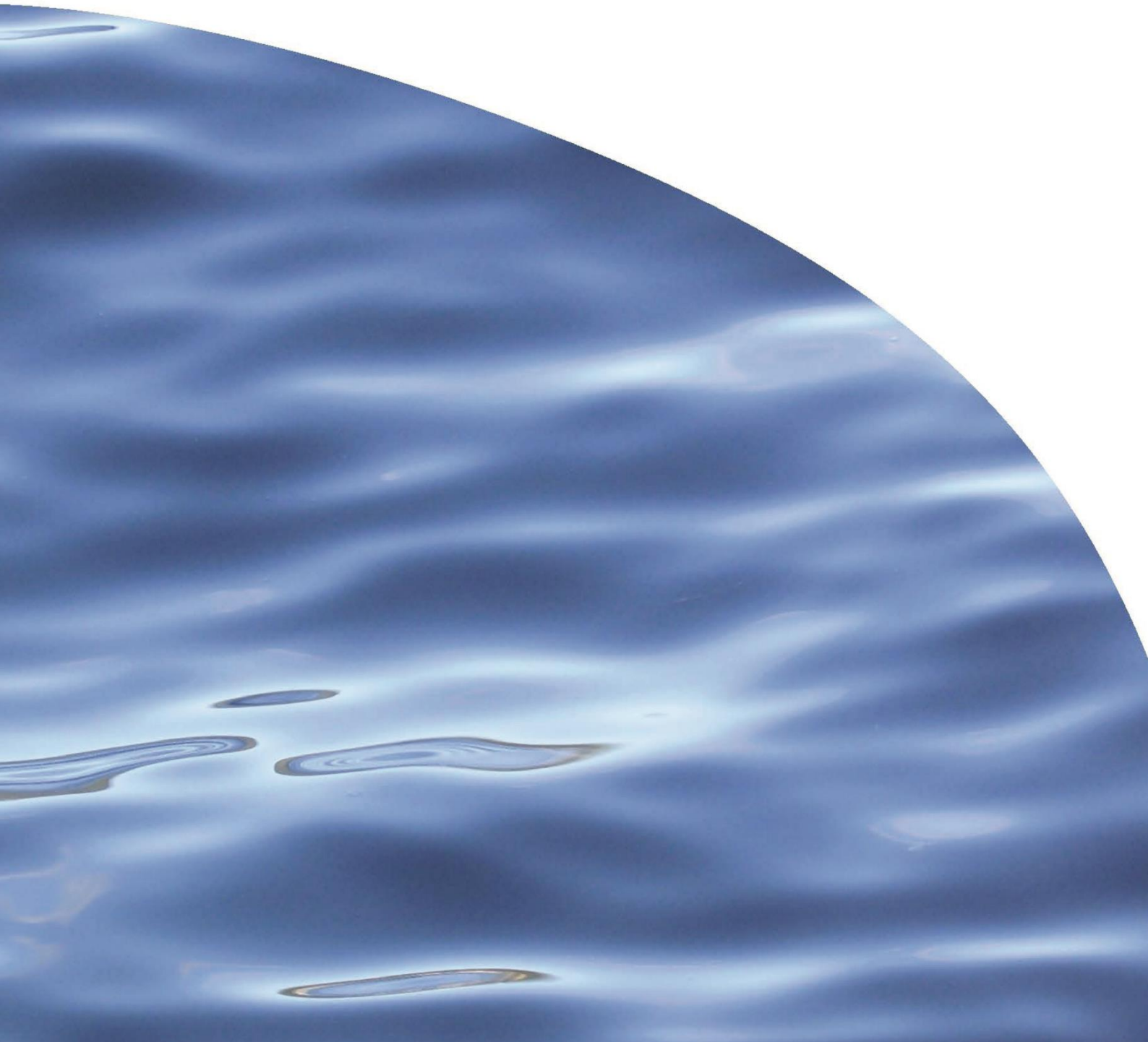
CAWTHRON
The power of science®

REPORT NO. 3631

ANALYSIS OF EMERGING ORGANIC CONTAMINANTS (EOCS) IN EFFLUENT OF THE RAGLAN WASTEWATER TREATMENT PLANT



ANALYSIS OF EMERGING ORGANIC CONTAMINANTS (EOCS) IN EFFLUENT OF THE RAGLAN WASTEWATER TREATMENT PLANT

LOUIS A TREMBLAY[1], GRANT L NORTHCOTT[2]

[1] CAWTHRON INSTITUTE, NELSON
[2] NORTHCOTT RESEARCH CONSULTANTS LIMITED, HAMILTON

Prepared for Watercare Services Limited
a/o Stephen Howard, Senior Consenting and Strategic Planner

CAWTHRON INSTITUTE
98 Halifax Street East, Nelson 7010 | Private Bag 2, Nelson 7042 | New Zealand
Ph. +64 3 548 2319 | Fax. +64 3 546 9464
www.cawthron.org.nz

REVIEWED BY:
Andrew Barrick

APPROVED FOR RELEASE BY:
Chris Cornelisen

ISSUE DATE: 20 April 2021

RECOMMENDED CITATION: Tremblay LA, Northcott GL 2021. Analysis of Emerging Organic Contaminants (EOCs) in effluent of the Raglan wastewater treatment plant. Prepared for Watercare Services Limited. Cawthron Report No. 3631. 13 p. plus appendix.

GLOSSARY

EOCs	Emerging organic contaminants
WWTP	Waste water treatment plant
SPE	Solid phase extraction
GCMS	Gas chromatography mass-spectrometry
MSTFA	N-methyl-N-(trimethylsilyl)trifluoroacetamide
MTBSTFA	N-tert-butyldimethyl- silyl-N-methyltrifluoroacetamide
TBDMSCl	t-butyldimethylsilyl chloride
QA	Quality assurance
ppt	Part per trillion
MDL	Method detection limits
PNEC	Predicted no-effect concentration
ADF	Average daily flow
NOEC	No observable-effect concentration
NC	Negligible concentration
TCPP	Tris(1-chloro-2-propyl)phosphate
TDCP	Tris[2-chloro-1-(chloromethyl)ethyl]phosphate
TPP	Triphenylphosphate
TBEP	Tris(2-butoxyethyl)phosphate
TNP	Technical nonylphenol
BPA	Bisphenol A
DEET	N,N-Diethyl-meta-toluamide

1. INTRODUCTION

Emerging organic contaminants (EOCs) have been defined as synthetic or naturally-occurring chemicals or any microorganisms not commonly monitored in the environment, but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects (Stewart et al. 2016). Municipal wastewater treatment plant (WWTP) effluent is recognised as a major source of EOCs into the environment. Watercare Services Limited contracted the Cawthron Institute and Northcott Research Consultants (NRC) Ltd to undertake an investigation of EOCs in the treated effluent discharged from the Raglan WWTP. The results of this investigation will inform decisions on appropriate wastewater treatment and discharge options, as part of the resource consent renewal process for Raglan WWTP managed by Watercare Services Limited on behalf of Waikato District Council.

The objectives of this study were to:

- characterise EOCs present in treated wastewater effluent from the Raglan WWTP
- compare the concentrations of EOCs detected with those in effluents from other WWTPs in New Zealand
- assess the risks of EOCs detected in the treated effluent from the Raglan WWTP pose to the receiving environment.

2. METHODS

2.1. Sample delivery and extraction

A sample of treated effluent from the Raglan WWTP effluent (dated 23 March 2020) was obtained by Watercare Services and delivered by courier on the same day to Northcott Research Consultants at Plant and Food Research, Ruakura. On arrival, the samples were acidified (pH = 2.0) by the addition of concentrated sulphuric acid, and filtered through a glass microfiber filter (47 mm, Labservice) topped with diatomaceous earth filter aid medium (Hyflo SuperCel) to remove particulate material. Two aliquots of the filtered effluent were collected in pre-cleaned glass Schott bottles (a 2L and a 1L aliquot) and stored under refrigeration overnight.

The prepared samples were extracted for analysis the following morning. The 2 L acidifed and filtered effluent 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. Concentrations of EOCs found in the water samples are typically below the µg L^{-1} range, making extraction, pre-concentration, and cleanup prior to detection an important step. The addition of carbon-13 labelled analogues is used as a quality control to characterise

the extraction efficacy of chemicals found at very low trace levels in a complex matrix like sewage effluent. The corresponding 1-L acidified and filtered effluent sample destined for analysis of acidic pharmaceuticals was spiked with a surrogate recovery solution containing the acidic herbicides dichlorprop, flamprop and MCPB, and the plant growth regulator naphthalene acetic acid.

Neutral and phenolic EOCs were extracted from the 2-L effluent sample by solid phase extraction (SPE) using Waters Oasis HLB cartridges. Acidic pharmaceuticals were extracted from the 1-L effluent sample using Waters Oasis MCX cartridges. EOCs eluted from the Oasis HLB SPE cartridge were purified using florosil adsorption chromatography followed by gel permeation chromatography to remove the large amount of residual fats and lipids that can be present in WWTP effluent 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 (GC-MS).

One 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).

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-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) with 1% t-Butyldimethylsilyl chloride (TBDMSCl).

2.3. Analysis of EOCs

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 an Agilent 5975C mass spectrometer operating in single ion monitoring mode. Precise measurement of target EOCs was achieved by internal standard quantitation using Agilent Chemstation MS software. Phthalate esters, monocaboxylate phthalate esters and pharmaceuticals were analysed using an Agilent 7000 series triple quadrupole GC-MS operating in MS/MS mode. Precise measurement of target EOCs was achieved by internal standard quantitation using Agilent Mass Hunter MS/MS software.

A total of 84 individual chemicals representing 9 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 (11 compounds)
- paraben preservatives (11 compounds)
- pharmaceuticals (10 compounds)
- phenolic antimicrobials (6 compounds)
- phthalate esters and plasticisers (13 compounds)
- steroid hormones (12 compounds).

3. RESULTS

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 1. The surrogate standard compounds spiked into the 2-L and 1-L samples of effluent for EOC and pharmaceutical analysis were added at an equivalent concentration of 50 ng/L (ppt) to assess the efficacy of extracting EOCs from the effluent sample.

The recovery of the surrogate standards meets the acceptance requirements of quality assurance (QA) criteria of > 70% for all carbon-13 labelled and acidic herbicide surrogate chemicals. The mean recovery of the carbon-13 labelled EOCs and acidic herbicide surrogate standards were 86.0% and 97.2%, 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 1. Recovery of EOC and pharmaceutical surrogate standard chemicals spiked into the Raglan WWTP effluent sample.

Recovery compound	Calculated mean percentage Recovery (%)
EOC surrogate	
^{13}C-methylparaben	88.2
^{13}C-ortho-phenylphenol	81.0
^{13}C-butylparaben	95.2
^{13}C-triclosan	96.4
^{13}C-bisphenol-A	81.6
^{13}C-estrone	80.0
^{13}C-17β-estradiol	79.8
Mean recovery	**86%**
Pharmaceutical surrogate	
Diclorprop	102.1
NAA	106.3
MCPB	97.9
Flamprop	82.5
Mean recovery	**97.2%**

3.1. Residues of EOCs

The EOC concentrations detected in the Raglan WWTP effluent sample are summarised in Table 2. All of the analysed EOCs together with their respective method detection limits (MDLs) are listed in Appendix 1. A total of 22 of the 84 individual EOCs analysed were detected in the effluent from the Raglan WWTP, including:

- 6 alkyl phosphate flame retardant
- 3 phenolic antimicrobial chemicals
- the industrial mixture of technical-nonylphenols
- the insect repellent DEET
- the polycyclic musk fragrance galaxolide
- 4 acidic pharmaceuticals
- 6 plasticisers.

Table 2. Concentration of EOCs detected in Raglan WWTP.

Emerging Organic Chemical	Concentration (ng/L)
Alkylphosphate Flame Retardants	
Tri-isobutylphosphate	33.0
Tri-butylphosphate	27.4
Tri-(2-chloroethyl)phosphate	183
Tris(1-chloro-2-propyl)phosphate	2199
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	173
Triphenylphosphate	2.15
Phenolic Anti-microbials	
Chloroxylenol	3.53
Chlorophene	9.41
Triclosan	8.13
Industrial alkylphenols	
Tech-NP-equivalents	84.0
Insect repellants	
DEET	101
Musk Fragrances	
Galaxolide	69.0
Acidic pharmaceuticals	
Carbamazepine	120
Diclofenac	16.0
Naproxen	35.6
Salicylic acid	7.91
Plasticisers	
Dimethylphthalate	4.16
Di-n-butylphthalate	40.9
Monomethyl-PAE	1.28
Monobutyl-PAE	6.19
MonoEH-PAE	2.56
Bisphenol A	4.47

[A]NA = not available

4. DISCUSSION

4.1. Comparison with other WWTPs in New Zealand

The national survey by Northcott et al. (2013) of EOCs in the influent and effluent of 13 WWTPs is the most comprehensive dataset in New Zealand. The plants selected represented a broad range of treatment technologies, catchment population, balance of domestic to industrial inputs, and geographic distribution throughout New Zealand The concentrations of EOCs in the dissolved phase of effluent from the thirteen

WWTPs surveyed by Nothrcott et al. (2013) are compared with the concentrations measured in the Raglan WWTP effluent in Table 3. The concentrations of EOCs from the thirteen WWTPs are presented as the range of the minimum to maximum measured concentration and the corresponding average concentration (mean).

The comparison of the measured concentrations for the acidic pharamaceuticals detected in the treated effluent from the Raglan WWTP is made against data collected over the last seven years from the analysis of treated effluent from six different WWTPs in New Zealand.

The concentration of EOCs detected in the effluent of the Raglan WWTP are largely comparable to that of other WWTPs in New Zealand (Table 3). Of the 22 EOCs detected in the Raglan WWTP effluent, the concentration of only one (the alkylphosphate flame retardant TCPP (Tris(1-chloro-2-propyl)phosphate**)** exceeded the previously determined maximum concentration but this is still well below the PNEC threshold (refer to Table 4). The concentration of the other 21 EOCs detected in the treated effluent from the Raglan WWTP either fell below or within the range of concetrations previously measured in treated effluent from New Zealland WWTPs. The data indicate that the Raglan WWTP achieves a level of EOC removal similar to other WWTPs in New Zealand, some of which are operating more advanced treatment technologies.

Table 3. Comparison of the concentration of EOCs detected in treated effluent from the Raglan wastewater treatment plant with that in other New Zealand wastewater treatment plants (Northcott et al. 2013).

	Concentration in ng/L (ppt)			
	Min	**Max**	**Mean**	**Raglan**
Musk fragrance				
Galaxolide	24.4	902.0	243.0	69.0
		Alkylphosphate flame retardant		
TiBP	ND	103.0	29.2	33.0
TnBP	26.9	499.0	128.0	27.4
TCEP	16.3	303.0	108.0	183.0
TCPP	70.5	1024.0	321.0	2199.0
TDCP	1.9	630.0	222.0	173.0
TPP	6.1	3277.0	301.0	2.1
Insect repellent				
DEET	15.2	1836.0	220.0	101.0
Antimicrobial				
Chloroxylenol	4.1	2633.0	322.0	3.5
Chlorophene	ND	10.3	NA	9.4
Triclosan	4.4	158.0	38.3	8.1
Plasticiser				
Bisphenol-A	N.D	66.9	17.0	4.5
Monomethyl-PAE	1.2	65.7	17.5	1.3
Monobutyl-PAE	5.3	52.0	20.3	6.2
Monoethylhexyl-PAE	15.2	1596.0	380.0	2.6
Acidic pharmaceuticals				
Carbamazepine	233.0	719.0	487.0	120.0
Diclofenac	19.4	913.0	512.0	16.0
Naproxen	9.2	770.0	312.0	35.5
Salicylic acid	ND	118.0	44.6	7.9

[A] values in green highlight represent those less than the minimum value of the range
[B] values in orange highlight represent those falling within the range of minimum to maximum
[C] values in red highlight represent those falling exceeding the maximum of the range

4.2. What is the risk of EOCs in the treated effluent of the Raglan WWTP to the receiving environment?

The risk the residual EOCs in Raglan WWTP effluent present to the receiving environment has been assessed by comparing the concentrations of the EOCs with available predicted no-effect concentrations (PNECs), an estimate of the concentration below which exposure to a substance is not expected to cause adverse effects. For those EOCs where a PNEC is not available, the no observable-effect

concentration (NOEC) was used. The results from the analyses along with available guideline limits are summarised in Table 4. Some PNECs were derived for freshwater environments that would tend to overestimate risk to marine environments. The concentrations of phthalate plasticisers fell significantly below the available PNEC values.

Overall, the results indicate that the risk to the receiving environment represented by the EOCs detected in the treated effluent of the Raglan WWTP can be considered negligible. It should be noted however, that this conclusion is based on the analysis of a single sampling event.

Table 4. Raglan WWTP effluent concentrations of some emerging organic contaminants compared to some recommended limits from world-wide agencies. PNEC = predicted no-effect concentration; NOEC = no observed effect concentration. The latter are indicated by *. Order of magnitude: 1 order of magnitude is a 10-fold difference, 2 orders of magnitude is a 100-fold difference, and so forth.

Emerging organic contaminant	Abbreviation	Raglan concentration (µg/L)	Above/below PNEC/NOEC	Order of magnitude	PNEC or NOEC* (µg/L)	Source
Tri-butylphosphate	TBP	0.027	Below	7	370,000 (algae)	OECD 2002
Tris(1-chloro-2-propyl)phosphate	TCPP	2.2	Below	3	1,700 (aquatic ecosystems)	Env Canada 2016
			Below	2-3	640 (inverts) 260 (algae) 64 (fish)	European Union (EU 2008a)
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	TDCP	0.173	Below	1	1.3 (aquatic ecosystems)	Env Canada 2016
				1-2	1 (seawater) 10 mg/L (freshwater)	European Union (EU 2008b)
Triphenylphosphate	TPP	0.002	Below	2-3	0.16 (aquatic organisms)	Netherlands (Verbruggen et al. 2005)
					0.74 (surface waters) 0.074 (marine water)	European Commission Water Framework Directive Annex VIII (WFD-UKTAG 2009)
Triclosan	TCS	0.0081	Below	2	0.1 (fresh water)	European Commission Water Framework Directive Annex VIII (WFD-UKTAG 2009)
technical nonylphenol	TNP	0.048	Below	1	0.20 (water)	Europe (WHO 2004)
			Below	1	0.330	European Union (EU 2002)

Table 4, continued

Emerging organic contaminant	Abbreviation	Raglan concentration (µg/L)	Above/below PNEC/NOEC	Order of magnitude	PNEC or NOEC* (µg/L)	Source
DEET		0.1	Below	3	407 (algae, daphnia zebrafish)	Sun et al. 2016
				2	43 (aquatic organisms)	European Union (EU 2010)
galaxolide	HHCB	0.069	Below	3	68 (freshwater fish) 39 (marine copepods)	United States EPA (US EPA 2014)
			Below	2	6,800 (marine organisms)	European Union (HERA 2004, EU 2008c)
Bisphenol A	BPA	0.0045	Below	3	1.5	European Union (EU 2008d)
				3	1.6	Japan (AIST 2007)
				2	0.175	Env Canada 2008
				Same	0.06 (aquatic organisms)	Meta analysis: Wright-Walters et al. 2011
Dimethylphthalate	DMPAE	0.004	Below	10	3,125,000	Staples et al. 2000
Di-n-butylphthalate	DnBPAE	0.041	Below	6	57,000	Staples et al. 2000
Carbamazepine		0.12	Below	2	25	Li 2014
Diclofenac		0.016	Below	2	9.8	Zhao et al. 2017
Naproxen		0.036	Below	3	37	Li 2014
Salicylic acid		0.045	Below	4	119	Ortez de Garcia et al. 2014

`

5. CONCLUSIONS

Concentrations of EOCs measured in the treated effluent of the Raglan WWTP are considerably lower than those recognised to represent a risk to freshwater and marine organisms. Furthermore, effluent will be subject to dispersion and dilution upon discharge to the environment, which will further reduce the concentrations of the detected EOCs and their potential risks. The EOCs entering the receiving environment will be subjected to loss and removal through a range of microbial and chemical degradation processes, and potential adsorption to sediment particles.

Therefore, taking into account the current state of knowledge regarding the toxicity of measured EOCs towards organisms within freshwater and marine environments, we conclude that the EOCs measured in the treated effluent of the Raglan WWTP do not pose an immediate risk to aquatic organisms in the receiving environment.

There is currently limited information on the characterisation of the impacts of EOCs in combination with other stressors like reduced dissolved oxygen, metals and nutrients on organisms in the receiving environment. Therefore, it is important to keep abreast of the latest research assessing the potential risks of EOCs so that effective mitigation actions can be implemented to manage them as required.

6. ACKNOWLEDGEMENTS

The authors thank the Watercare Services staff for sampling the Raglan effluent.

7. REFERENCES

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

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

Env 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 2008a. European Union risk assessment report. Tris(2-chloro-1-methylethyl)Phosphate (TCPP). CAS No. 13674-84-5. EINECS No: 237-158-7. Risk Assessment. Published by the European Commission. http://europa.eu.int. 408 p.

EU 2008b. European Union risk assessment report. Tris[2-chloro-1-(chloromethyl)ethyl]Phosphate (TDCP). CAS No. 13674-87-8. EINECS No: 237-156-2. Risk Assessment. published by the European Commission. 251 p. http://europa.eu.int. 294 p.

EU 2008c. European Union risk assessment report. 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran (HHCB). CAS No: 122-05-5. Published by the European Commission. 251 p. http://europa.eu.int.

EU 2008d. 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.

EU 2010. Directive 98/8/EC concerning the placing of biocidal products on the market. Inclusion of active substances in Annex I or IA to Directive 98/8/EC N,N-diethyl-meta-toluamide (DEET) Product-type 19.

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.

Li WC 2014. Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environmental Pollution 187: 193-201.

Northcott GL, Strong J, Tremblay LA, Wilkins A 2013. Emerging organic contaminants enter New Zealand's aquatic environments with waste water treatment plant effluents. In Gielen G, Heaphy M (eds) Proceedings of the 2013 New Zealand Land Treatment Collective annual conference, 10-12 April 2013, Blenheim, New Zealand.

Ortiz de Garcia SA, Pinto GP, Garcia-Encina PA, 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 CA, Parkerton TF, Peterson DR 2000. A risk assessment of selected phthalate esters in North American and western European surface waters. Chemosphere 40: 885-891.

Stewart M, Northcott G, Gaw S, Tremblay LA 2016. An update on emerging organic contaminants of concern for New Zealand with guidance on monitoring approaches for councils. Prepared by Streamlined Environmental Ltd, Northcott Research Consultants Ltd, University of Canterbury, Cawthron Institute and the University of Auckland for Auckland Council, Greater Wellington Regional Council and Environment Canterbury Regional Council. Auckland Council technical report TR2016/006.

Sun HQ, Du Y, Zhang ZY, Jiang WJ, Guo YM, Lu XW, Zhang YM, Sun LW 2016. Acute toxicity and ecological risk assessment of benzophenone and N,N-diethyl-3-methylbenzamide in personal care products. International Journal of Environmental Research and Public Health 13(9): 925.

US EPA 2014. TSCA work plan chemical risk assessment HHCB 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcylcopenta-γ-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.

8. APPENDIX

Appendix 1. List of analysed emerging organic contaminants and their method detection limits (MDLs) in Raglan WWTP effluent.

Emerging Organic Chemical	Concentration (ng/L)	MDL (ng/L)
Alkylphosphate Flame Retardants		
Tri-isobutylphosphate	33.0	0.10
Tri-butylphosphate	27.4	0.10
Tris(2-chloroethyl)phosphate	183	0.10
Tris(1-chloro-2-propyl)phosphate	2199	0.10
Tris[2-chloro-1-(chloromethyl)ethyl]phosphate	173	0.10
Tri-phenylphosphate	2.15	0.10
Tris(2-butoxyethyl)phosphate	ND[A]	0.10
Tris(2-ethylhexyl)phosphate	ND	0.10
Tri-o-cresylphosphate	ND	10.00
Tri-m-cresylphosphate	ND	10.00
Tri-p-cresylphosphate	ND	10.00
Phenolic Anti-microbials		
Chloroxylenol	3.53	0.05
o-phenylphenol	ND	0.10
Chlorophene	9.41	0.10
methyl triclosan	ND	0.05
Triclosan	813	0.10
Dichlorophen	ND	0.50
Paraben preservatives		
Methylparaben	ND	0.05
Ethylparaben	ND	0.05
Isopropylparaben	ND	0.05
Propylparaben	ND	0.05
isobutylparaben	ND	0.05
Butylparaben	ND	0.05
Pentylparaben	ND	0.05
Hexylparaben	ND	0.05
Phenylparaben	ND	0.05
Heptylparaben	ND	0.05
Benzylparaben	ND	0.05

[A] ND = not detected above the method detection limit

Appendix 1 continued, Analysed emerging organic contaminants and their method detection limits (MDLs) in Raglan WWTP effluent.

Emerging Organic Chemical	Concentration (ng/L)	MDL (ng/L)
Industrial alkylphenols		
4-t-Amylphenol	ND	0.10
4-n-Amylphenol	ND	0.10
4-t-octylphenol	ND	0.10
4-t-heptylphenol	ND	0.10
4-n-octylphenol	ND	0.10
4-n-nonylphenol	ND	0.10
Tech-NP-equivalents	84.0	5.00
Insect repellants		
DEET	101	1.00
Picaradin	ND	1.00
Benzylbenzoate	ND	1.00
Musk fragrances		
Cashmeran	ND	1.00
Celestolide	ND	1.00
Phantolide	ND	1.00
Musk ambrette	ND	1.00
Traseolide	ND	1.00
Galaxolide	69.0	5.00
Musk xylene	ND	1.00
Tonalide	ND	1.00
Musk moskene	ND	1.00
Musk tibetene	ND	1.00
Musk ketone	ND	1.00
Acidic pharmaceuticals		
Acetaminophen	ND	0.10
Aspirin	ND	0.10
Carbamazepine	120	0.10
Clofibric acid	ND	0.50
Diclofenac	16.0	0.10
Ibuprofen	ND	0.10
Ketoprofen	ND	0.10
Meclofenamic	ND	0.50
Naproxen	35.6	0.10
Salicylic acid	7.9	2.00

[A] ND = not detected above the method detection limit

Appendix 1, continued. List of analysed Emerging Organic Contaminants and their Method Detection Limits (MDLs) in Raglan WWTP effluent.

Emerging Organic Chemical	Concentration (ng/L)	MDL (ng/L)
Plasticisers		
Chloro-ethoxymethane	ND[A]	5.00
Dimethylphthalate	4.16	1.00
Diethylphthalate	ND	5.00
4-Chlorophenyl phenyl ether	ND	0.10
4-bromophenyl phenyl ether	ND	0.10
Di-n-butylphthalate	40.9	5.00
Butylbenzyl phthalate	ND	0.10
Diethylhexylphthalate	ND	25.00
Di-n-octylphthalate	ND	5.00
Monomethyl-PAE	1.28	1.00
Monobutyl-PAE	6.19	1.00
MonoEH-PAE	2.56	1.00
Bisphenol A	4.47	0.50
Steroid hormones		
Estrone	ND	0.02
17□-estradiol	ND	0.02
17□-estradiol	ND	0.02
Estriol	ND	0.05
Mestranol	ND	0.02
17□-ethynylestradiol	ND	0.02
Androstenediol	ND	0.10
19-Nortestosterone	ND	1.00
Androstenedione	ND	0.10
Testosterone	ND	0.10
19-Norethindrone	ND	1.00
Norgestrel	ND	1.00

[A] ND = not detected above the method detection limit