presence and measured concentration of the corresponding metabolites of di-n-butyl phthalate and diethylhexyl phthalate, mono-butylphthalate acid ester and mono-ethylhexyl phthalate acid ester.

Table 8. Concentration of phthalate esters and plasticisers detected in MBR permeate samples

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
Butylbenzyl phthalate	1.72	1.93	1.80
4-Chlorophenyl phenyl ether	N.D ^A	22.6	7.52
Diethylphthalate	N.D	55.9	35.9
Diethylhexylphthalate	N.D	63.6	21.2
Dimethylphthalate	0.48	0.85	0.71
Di-n-butylphthalate	13.6	22.3	17.1
Monobutyl-PAE	9.24	11.5	10.5
Monoethylhexyl-PAE	33.3	38.0	35.2
Monomethyl-PAE	3.53	5.61	4.61
Bisphenol A	31.2	37.3	33.7

^AN.D = not detected

The concentration of phthalate esters in the MBR permeate displayed more variability than that of other classes of detected EOCs. However, the concentration of the mono-phthalate acid ester metabolites of the parent phthalate esters and the plasticiser compound bisphenol-A were reasonably consistent in all three samples (Appendix 2 and table 8).

Steroid hormones

Six of the total number of twelve steroid hormones analysed in the three MBR permeate samples (Appendix 2 and Table 9) were detected in one or more samples. The natural and synthetic estrogenic steroid hormones estriol and 17 α -ethinylestradiol, androgenic steroid hormones androstenediol, androstendione and 19-nortestosterone, and progestogen norethisterone were not detected in any of the samples. Residues of 17 α -ethinylestradiol and androstenedione are typically present in treated WWTP effluent, so their absence in MBR permeate along with other steroid hormones may result from their preferential removal during MBR treatment.

Table 9. Concentration of steroid hormones detected in MBR permeate samples

Emerging Organic Chemical	MBR Min	MBR Max	MBR Mean
<u>Estrogens</u>			
17 α -estradiol	N.D ^A	0.91	0.55
17 β -estradiol	2.04	3.23	2.65
Estrone	54.3	57.3	55.4
Mestranol	1.57	2.36	1.93
<u>Androgens</u>			
Testosterone	1.24	1.66	1.45
<u>Progestin</u>			
Norgestrel	N.D	1.1	0.53

^AN.D = not detected

Estrone, the principle metabolite of the natural steroid hormone 17 β -estradiol, was present at the highest concentration. Residues of 17 β -estradiol (a natural estrogenic steroid produced by female

humans) were also present at an order of magnitude lower concentration, along with residues of mestranol a synthetic steroid estrogen used as an oral contraceptive. Mestranol, is the 3-methoxy derivative of the synthetic steroid estrogen 17α -ethinylestradiol that is also used as an oral contraceptive. While the residues of mestranol in the samples may represent non degraded mestranol it is possible that mestranol has been produced by bacterial methylation of 17α -ethinylestradiol (also a synthetic oral contraceptive) during MBR treatment of wastewater. The natural androgenic steroid hormone testosterone was detected in the MBR permeate samples at a relatively low concentration, as was norgestrel a synthetic progestogen used as an oral contraceptive.

Comparison with other treated effluent discharges from WWTPs in New Zealand

The most comprehensive set of data with which to compare the concentration of EOCs in the RLC WWTP MBR permeate samples against is that obtained from a national survey of EOCs in the influent and effluent of 13 WWTPs in New Zealand (Northcott et al, 2013). The characteristics of the thirteen WWTPs included in this study are listed in Table 10.

The concentration of EOCs detected in the MBR permeate samples are compared against that measured in the discharged effluent from these thirteen WWTPs in Table 11. The concentration of EOCs measured in the effluent from the thirteen WWTPs is presented as the range from the minimum to maximum measured concentration and the corresponding average concentration (mean). The concentration of EOC measured in the MBR permeate samples in Table 11 represents the mean concentration measured in the three consecutive 24-hour composite MBR permeate samples.

The WWTPs selected in this national survey represented a broad range of treatment technologies, catchment population, balance of domestic to industrial inputs, and geographic distribution throughout New Zealand (Northcott et al, 2013).

The values highlighted in **green** in table eleven represent the average concentration of EOCs in the RLC WWTP MBR permeate that fall within the range of concentration obtained from thirteen WWTPs across New Zealand. The values highlighted in **red** in table three represent the average concentration of EOCs in the RLC WWTP MBR permeate that exceed the maximum concentration measured in thirteen WWTPs across New Zealand.

The data in Table 11 clearly demonstrates the concentration of nineteen of the EOCs analysed in the MBR permeate samples fall below or are highly comparable to the concentration measured in the treated effluent of thirteen WWTPs in New Zealand. The average concentration of four EOCs measured in the MBR permeate exceeds the maximum concentration previously measured in the effluent of thirteen WWTPs in New Zealand.

Table 10. Characteristics of WWTPs included in the 2012 National Survey project

WWTP	Description	ADF ^A (m ³)	Population	Industrial	Domestic
1	Milli-screened	20,000	55,000	25	75
2	BTF (domestic)	51,000	60,000	50	50
3	Primary sedimentation	2,330	4,000	40	60
4	Primary sedimentation	940	1,900	25	75
5	Primary sedimentation	1300	7000	5	95
6	Sedimentation and UVB	1,170	3,330	0	100
7	Sedimentation, activated sludge digestion, UV	45,000	140,000	10	90
8	Sedimentation, BTF, sedimentation	16,000	20,000	20	80
9	Sedimentation, BTF, sedimentation	25,000	48,000	20	80
10	Primary sedimentation	900	4,000	0	100
11	Primary sedimentation, UV	No Data	700	0	100
12	Sedimentation, BTF, sedimentation	180,000	360,000	10	90
13	Sedimentation, activated sludge digestion, clarification, UV	300,000	1,000,000	40	60

^A ADF = average daily flow, ^B UV = UV treatment of final effluent

The concentration of two of these EOCs in MBR permeate, the polycyclic and nitro musk celestolide and musk ketone, are the same order of magnitude as that measured in treated effluent of thirteen WWTPs in New Zealand. The phenolic antimicrobial chemicals chlorophene was not previously detected in treated effluent of thirteen WWTPs in New Zealand but was present in all three analysed MBR permeate samples. This suggests there is a unique source of chlorophene within Rotorua that is entering the WWTP, possibly related to its use as a biocide in air washer water systems, evaporative condenser water systems, or water cooling systems.

The concentration of methyl-triclosan, the principal metabolite of the phenolic antimicrobial chemical triclosan, was an order of magnitude greater in the MBR permeate samples than the treated effluent of thirteen WWTPs in New Zealand.

None of the thirteen WWTPs previously assessed and used in this comparison incorporated MBR treatment, therefore it is possible the higher concentrations of the four EOCs measured in the MBR permeate samples may be unique to this specific wastewater treatment process.

The conclusion of this comparison is that the concentration of EOCs measured in the MBR permeate from the RLC WWTP is remarkably similar to, or lower than, those measured in treated effluent from other WWTPs across New Zealand. The exceptions are the two musk fragrances celestolide and musk ketone, the antimicrobial chlorophene, and methyl-triclosan a by-product from the breakdown of triclosan.

Table 11. Comparison of the concentration of EOCs in the influent and effluent of WWTPs in New Zealand and RLC WWTP MBR permeate

Concentration of EOCs in ng/L							
	Influent			Discharged effluent			MBR Permeate
<u>Musk fragrance</u>	<u>Min</u>	<u>Max</u>	<u>Mean</u>	<u>Min</u>	<u>Max</u>	<u>Mean</u>	
Cashmeran	N.D	64.4	26.2	N.D. ^A	58.6	14.9	N.D.
Celestolide	N.D	8.63	4.80	N.D.	24.2	6.59	28.7 ^B
Galaxolide	9.03	432	81.4	24.4	902	243	341 ^C
Tonalide	5.22	89.5	54.2	9.83	168	60.9	137
Musk Ketone	7.36	44.6	20.2	N.D.	36.7	13.8	59.5
<u>Alkyl phosphate flame retardant</u>							
TiBP	N.D	283	69.1	N.D.	103	29.2	46.1
TnBP	N.D	1508	209	26.9	499	128	N.D.
TCEP	15.0	451	101	16.3	303	108	N.D.
TCPP	25.5	1009	383	70.5	1024	321	N.D.
TDCP	N.D	516	185	1.92	630	222	287
TBEP	N.D	6302	1396	N.D.	3441	783	1529
TPP	N.D	128	59.9	6.10	3277	301	29.1
<u>Insect repellent</u>							
DEET	28.2	798	279	15.2	1836	220	N.D.
Benzylbenzoate	N.D	220	90.3	N.D	270	30.4	N.D.
<u>Antimicrobial</u>							
Chloroxylonol	104	3750	1241	4.07	2633	322	3.53
o-Phenylphenol	N.D	294	55.2	N.D	6825	549	29.0
Chlorophene	N.D	21.4	3.42	N.D	N.D	N.D	10.3
methyl-Triclosan	N.D	106	11.4	N.D	5.45	1.38	66.2
Triclosan	24.7	100	60.5	4.43	158	38.3	98.6
<u>Paraben preservatives</u>							
Methyl-Paraben	89.5	2670	1147	N.D.	772	81.6	N.D.
Ethyl-Paraben	N.D	296	104	N.D.	39	4.11	N.D.
Propyl-Paraben	43.4	696	328	N.D.	177	29.4	N.D.
Butyl-Paraben	17.1	177	76.9	N.D.	13.0	2.70	N.D.
<u>Plasticiser</u>							
Bisphenol-A	5.59	199	40.6	N.D	66.9	17.0	33.7

^A N.D. = not detected

^B values in red highlight represent those falling exceeding the maximum range

^C values in green highlight represent those falling below the minimum or within the range of minimum to maximum

BACKGROUND CONCENTRATION OF EOCs IN LAKE ROTORUA WATER SAMPLES

Analysis of the two water samples obtained from Lake Rotorua demonstrated the lake water contained twenty-eight individual EOCs from eight different classes of EOCs (Table 12 summarised data, Appendix 2 for full data). The concentration of individual EOCs detected in water samples from the two sampling sites in Lake Rotorua are displayed together with their respective mean concentration in the RLC WWTP MBR permeate samples for comparison (Table 12).

The concentration of EOCs in the two water samples from Lake Rotorua is, as expected, generally much lower than that measured in the MBR permeate samples (Table 12 and Appendix 2). However, the concentration of five EOCs in the lake water samples, namely TCPP, ethyl- and methyl-paraben, aspirin, and salicylic acid was higher than that measured in the MBR permeate samples. With the exception of salicylic acid these EOCs were not detected in any of the three samples of MBR permeate but were present in samples from Lake Rotorua. This indicates the residues of TCPP (a flame retardant), ethyl- and methyl-paraben (preservatives in personal care products, and aspirin (pain medicine) in Lake Rotorua water samples originate from an alternative, and most likely fresh source that has not been subject to waste water treatment. In comparison to these four EOCs salicylic acid is a common chemical in terrestrial plants, so it's presence in the two Lake Rotorua water samples could be from a combination of natural and man-made sources.

The concentration of 50% (14 out of 28) of the EOCs detected in Lake Rotorua water samples were higher at Site 5 compared to their concentration in the water sample from Site 4 which is located further off-shore. The concentration of two EOCs in water sampled from Sites 4 and 5 was similar (TPP and ibuprofen), and the concentration of 12 of the 28 EOCs was lower in lake water sampled from Site 4 compared to Site 5. These results suggest there may be a near shore source of the EOCs detected in the lake water samples, and their concentration decreases with increasing distance off-shore. However, these measurements are based single samples obtained from one day of the year, and as such should be treated with caution.

The presence of EOCs in the samples of Lake Rotorua water demonstrates there are sources of these chemicals into Lake Rotorua other than the discharge of treated effluent from the RLC WWTP. These sources could include run-off from the urban landscape, storm water discharges from urban and industrial zones, discharge from public bathing pools, septic tank discharges, and leakage, infiltration or overflow of wastewater from the Rotorua municipal wastewater reticulation network. In the absence of direct investigation, the possibility that EOCs in treated effluent irrigated onto the plantation forest within Whakarewarewa forest, other than TCPP, ethyl- and methyl-paraben, and aspirin are entering Lake Rotorua via site run-off and transportation within the Puarenga stream cannot be excluded. If the current discharge is a contributing source of any of the EOCs identified in the Lake Rotorua water samples, this input will reduce over time after the current discharge to the forest ceases.

Regardless of the specific source(s) it is apparent EOCs are already present in Lake Rotorua. While the discharge of treated effluent from the RLC WWTP represents a future source of EOCs into Lake Rotorua one or more other sources already exist.

Table 12. Concentration of EOCs detected Lake Rotorua water samples and RLC WWTP MBR permeate

Emerging Organic Chemical	MBR Mean	Lake Site 4	Lake Site 5
<u>Alkylphosphate Flame Retardants</u>			
TCPP	N.D. ^A	20.1	23.9
TDCP	287	1.23	1.06
TPP	29.1	0.41	0.39
<u>Phenolic Antimicrobials</u>			
Chloroxlenol	3.53	0.12	0.35
o-phenylphenol	29.0	4.52	5.39
Triclosan	98.6	25.1	26.8
<u>Parabens</u>			
Ethylparaben	N.D	65.6	57
Methyl paraben	N.D	0.11	0.26
<u>Industrial Alkylphenols</u>			
4-n-nonylphenol	18.5	1.52	1.36
Tech-NP-equivalents	541	12.6	11.7
<u>Nitro- and Polycyclic Musk Fragrances</u>			
Celestolide (ADBI)	28.7	0.53	N.D
Galaxolide (HHCB)	341	2.82	4.13
Phantolide	1.62	0.66	N.D
<u>Acidic Pharmaceuticals</u>			
Acetaminophen	12.7	1.31	0.92
Aspirin	N.D.	5.67	4.77
Carbamazepine	383	1.38	3.26
Diclofenac	304	0.58	0.81
Ibuprofen	32.3	0.29	0.28
Salicylic acid	35.2	89.2	105
<u>Phthalate esters and plasticisers</u>			
Butylbenzyl phthalate	1.80	1.26	0.70
Diethylphthalate	35.9	4.59	1.75
Diethylhexylphthalate	21.2	N.D	12.7
Di-n-butylphthalate	17.1	18.4	6.78
Monobutyl-PAE	10.5	2.15	1.21
Monoethylhexyl-PAE	35.2	6.42	7.04
Monomethyl-PAE	4.61	1.00	0.90
Bisphenol A	33.7	8.39	15.3
<u>Estrogenic steroid hormones</u>			
Mestranol	1.93	0.67	N.D

^A N.D. = not detected

PREDICTED CONCENTRATION AND RISK OF EOCs IN RLC WWTP MBR PERMEATE DISCHARGED INTO LAKE ROTORUA

The concentration of EOCs in lake water at sites 4 and 5 within Lake Rotorua (Figure 1) has been predicted by taking into consideration the portion of MBR-permeate and lake water that would be at each site, obtained from a modelling assessment, and the mean concentration of EOCs measured in the MBR permeate from this study. To assess the effect of EOCs in the proposed MBR discharge on exposed organisms, including the long-term effect on populations, a precautionary approach was adopted when estimating the concentration of EOCs in the lake water, and this concentration was compared to published predicted no-effect concentrations' (PNECs).

A precautionary approach was adopted in this scenario by:

- using the mean concentration of EOCs measured in the three consecutive 24-hour composite MBR samples
- adopting the conservative values of the 95th percentile for the dilution of MBR permeate in Lake Rotorua of 3.0% and 34.6% respectively at Sites 4 and 5 obtained from the modelling exercise (table 13; Data et al, 2017)
- excluding the loss of EOCs in Lake Rotorua, particularly degradation by hydrolysis that will be enhanced within the discharge point mixing zone (Site 5) due to the prevalent low pH and elevated temperature of the lake water.

Table 13. Statistical summary of the percentage dilution of MBR permeate in Lake Rotorua

Dilution parameter	Site 5	Site 4
Minimum %	3.0	0.1
25 th percentile	18.2	0.3
50 th percentile	21.1	0.7
75 th percentile	27.5	1.3
95 th percentile	34.6	3.0
Maximum %	41.2	4.0

Sourced from Dada et al, 2017.

The outcome of the concentration prediction of the EOCs is summarised in Table 14. Table 14 contains the baseline concentration of EOCs measured in the lake water samples at Sites 4 and 5, and the MBR permeate, prior to the WWTP upgrade. The predicted concentration of EOCs in lake water at sites 4 and 5 following the WWTP upgrade are included in Table 14 together with available PNEC values, and an assessment of the risk EOCs present to aquatic life at site 4 beyond the zone of reasonable mixing within Puarenga Bay.

The PNEC value is the concentration of a chemical below which no adverse effects of exposure in an ecosystem occur. PNEC values are intended to be conservative and predict the concentration at which a chemical will likely have no toxic effect. For those EOCs where a PNEC is not available, the no observable-effect concentration (NOEC) has instead been used. If the predicted concentration for

an EOC is less than the PNEC value it will not cause an adverse effect on aquatic organisms exposed to the EOC, and therefore represents no risk to aquatic organisms.

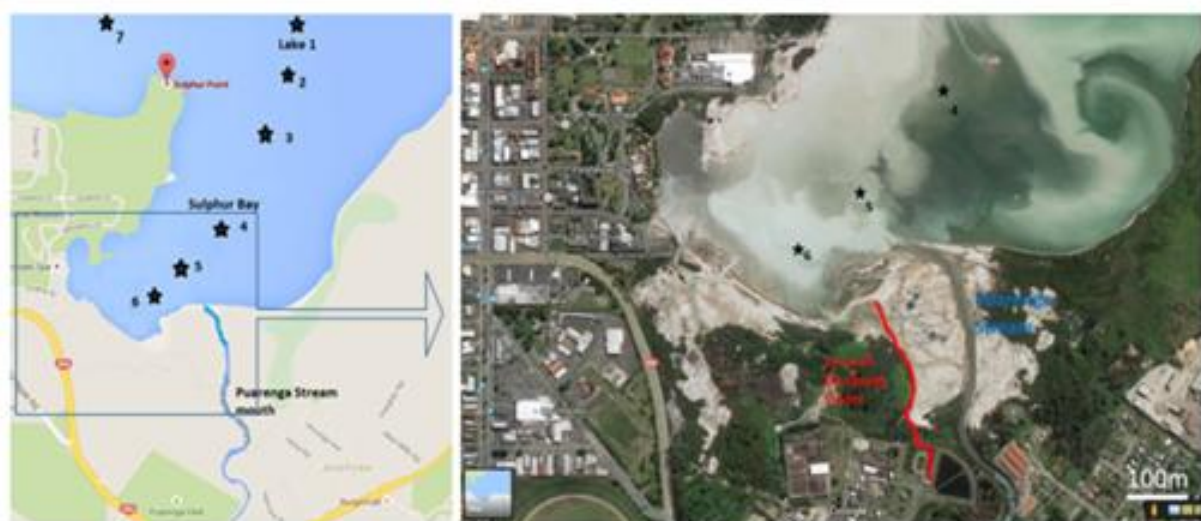


Figure One: Location of water sampling sites within (Site 5) and beyond (Site 4) the WWTP discharge point mixing zone in Puarenga Bay Lake Rotorua (Dada et al, 2017).

The data presented in Table 14 demonstrates there is a general absence of effect measures for the majority of the analysed EOC, as evidenced by the low number of EOCs for which PNEC/NOEC values are available.

The predicted concentration of EOCs (in ng/L, ppt) in the water of Lake Rotorua at Site 4 beyond the zone of reasonable mixing is compared to the corresponding PNEC/NOEC values (in ng/L, ppb) reported in the scientific literature in Table 14. The estimated concentration of all of the EOCs in lake water at site 4 beyond the zone of reasonable mixing were lower than their respective PNEC values, most by two to three orders of magnitude.

The estimated concentration for the estrogenic steroid hormone estrone at site 4 beyond the zone of reasonable mixing (1.70 ng/L) was same order of magnitude as, but remained lower than, its PNEC value (6.00 ng/L).

Table 14. Predicted concentration of EOCs in water samples (parts per trillion (ng/L)) at modelled sites in Lake Rotorua and comparison with Predicted No-Effects concentrations (PNECs)

Emerging Organic Chemical	Baseline concentrations pre-upgrade (ng/L)			Predicted concentrations post-upgrade (ng/L)		PNEC or NOEC (ng/L)	Risk of the proposed discharge to aquatic organisms beyond zone of reasonable mixing and comment. (GREEN=no risk; RED=risk)	Source
	MBR Mean	Lake Site 5	Lake Site 4	In lake within mixing zone (Site 5)	In lake beyond mixing zone (Site 4)			
<u>Alkylphosphate Flame Retardants</u>								
TiBP	46.1	N.D ^A	N.D	16.0	1.40	NA ^B	Unknown	
TBP	135	N.D	N.D	46.7	4.10	370000000	8 orders of magnitude < PNEC/NOEC	OECD 2002
TCEP	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
TCPP	N.D	23.9	20.1	15.6	19.5	NA	not detected in WWTP discharge	
TDCP	287	1.10	1.20	100	9.80	1300	3 orders of magnitude < PNEC/NOEC	Env Canada 2016
TPP	29.1	0.40	0.40	10.3	1.30	160	2 orders of magnitude < PNEC/NOEC	Verbruggen 2005
TBEP	1529	N.D	N.D	529	45.9	130	1 order of magnitude < PNEC/NOEC	Verbruggen 2005
TEHP	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
ToCP	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
TmCP	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
TpCP	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	

^AN.D = not detected; ^BNA = not available

Analyte key

TiBP = Tri-isobutyl-phosphate

TBP = Tributyl-phosphate

TCEP= Tris(2-chloroethyl) phosphate

TCPP = Tris (1-chloro-2-propyl) phosphate

TDCP = Tris[2-chloro-1-(chloromethyl)ethyl] phosphate

TPP = Triphenylphosphate

TBEP = Tris-(2-butoxyethyl) phosphate

TEHP = Tris(2-ethylhexyl) phosphate

ToCP = Tri-o-cresyl phosphate

TmCP = Tri-m-cresyl phosphate

TpCP = Tri-p-cresyl phosphate

Table 14. Predicted concentration of EOCs in water samples (parts per trillion (ng/L)) at modelled sites in Lake Rotorua and comparison with Predicted No-Effects concentrations (PNECs) – continued

Emerging Organic Chemical	Baseline concentrations pre-upgrade (ng/L)			Predicted concentrations post-upgrade (ng/L)		PNEC or NOEC (ng/L)	Risk of the proposed discharge to aquatic organisms beyond zone of reasonable mixing and comment. (GREEN=no risk; RED=risk)	Source
	MBR Mean	Lake Site 5	Lake Site 4	In lake within mixing zone (Site 5)	In lake beyond mixing zone (Site 4)			
Phenolic Antimicrobials								
Chlorophene	10.3	N.D ^A	N.D	3.60	0.30	NA ^B	Unknown	WFD-UKTAG 2009
Chloroxylonol	3.50	0.40	0.10	1.50	0.20	NA	no discernible change	
o-phenylphenol	29.0	5.40	4.50	13.6	5.30	NA	Unknown	
Methyl triclosan	66.2	N.D	N.D	22.9	2.00	NA	Unknown	
Triclosan	98.6	26.8	25.1	51.6	27.3	100	1 order of magnitude < PNEC/NOEC	
Tetra-bromocresol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Parabens								
Benzylparaben	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	Ortez de Garcia, 2014
Butylparaben	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Ethylparaben	N.D	57.0	65.6	37.3	63.6	2780	2 orders of magnitude < PNEC/NOEC	
Methyl paraben	N.D	0.30	0.10	0.20	0.10	6846	not detected in WWTP discharge	
Propylparaben	N.D	N.D	N.D	N.D	N.D	1642	not detected in WWTP discharge	
Industrial Alkylphenols								
4-t-Amylphenol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	WHO IPCS 2004 European Union 2002
4-n-Amylphenol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
4-t-octylphenol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
4-t-heptphenol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
4-n-octylphenol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
4-n-nonylphenol	18.5	1.4	1.5	7.30	2.00	200	2 orders of magnitude < PNEC/NOEC	
Tech-NP-equivalents	541.0	11.7	12.6	195	28.5	330	1 order of magnitude < PNEC/NOEC	

^A N.D = not detected; ^B NA = not available

Table 14. Predicted concentration of EOCs in water samples (parts per trillion (ng/L)) at modelled sites in Lake Rotorua and comparison with Predicted No-Effects concentrations (PNECs)- continued.

Emerging Organic Chemical	Baseline concentrations pre-upgrade (ng/L)			Predicted concentrations post-upgrade (ng/L)		PNEC or NOEC (ng/L)	Risk of the proposed discharge to aquatic organisms beyond zone of reasonable mixing and comment. (GREEN=no risk; RED=risk)	Source
	MBR Mean	Lake Site 5	Lake Site 4	In lake within mixing zone (Site 5)	In lake beyond mixing zone (Site 4)			
Nitro- and Polycyclic Musk								
Fragrances								
Cashmeran (DPMI)	N.D ^A	N.D	N.D	N.D	N.D	NA ^B	not detected in WWTP discharge	
Celestolide (ADBI)	28.7	N.D	0.50	9.90	1.40	NA	Unknown	
Galaxolide (HHCB)	341	4.10	2.80	121	13.0	68000	3 orders of magnitude < PNEC/NOEC	
Musk ambrette	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Musk ketone	59.5	N.D	N.D	20.6	1.80	NA	Unknown	
Musk moskene	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Musk tibetene	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Musk xylene	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Phantolide	1.60	N.D	0.70	0.60	0.70	NA	no discernible change	
Tonalide(AHTN)	137	N.D	N.D	47.4	4.10	3500	3 orders of magnitude < PNEC/NOEC	
Traseolide (ATII)	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Acidic pharmaceuticals								
Acetaminophen	12.7	0.90	1.30	5.00	1.70	310,700	5 orders of magnitude < PNEC/NOEC	Ortez de Garcia, 2014
Aspirin	N.D	4.80	5.70	3.10	5.50	118,700	not detected in WWTP discharge	Ortez de Garcia, 2014
Carbamazepine	383	3.30	1.40	135	12.8	9000	2 orders of magnitude < PNEC/NOEC	Zhao et al 2017
Clofibric acid	1.00	N.D	N.D	0.4	N.D	102,699	Not detected at site 4	Ortez de Garcia, 2014
Diclofenac	304	0.80	0.60	105.7	9.70	9800	3 orders of magnitude < PNEC/NOEC	Zhao et al 2017
Ibuprofen	32.3	0.30	0.30	11.4	1.30	13,875	4orders of magnitude < PNEC/NOEC	Ortez de Garcia, 2014
Ketoprofen	34.6	N.D	N.D	12.0	1.00	NA	Unknown	
Meclofenamic acid	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Naproxen	10.5	N.D	N.D	3.60	0.30	14,199	5 orders of magnitude < PNEC/NOEC	Ortez de Garcia, 2014
Salicylic acid	35.2	105	89.2	80.8	87.6	118,700	4 orders of magnitude < PNEC/NOEC	Ortez de Garcia, 2014

^AN.D = not detected; ^BNA = not available

Table 14. Predicted concentration of EOCs in water samples (parts per trillion (ng/L)) at modelled sites in Lake Rotorua and comparison with Predicted No-Effects concentrations (PNECs)- continued.

Emerging Organic Chemical	Baseline concentrations pre-upgrade (ng/L)			Predicted concentrations post-upgrade (ng/L)		PNEC or NOEC (ng/L)	Risk of the proposed discharge to aquatic organisms beyond zone of reasonable mixing and comment. (GREEN=no risk; RED=risk)	Source
	MBR Mean	Lake Site 5	Lake Site 4	In lake within mixing zone (Site 5)	In lake beyond mixing zone (Site 4)			
Phthalate esters and plasticisers								
4-bromophenyl phenyl ether	N.D ^A	N.D	N.D	N.D	N.D	NA ^B	not detected in WWTP discharge	Staples, 2000
Butylbenzyl phthalate	1.80	0.70	1.30	1.10	1.30	51,000	4 orders of magnitude < PNEC/NOEC	
4-Chlorophenyl phenyl ether	7.50	N.D	N.D	2.60	0.20	NA	Unknown	
Chloro-ethoxymethane	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	Staples, 2000
Diethylphthalate	35.9	1.80	4.60	13.6	5.50	940,000	5 orders of magnitude < PNEC/NOEC	
Diethylhexylphthalate	21.2	12.7	N.D	15.6	0.60	NA	Unknown	
Dimethylphthalate	0.70	N.D	N.D	0.20	N.D	3,251,000	no discernible change	Staples, 2000
Di-n-butylphthalate	17.1	6.80	18.4	10.4	18.4	57,000	3 orders of magnitude < PNEC/NOEC	Staples, 2000
Di-n-octylphthalate	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	Wright-Walters, 2011
Monobutyl-PAE	10.5	1.20	2.20	4.40	2.40	NA	no discernible change	
Monoethylhexyl-PAE	35.2	7.00	6.40	16.8	7.30	NA	no discernible change	
Monomethyl-PAE	4.60	0.90	1.00	2.20	1.10	NA	no discernible change	
Bisphenol A	33.7	15.3	8.40	21.7	9.10	60	1 order of magnitude < PNEC/NOEC	

^AN.D = not detected; ^BNA = not available

Table 14. Predicted concentration of EOCs in water samples (parts per trillion (ng/L)) at modelled sites in Lake Rotorua and comparison with Predicted No-Effects concentrations (PNECs) - continued.

Emerging Organic Chemical	Baseline concentrations pre-upgrade (ng/L)			Predicted concentrations post-upgrade (ng/L)		PNEC or NOEC (ng/L)	Risk of the proposed discharge to aquatic organisms beyond zone of reasonable mixing and comment. (GREEN=no risk; RED=risk)	Source
	MBR Mean	Lake Site 5	Lake Site 4	In lake within mixing zone (Site 5)	In lake beyond mixing zone (Site 4)			
<u>Estrogenic steroid hormones</u>								
17α-estradiol	0.60	N.D ^A	N.D	0.20	N.D	NA ^B	no discernible change	Caldwell et al 2012
17β-estradiol	2.70	N.D	N.D	0.90	0.10	2.00	no discernible change	
Estriol	N.D	N.D	N.D	N.D	N.D	60.0	not detected in WWTP discharge	
Estrone	55.4	N.D	N.D	19.2	1.70	6.00	same order of magnitude as PNEC/NOEC	
17α-ethinylestradiol	N.D	N.D	N.D	N.D	N.D	0.10	not detected in WWTP discharge	
Mestranol	1.90	N.D	0.70	0.70	0.70	NA	no discernible change	
<u>Androgenic steroid hormones</u>								
Androstenediol	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	Caldwell et al 2012
Androstenedione	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
19-Nortestosterone	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	
Testosterone	1.50	N.D	N.D	0.50	N.D	NA	no discernible change	
<u>Progestogens</u>								
Norethisterone	N.D	N.D	N.D	N.D	N.D	NA	not detected in WWTP discharge	Caldwell et al 2012
Norgestrel	0.50	N.D	N.D	0.20	N.D	NA	no discernible change	

^A N.D = not detected; ^B NA = not available

SUMMARY OF THE RISK

The predicted concentrations for EOCs at Site 4 beyond the zone of reasonable mixing post the RLC WWTP upgrade were lower than their respective PNEC values. The Risk Quotient for the EOCs for which PNEC values are available, calculated by dividing their predicted concentrations by their PNEC values, are all below 1 beyond the zone of reasonable mixing. The risk Quotient of 0.28 obtained for the estrogenic steroid hormone estrone was the highest of all the EOCs.

Risk Quotients less than 1 indicate the predicted concentration of EOCs in the water at Site 4 in Lake Rotorua present no risk to aquatic organism that may be exposed to them.

As previously stated the predicted concentrations of EOCs have been calculated to present a conservative scenario, or higher predicted concentration of EOCs at each site within Lake Rotorua, by adopting the 95th percentile value for the dilution of MBR permeate at each site. Importantly, these predicted concentrations do not take account of loss processes that will occur in the receiving environment within Lake Rotorua. These loss/removal processes including sorption to stream and lake bed sediments, microbial degradation, and chemical degradation will reduce the concentration of EOCs in the treated effluent discharged from the RLC WWTP within and beyond the zone of reasonable mixing. A higher than usual rate of degradation of EOCs can be expected within the waters of Puarenga Bay as a result of enhanced chemical degradation (hydrolysis) facilitated by the combination of low pH and elevated water temperature prevailing in the bay. The susceptibility of the estrogenic steroid hormone estrone to degradation by hydrolysis will result in a significant and rapid reduction in its concentration under these environmental conditions.

The predicted concentration of EOCs used in this risk assessment therefore “over predict” the concentration of EOCs in lake water, and the real concentration of EOCs beyond the zone of reasonable mixing will be even lower, and result in a further reduction of their RQs.

Those EOCs that were not detected in MBR permeate do not present any risk to aquatic organisms in Lake Rotorua within and beyond the zone of reasonable mixing. The background concentrations obtained for EOCs that are present in lake water beyond the zone of reasonable mixing (Site 4) prior to the upgrade of the RLC WWTP similarly fall below their respective PNECs, have RQs less than 1, and therefore present no risk to aquatic organisms.

Overall, these results indicate the EOCs that will enter Lake Rotorua following the RLC WWTP upgrade present no risk to aquatic organisms beyond the zone of reasonable mixing.

The relevance of microplastics

Microplastics (MPs) are generally defined as plastic fragments smaller than five millimetres in any dimension. The lower size limit for MPs is generally considered to be 1µm, however the lower limit in most studies is 300µm. Currently, MPs are categorised as large (1 mm to 5 mm) and small (<1 mm). MPs are also often categorised as either primary or secondary MP. Primary MPs are produced and released into the environment as micro particles and include raw plastic granules (nurdles) used in the manufacture of plastic materials, and microbeads in cosmetics, skin care scrubs, cleaning

products, and as abrasives in industrial applications. Secondary MPs are produced in the environment from the breakdown of macroplastics (plastic particles >5mm in any dimension).

MPs have recently been discovered in high and increasing concentrations in the world's oceans and inland waterways, and are a subject of increasing concern to the public, regulators and governments worldwide. Consequently there is a significant international effort underway to identify the sources, fate, and impacts of MPs in aquatic ecosystems.

WWTPs are one of the recognised sources of MPs into the environment, receiving inputs of MPs from both industrial and domestic sources. Domestic sources of MPs include microbeads in cosmetic, personal care and cleaning products, and fibres produced by the washing of synthetic textiles. Up to 1900 MP synthetic fibres can be released from the washing of a single item of clothing made from synthetic fabric (Brown et al, 2011).

The removal of MPs from wastewater by tertiary wastewater treatment processes is reasonably high. For example, wastewater entering European wastewater treatment plants (WWTPs) contained 15 to 200 particles per L (ppL) of which 90 % to 99.9 % was removed by wastewater treatment, with higher removal efficiency achieved for larger particles and lower removal efficiency for MPs of 20µm to 300µm diameter (GWRC, 2015). Under conventional treatment most of the MPs are retained by sedimentation and therefore accumulate in sewage sludge and biosolids. However, the constant input of MPs into WWTPs means that treated WWTP effluents contain residues of MPs that are released into the environment. For example, in the United States WWTPs are the largest source of MPs into aquatic environments, principally through the discharge of microbeads and microfibers (McCormick, et al, 2015; Mason et al, 2016).

In New Zealand new regulations to ban the sale of products containing intentionally added, solid plastic particles less than 5mm in size, come into effect on 7 June 2018. Under section 23 of the Waste Minimisation Act 2008, the sale and manufacture of wash-off products that contain plastic microbeads for the purposes of exfoliation, cleaning, abrasive cleaning or visual appearance of the product will be prohibited. The prohibited sale of these products will result in the removal of microbeads from WWTP effluent in New Zealand, with the result that microfibers originating from the washing of synthetic textiles will become the predominant MP within WWTP effluent discharged into the New Zealand environment.

Filtration is the optimal treatment for removing MPs from WWTP effluents. Sand filters have been applied to remove MPs from treated effluent but with variable removal rates due to the variation in the size fraction of MPs that have been investigated.

The smaller size of plastic microfibers (generally <100µm in one dimension) makes them more challenging to remove from treated wastewater. However, the application of membrane technologies with small sub-micron pore size provides the best state of the art technology to remove plastic microfibers and the upper size range of plastic and other types of nanoparticles from wastewater effluent.

The proposed upgrade for RLC WWTP will result in all effluent being subject to ultrafiltration at 0.04 microns, or 40 nanometers. Ultrafiltration through pores of this size will remove all microplastics and a significant proportion of nano-sized plastic and other nano-sized residues from the treated

effluent. The introduction of ultrafiltration at 0.04 microns for the treatment of effluent will result in RLC WWTP achieving the most efficient and highest level of reduction of microplastics and nanoplastics in wastewater effluent in New Zealand

RECOMMENDATIONS FOR FUTURE WORK

Identification of representative model EOCs

In the absence of comprehensive data on the type and concentration of EOCs that were present in the RLC WWTP MBR permeate this study analysed a total of seventy-eight individual EOCs from nine different classes of EOCs. The analysis of this number and range of EOCs together with the assessment of their risk represents one of the most comprehensive studies to date of the potential impact of EOCs in WWTP effluent entering the New Zealand environment.

As highlighted by the analysis results a total of forty-one EOCs were detected in MBR permeate and a reduced number of these dominated the profile of EOCs within each class of compounds. Some of the EOCs present in the MBR permeate can be adopted as representative model EOCs to include in future studies of the fate and effects of EOCs in RLC WWTP discharged into Lake Rotorua

The twelve 12 EOCs identified as representative model EOCs are listed in Table 15 along with their respective chemical classes.

These chemicals provide a useful subset of model EOCs to incorporate into future assessments of the efficacy of modifications incorporated into the RLC WWTP to remove and/or reduce the concentration of residual EOCs in discharged effluent, and assess the fate and effects of EOCs in treated effluent discharged into Lake Rotorua.

Table 15. Representative model EOCs in MBR permeate

Emerging Organic Chemical	Class	MBR Mean
TBP	Alkylphosphate Flame Retardant	135
TDCP	Alkylphosphate Flame Retardant	287
TBEP	Alkylphosphate Flame Retardant	1529
Methyl-triclosan	Phenolic Antimicrobial	66.2
Triclosan	Phenolic Antimicrobial	98.6
Technical-NP equivalents	Industrial alkylphenol	541
Galaxolide (HHCB)	Polycyclic musks	341
Tonalide(AHTN)	Polycyclic musks	137
Carbamazepine	Acidic Pharmaceutical	383
Diclofenac	Acidic Pharmaceutical	304
Bisphenol-A	Plasticiser	33.7
Estrone	Steroid hormone	55.4

Analyte key

TBP = Tributyl-phosphate

TDCP = Tris[2-chloro-1-(chloromethyl)ethyl] phosphate

TBEP = Tris-(2-butoxyethyl) phosphate

Reviewing the science on the fate and effects of EOCs

As demonstrated by the absence of PNEC values for most of the EOCs assessed in this study there is limited information available to characterise the impacts of EOCs within aquatic environments. The continual development and introduction of new techniques to assess the broader effects of chemicals to exposed organisms within the field of ecotoxicity is beginning to produce new effects based data, particularly with respect to long-term chronic impacts, that can have a profound effect at the population level, so that effective actions can be implemented to manage their long-term impacts.

Periodic review of the latest research assessing the potential risks of EOCs to aquatic organisms is recommended so that effective actions can be implemented to manage their long-term impacts and ensure aquatic organisms in Lake Rotorua are not adversely affected by EOCs in treated effluent discharged from the RLC WWTP.

REFERENCES

AIST (Japan National Institute of Advanced Industrial Science and Technology) 2007. AIST Risk Assessment Document Series 4. Bisphenol A.

Browne, M. A.; Crump, P.; Niven, S. J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environmental Science & Technology*. 45: 9175–9179.

Caldwell, D.J., Mastrocco, F., Anderson, P.D., Länge, R., Sumpter, J.P., 2012. Predicted no-effect concentrations for the steroid estrogens estrone, 17 β -estradiol, estriol, and 17 α -ethinylestradiol. *Environmental Toxicology and Chemistry*. 31: 1396–1406.

Dada, A.C., Hicks, B. J. M., Ling, N., Hamilton, D. P. 2017. Assessment of Effects of Proposed Treated Wastewater Discharge to the Te Arikioa Thermal Channel and Sulphur Bay (Lake Rotorua). Report prepared for Rotorua Lakes Council by the Environmental Research Institute University of Waikato. ERI Report 91.

Env Canada/ Health Canada 2008. Screening assessment for the challenge phenol, 4,4' (1-methylethylidene)bis- (Bisphenol A) CAS 80-05-7. October 2008
http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_80-05-7_en.pdf

Environment Canada /Health Canada 2016. Draft screening assessment, certain organic flame retardants substance grouping. 2-Propanol,1-chloro-,phosphate (3:1) (TCPP). Chemical Abstracts Service Registry Number 13674-84-5. 2-Propanol, 1,3-dichloro-,phosphate (3:1) (TDCPP). Chemical Abstracts Service Registry Number 13674-87-8. 149 p.

EU 2002. European Union summary risk assessment report: 4-nonylphenol (branched) and nonylphenol. CAS Nos: 84852-15-3 and 25154-52-3. EINECS Nos: 284-325-5 and 246-672-0. Special Publication I.02.69.

EU 2008. European Union updated risk assessment report. Bisphenol A, CAS No: 80-05-7. Institute for Health and Consumer Protection, European Chemicals Bureau, European Commission Joint Research Centre, 3rd Priority List, Luxembourg: Office for Official Publications of the European Communities.

Global Water Research Coalition. 2015. Science Brief. Microplastics in fresh water resources. Prepared for GWRC by Storck, F. R., Kools, S.A.E., and Rinck-Pfeiffer, S.

HERA 2004. Human and environmental health assessment on ingredients of household cleaning products. Polycyclic musks AHTN (CAS 1506-02-1) and HHCB (CAS 122-05-05). Environmental Section. Version 2. November 2004. 81 p.

Mason, S.A., Garneau, D., Sutton, R., Chu, Y., Ehmann, K., Barnes, J., Fink, P., Papazissimos, D., Rogers, D.L. 2017. Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. *Environmental Pollution*. 218:1045-1054.

McCormick A, Hoellein, T.J., Mason, S.A., Schluep, J., Kelly, J.J. 2014. Microplastic is an abundant and distinct microbial habitat in an urban river. *Environmental Science and Technology*. 48:11863-11871.

Mott MacDonald. Rotorua Wastewater- Design statement for preferred treatment arrangement. 2017. Report prepared for Rotorua Lakes Council.

Northcott, G.L., Strong, J., Tremblay, L., Wilkins, A.L., 2013. WWTPs contribute significant loadings of emerging organic contaminants to NZs aquatic environment. SETAC Australasia 'What's in our Water Symposium'. 2nd October 2013, Melbourne Australia.

Ortiz de Garcia, S.A., Pinto, G.P., Garcia-Encina, P. A., Irusta-Mata, R. 2014. Ecotoxicity and environmental risk assessment of pharmaceuticals and personal care products in aquatic environments and wastewater treatment plants. *Ecotoxicology*. 23: 1517-1533.

Staples, C. A., Parkerton, T.F., Peterson, D. R. 2000. A risk assessment of selected phthalate esters in North American and Western European surface waters. *Chemosphere*. 40: 885-891.

OECD SIDS 2002. SIDS initial assessment report for 12th SIAM. Tributyl phosphate. CAS No: 126-73-8. UNEP Publications. 132 p.

US EPA 2014. TSCA work plan chemical risk assessment HHCB 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- $\bar{b}$ -2-benzopyran. CASRN 1222-05-5. EPA Document # 746-R1-4001. August 2014. Office of Chemical Safety and Pollution Prevention. 136 p.

Verbruggen EMJ, Rila JP, Traas TP, Posthuma-Doodeman CJAM, Posthumus R 2005. Environmental risk limits for several phosphate esters, with possible application as flame retardant. RIVM Report 601501024/2005. 118 p.

Water Framework Directive—United Kingdom Technical Advisory Group (WFD-UKTAG) 2009. Proposed EQS for Water Framework Directive Annex VIII substances: triclosan (for consultation). Report commissioned for the Environment Agency and the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER).

WHO (World Health Organisation) 2004. Integrated risk assessment: nonylphenol case study. International Programme on Chemical Safety, WHO, Geneva, Switzerland.

Wright-Walters M, Volz C, Talbott E, Davis D 2011. An updated weight of evidence approach to the aquatic hazard assessment of Bisphenol-A and the derivation of a new predicted no effect concentration (PNEC) using a non-parametric methodology. *Science of the Total Environment*. 409: 676-85.

Zhao, W., Wang, B., Wang, Y., Deng, S., Huang, J., Yu, G. 2017. Deriving acute and chronic predicted no effect concentrations of pharmaceuticals and personal care products based on species sensitivity distributions. *Ecotoxicology and Environmental Safety*. 144: 537-542.

APPENDIX ONE

Emerging Organic Chemicals and their expected Method Detection Limits

Emerging Organic Chemical	MDL (ng/L)
<u>Alkylphosphate Flame Retardants</u>	
TiBP	0.10
TBP	0.10
TCEP	0.10
TCPP	0.10
TDCP	0.10
TPP	0.40
TBEP	0.10
TEHP	0.10
ToCP	10
TmCP	10
TpCP	10
<u>Phenolic Antimicrobials</u>	
Chloroxylenol	0.05
o-phenylphenol	0.10
Chlorophene	0.10
methyl triclosan	0.05
Triclosan	0.10
Tetra-bromocresol	1.00
<u>Parabens</u>	
Methylparaben	0.05
Ethylparaben	10.0
Propylparaben	0.05
Butylparaben	0.05
Benzylparaben	0.05
<u>Industrial Alkylphenols</u>	
4-t-Amylphenol	0.10
4-n-Amylphenol	0.10
4-t-octylphenol	0.10
4-t-heptphenol	0.10
4-n-octylphenol	0.10
4-n-nonylphenol	0.10
Tech-NP-equivalents	5.0
<u>Insect Repellants</u>	
DEET	1.0
Picaradin	1.0
Benzylbenzoate	1.0

APPENDIX ONE

Emerging Organic Chemicals and their expected Method Detection Limits- continued

Emerging Organic Chemical	MDL (ng/L)
<u>Nitro- and Polycyclic Musk Fragrances</u>	
Cashmeran	1.0
Celestolide	1.0
Phantolide	1.0
Musk ambrette	1.0
Traseolide	1.0
Galaxolide	2.5
Musk xylene	1.0
Tonalide	5.0
Musk moskene	1.0
Musk tibetene	1.0
Musk ketone	1.0
<u>Acidic Pharmaceuticals</u>	
Acetaminophen	0.20
Aspirin	20.0
Carbamazepine	0.10
Clofibric acid	0.50
Diclofenac	0.10
Ibuprofen	0.10
Ketoprofen	0.10
Meclofenamic acid	0.50
Naproxen	0.10
Salicylic acid	2.0
<u>Phthalate esters and plasticisers</u>	
Chloro-ethoxymethane	5.0
Dimethylphthalate	1.0
Diethylphthalate	15
4-Chlorophenyl phenyl ether	0.10
4-bromophenyl phenyl ether	0.10
Di-n-butylphthalate	20
Butylbenzyl phthalate	1.0
Diethylhexylphthalate	25
Di-n-octylphthalate	5.0
Monomethyl-PAE	1.0
Monobutyl-PAE	1.0
MonoEH-PAE	1.0
Bisphenol A	1.0

APPENDIX ONE

Emerging Organic Chemicals and their expected Method Detection Limits- continued

Emerging Organic Chemical	MDL (ng/L)
<u>Steroid Hormones</u>	
Estrone	0.02
17 α -estradiol	0.02
17 β -estradiol	0.02
Estriol	0.05
Mestranol	0.02
17 α -ethinylestradiol	0.02
Androstenediol	0.1
19-Nortestosterone	1.0
Androstenedione	0.1
Testosterone	0.1
19-Norethindrone	1.0
Norgestrel	1.0

APPENDIX TWO

Concentration of EOCs in MBR permeate and Lake Rotorua water samples in parts per trillion (ng/L)

Emerging Organic Chemical	MBR 22/23	MBR 23/24	MBR 24/25	MBR Min	MBR Max	MBR Mean	Lake Site 4	Lake Site 5
<u>Alkylphosphate Flame Retardants</u>								
TiBP	44.5	46.6	47.3	44.5	47.3	46.1	N.D ^A	N.D
TBP	167	152	87.1	87.1	167	135	N.D	N.D
TCEP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
TCPP	N.D	N.D	N.D	N.D	N.D	N.D	20.1	23.9
TDCP	272	267	322	267	322	287	1.23	1.06
TPP	28.5	29.3	29.6	28.5	29.6	29.1	0.41	0.39
TBEP	819	1062	2707	819	2707	1529	N.D	N.D
TEHP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
ToCP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
TmCP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
TpCP	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

^AN.D = not detected

Analyte key

TiBP = Tri-isobutyl-phosphate

TBP = Tributyl-phosphate

TCEP= Tris(2-chloroethyl) phosphate

TCPP = Tris (1-chloro-2-propyl) phosphate

TDCP = Tris[2-chloro-1-(chloromethyl)ethyl] phosphate

TPP = Triphenylphosphate

TBEP = Tris-(2-butoxyethyl) phosphate

TEHP = Tris(2-ethylhexyl) phosphate

ToCP = Tri-o-cresyl phosphate

TmCP = Tri-m-cresyl phosphate

TpCP = Tri-p-cresyl phosphate

APPENDIX TWO:- continued.

Concentration of EOCs in MBR permeate and Lake Rotorua water samples in parts per trillion (ng/L)

Emerging Organic Chemical	MBR 22/23	MBR 23/24	MBR 24/25	MBR Min	MBR Max	MBR Mean	Lake Site 4	Lake Site 5
<u>Phenolic Antimicrobials</u>								
Chlorophene	8.57	10.6	11.6	8.57	11.6	10.3	N.D ^A	N.D
Chloroxylenol	4.63	3.06	2.91	2.91	4.63	3.53	0.12	0.35
o-phenylphenol	28.7	33.1	25.1	2.51	33.1	29.0	4.52	5.39
Methyl triclosan	65.7	61.5	71.3	61.5	71.3	66.2	N.D	N.D
Triclosan	93.4	90.9	112	90.9	112	98.6	25.1	26.8
Tetra-bromocresol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<u>Parabens</u>								
Benzylparaben	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Butylparaben	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Ethylparaben	N.D	N.D	N.D	N.D	N.D	N.D	65.6	57
Methyl paraben	N.D	N.D	N.D	N.D	N.D	N.D	0.11	0.26
Propylparaben	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<u>Industrial Alkylphenols</u>								
4-t-Amylphenol	N.D ^A	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4-n-Amylphenol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4-t-octylphenol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4-t-heptphenol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4-n-octylphenol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
4-n-nonylphenol	12.3	16.8	26.5	12.3	26.5	18.5	1.52	1.36
Tech-NP-equivalents	484	484	655	484	655	541	12.6	11.7

^AN.D = not detected

APPENDIX TWO:- continued.

Concentration of EOCs in MBR permeate and Lake Rotorua water samples in parts per trillion (ng/L)

Emerging Organic Chemical	MBR 22/23	MBR 23/24	MBR 24/25	MBR Min	MBR Max	MBR Mean	Lake Site 4	Lake Site 5
<u>Insect Repellants</u>								
DEET	N.D ^A	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Picaradin	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Benzylbenzoate	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
<u>Nitro- and Polycyclic Musk</u>								
<u>Fragrances</u>								
Cashmeran (DPMI)	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D
Celestolide (ADBI)	28.2	28.2	29.7	28.2	29.7	28.7	0.53	N.D
Galaxolide (HHCB)	330	339	354	330	354	341	2.82	4.13
Musk ambrette	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D
Musk ketone	58.3	58.7	61.5	58.3	61.5	59.5	N.D	N.D
Musk moskene	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D
Musk tibetene	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D
Musk xylene	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D
Phantolide	1.38	1.67	1.80	1.38	1.80	1.62	0.66	N.D
Tonalide(AHTN)	137	134	141	134	141	137	N.D	N.D
Traseolide (ATII)	N.D	N.D	N.D	NA	NA	N.D	N.D	N.D

^AN.D = not detected

APPENDIX TWO:- continued.

Concentration of EOCs in MBR permeate and Lake Rotorua water samples in parts per trillion (ng/L)

Emerging Organic Chemical	MBR 22/23	MBR 23/24	MBR 24/25	MBR Min	MBR Max	MBR Mean	Lake Site 4	Lake Site 5
<u>Acidic Pharmaceuticals</u>								
Acetaminophen	12.7	12.5	13.0	12.5	13.0	12.7	1.31	0.92
Aspirin	N.D. ^A	N.D.	N.D.	N.D.	N.D.	N.D.	5.67	4.77
Carbamazepine	361	408	381	361	408	383	1.38	3.26
Clofibric acid	1.09	0.96	1.03	0.96	1.09	1.03	N.D.	N.D.
Diclofenac	328	292	290	290	328	304	0.58	0.81
Ibuprofen	34.4	31.8	30.8	30.8	34.4	32.3	0.29	0.28
Ketoprofen	38.9	32.1	32.8	32.1	38.9	34.6	N.D.	N.D.
Meclofenamic acid	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Naproxen	9.24	10.7	11.5	9.24	11.5	10.5	N.D.	N.D.
Salicylic acid	38.0	34.4	33.3	33.3	38.0	35.2	89.2	105
<u>Phthalate esters and plasticisers</u>								
4-bromophenyl phenyl ether	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Butylbenzyl phthalate	1.77	1.72	1.93	1.72	1.93	1.80	1.26	0.70
4-Chlorophenyl phenyl ether	N.D	N.D	22.6	N.D	22.6	7.52	N.D	N.D
Chloro-ethoxymethane	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Diethylphthalate	N.D	51.9	55.9	N.D	55.9	35.9	4.59	1.75
Diethylhexylphthalate	N.D	N.D	63.6	N.D	63.6	21.2	N.D	12.7
Dimethylphthalate	0.85	0.78	0.48	0.48	0.85	0.71	N.D	N.D
Di-n-butylphthalate	13.6	15.4	22.3	13.6	22.3	17.1	18.4	6.78
Di-n-octylphthalate	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Monobutyl-PAE	9.24	10.7	11.5	9.24	11.5	10.5	2.15	1.21
Monoethylhexyl-PAE	38.0	34.4	33.3	33.3	38.0	35.2	6.42	7.04
Monomethyl-PAE	5.61	4.69	3.53	3.53	5.61	4.61	1.00	0.90
Bisphenol A	32.5	31.2	37.3	31.2	37.3	33.7	8.39	15.3

^AN.D = not detected

APPENDIX TWO:- continued.

Concentration of EOCs in MBR permeate and Lake Rotorua water samples in parts per trillion (ng/L)

Emerging Organic Chemical	MBR 22/23	MBR 23/24	MBR 24/25	MBR Min	MBR Max	MBR Mean	Lake Site 4	Lake Site 5
<u>Estrogenic steroid hormones</u>								
17 α -estradiol	0.73	N.D	0.91	N.D	0.91	0.55	N.D	N.D
17 β -estradiol	3.23	2.68	2.04	2.04	3.23	2.65	N.D	N.D
Estriol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Estrone	57.3	54.7	54.3	54.3	57.3	55.4	N.D	N.D
17 α -ethinylestradiol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Mestranol	2.36	1.87	1.57	1.57	2.36	1.93	0.67	N.D
<u>Androgenic steroid hormones</u>								
Androstenediol	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Androstenedione	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
19-Nortestosterone	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Testosterone	1.44	1.24	1.66	1.24	1.66	1.45	N.D	N.D
<u>Progestogens</u>								
Norethisterone	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Norgestrel	1.1	0.49	N.D	N.D	1.1	0.53	N.D	N.D

^AN.D = not detected