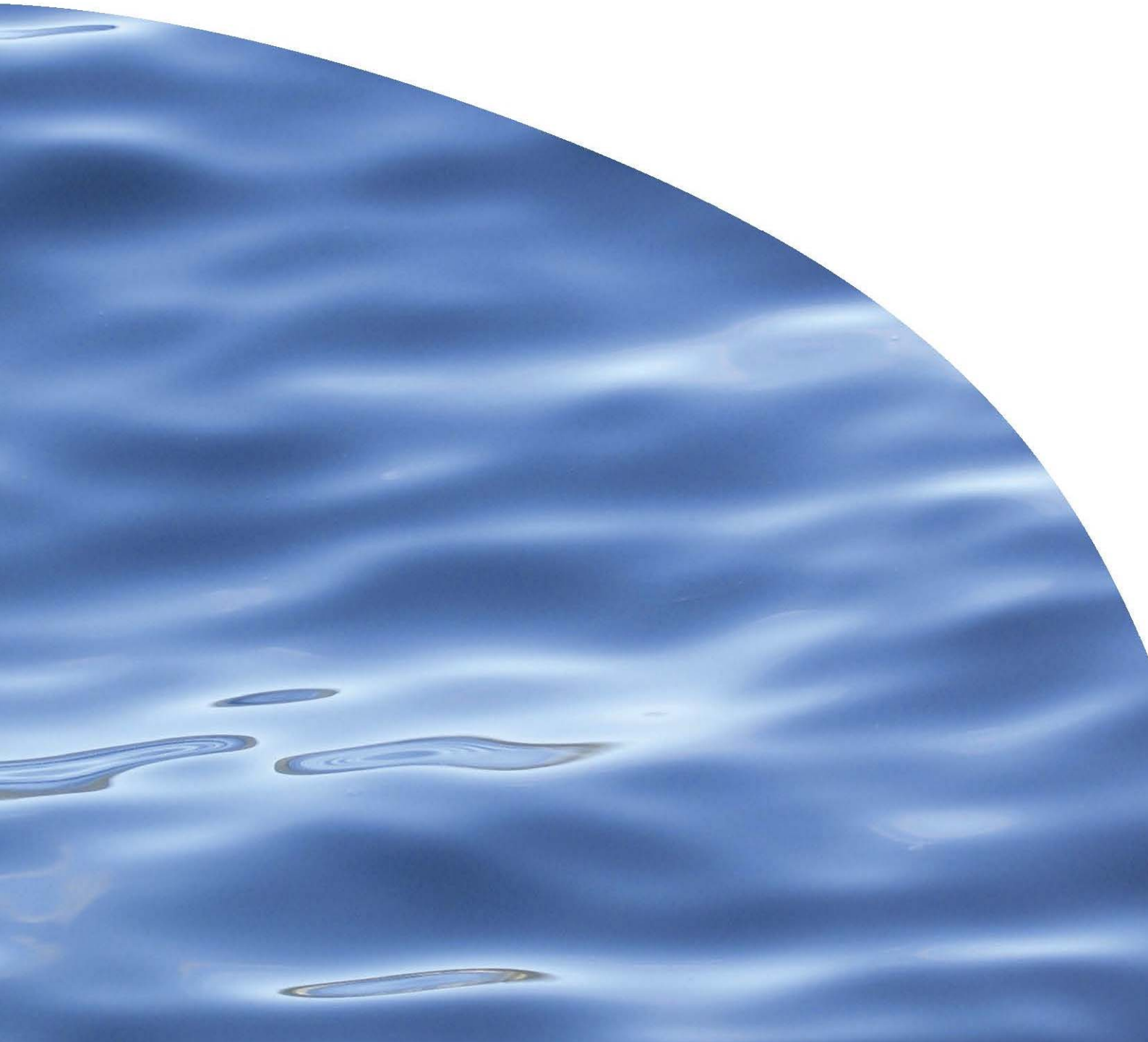
CAWTHRON INSTITUTE

REPORT NO. 2667

RISK ASSESSMENT OF EMERGING CONTAMINANTS IN TREATED WASTEWATER IN THE AUCKLAND REGION



RISK ASSESSMENT OF EMERGING CONTAMINANTS IN TREATED WASTEWATER IN THE AUCKLAND REGION

LOUIS TREMBLAY[1], GRANT NORTHCOTT[2]

[1] CAWTHRON INSTITUTE
[2] NORTHCOTT RESEARCH CONSULTANTS LIMITED

Prepared for Watercare Services Limited

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:
Cora Drijver
Cope Environmental Consulting

APPROVED FOR RELEASE BY:
Roger Young

ISSUE DATE: 13 April 2015

RECOMMENDED CITATION: Tremblay LA, Northcott GE 2015. Risk assessment of emerging contaminants in treated wastewater in the Auckland region. Prepared for Watercare Services Limited. Cawthron Report No. 2667. 45 p.

EXECUTIVE SUMMARY

Scope of the review

Watercare Services Limited (Watercare) contracted Cawthron Institute (Cawthron) to assess the potential risk of residual emerging organic contaminants (EOCs) in treated wastewater including:

- Conduct a review of the literature on emerging contaminants such as pharmaceuticals and personal care products (PPCPs), which may be present in treated wastewater, and may be applied to land (*e.g.* the Omaha wastewater treatment plant).
- Assess the potential risks from the discharge of treated wastewater, which may contain these contaminants, on the receiving groundwaters, estuaries and harbours, and fish and shellfish.
- Provide comments and recommendations on attenuation and losses in these environments, including wastewater treatment plants.
- Provide recommendations on emerging contaminants of concern, which may require assessment in WWTP effluent and monitoring in receiving environments.

This review focuses on chemicals, collectively referred to as 'emerging organic contaminants' (EOCs), which are typically of an organic, rather than inorganic nature. Contaminants such as nanoparticles (carbon black, titanium dioxide, iron oxides), have not been considered in this report as their environmental risks may be less than previously expected.

Emerging organic contaminants are synthetic or naturally-occurring chemicals. The main sources include pharmaceuticals and personal care products (PPCPs), veterinary medicines, fire retardants and other industrial products and new generation pesticides. There is a growing negative public perception of the potential fate and undesirable effects of such chemicals on the environment.

There is limited information to assess the risk of EOCs, and a paucity of information in New Zealand. Most EOCs are not commonly monitored, so their potential impacts on environmental and human health remain poorly characterised. The importance of EOCs in terms of biological impacts in the natural environment relative to other chemical and non-chemical stressors is not clear.

EOCs with endocrine disrupting activity are the most studied. Endocrine disrupting chemicals (EDCs) have been the subject of extensive research due to their potential to interfere with endocrine processes. These contaminants have been linked to significant effects in wildlife, including sex reversal and infertility in several species of fish. A range of threshold values to manage EDCs with estrogenic activity have been estimated. The New Zealand studies on EDCs to date tend to indicate that they pose negligible risks to aquatic biota.

Effluents from WWTPs are a main source of EOCs. Preliminary data confirms that the concentration of EOCs in New Zealand WWTP effluents is comparable to that reported in

studies overseas. However, studies suggest that current wastewater treatment technologies have different levels of removal efficacy and this depends on the chemical characteristics of the EOCs.

The management of EOCs in wastewater is challenging. Advanced water treatment technologies can achieve consistent removal of EOCs, but are costly. As many EOCs are found in commonly-used household products, any reduction of the use and discharge of these products in wastewater would improve the efficacy of the treatment plants.

Conclusions and recommendations

There is a need to generate local information on EOCs of relevance to the Auckland region and to characterise the efficacy of the various methods of effluent treatments and disposal. In light of these conclusions the following recommendations are made:

1. **Assess the composition and concentration of emerging organic contaminants in wastewater treatment plant effluents**

   Because the ability of WWTPs to remove and reduce EOCs is so variable, effort should be made to characterise a range of representative EOCs within the final effluents of plants operating at or near optimum treatment conditions.

   The EOCs analysed in the final effluents of the three WWTPs should include the same chemicals being investigated in the Gisborne City biological trickling filter project. This would provide a direct comparison with residue data previously obtained for 13 other WWTPs in New Zealand, together with a wider range of EOCs being assessed in the Gisborne study. These include alkylphosphate flame retardants; nitro and polycyclic musks; phenolic anti-microbials; parabens; industrial alkylphenols; the insect repellents DEET and Piccaridin; estrogenic, androgenic and progestogenic steroid hormones; phenolic anti-microbial chemicals, ultra-violet (UV) filter chemicals, phthalate esters, and non-steroidal anti-inflammatory drugs. Because they represent the highest level of risk to organisms, special attention should be given to characterising the profile of individual endocrine disrupting chemicals (EDCs) and total endocrine activity in the influents and treated effluents through a combined approach of trace chemical and bioassay analyses. Bioassay analyses (e.g. reporter gene assays) should be used to determine estrogenic, androgenic and dioxin-like activities of the samples.

2. **Determine the risk of emerging organic contaminants in wastewater treatment plant effluent discharged into waterways**

   The results obtained for concentration of EOCs analysed in WWTP effluent should be combined with appropriate hydrological data to estimate the concentrations that organisms within relevant waterways are likely to be exposed to. The estimated exposure concentrations can be combined with predicted-no-effect concentrations (PNEC) to derive exposure quotients that provide a measure of the risk EOCs pose to various types of organisms residing within those waterways.

3. **Monitor emerging organic contaminants within the irrigation application sites**
   Numerous uncertainties were highlighted in this report regarding the risk of EOCs in irrigated wastewater effluent leaching through soil and into underlying groundwater. These risks can only be quantified and mitigated, if the necessary data is available. Completing a full assessment of the fate and transport of EOCs in soil within the irrigation application fields is complex and expensive. Alternatively we recommend adopting a tiered approach comprising:

   - Characterisation of EOCs in WWTP effluent as outlined above.
   - Analysing soil cores from the wastewater irrigation sites for residual EOCs following three years of continued wastewater irrigation.
   - Consider further on-site monitoring assessments if soil cores show any evidence of downward migration of EOCs, for example, installing porewater/groundwater sampling devices to sample and monitor the leaching and migration of EOCs.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY

Term/acronym	Definition
AWWA	American Water Works Association
BOD	Biological oxygen demand
BPA	bisphenol-A
CBIR	Centre for Integrated Biowaste Research
DTA	Direct toxicity assessment
EC_{50}	Concentration of a substance or material resulting in a specific response in 50% of the test organisms
EC_{20}	Concentration of a substance or material resulting in a specific response in 20% of the test organisms
EC_{10}	Concentration of a substance or material resulting in a specific response in 10% of the test organisms
EC(s)	Emerging contaminant(s)
EDC(s)	Endocrine disrupting chemical(s)
EOC(s)	Emerging organic contaminant(s)
EPA	Environmental Protection Authority
FR(s)	Flame retardant(s)
LOEL	Lowest observable effects level
NOEL	No observable effects level
NSAID	Non-steroidal anti-inflammatory drug
PAH(s)	Polycyclic aromatic hydrocarbon(s)
PCBs	Polychlorinated biphenyl
PNEC	Predicted-no-effect concentrations
PPCP(s)	Pharmaceuticals and personal care product(s)
SRT(s)	Sludge retention time(s)
SSRT(s)	Selective serotonin re-uptake inhibitor(s)
STP(s)	Sewage treatment plant(s)
TSS	Total suspended solids
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultra-violet
WERF	Water Environment Research Foundation
WRC	Waikato Regional Council
WWTP(s)	Wastewater treatment plant(s)

1. INTRODUCTION

Watercare Services Limited (Watercare) contracted Cawthron Institute (Cawthron) to assess the potential risk of residual emerging organic contaminants (EOCs) in treated wastewater including:

- Conduct a review of the literature on emerging contaminants such as pharmaceuticals and personal care products (PPCPs) that may be present in final treated wastewater that may be applied to land (*e.g*. at the Omaha wastewater treatment plant [WWTP]).
- Assess the potential risks from the discharge of treated wastewater, which may contain these contaminants, on the receiving groundwaters, estuaries and harbours, and fish and shellfish.
- Provide comments and recommendations on attenuation and losses in these environments including the treatment plants.
- Provide recommendations of EOCs of concern that may require assessment in WWTP effluent and monitoring in receiving environments.

2. EMERGING CONTAMINANTS

2.1. What are emerging contaminants?

In their daily activities, humans use multiple products and medications that contain numerous chemicals. Scientists and regulators have become increasingly aware of the burden these chemicals can have on the environment, and in recent years they have become the subject of intense research. There is a growing negative public perception of the potential fate and undesirable effects of such chemicals on the environment. Their collective description as 'emerging contaminants' (ECs) derives from the recent or increasing interest in these chemicals, rather than them representing 'new chemicals'.

2.1.1. Definition of emerging contaminants

The widely recognised United States Geological Survey (USGS) definition of an emerging contaminant is:

> *"…any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects. In some cases, release of emerging chemical or microbial contaminants to the environment has likely occurred for a long time, but may not have been recognised until new detection methods were developed. In other cases, synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of ECs*[1]*."*

2.1.2. Difference in composition of emerging contaminants and emerging organic contaminants

Emerging contaminants include chemicals, micro-organisms (such as pathogens), and nanomaterials that are structured chemical substances. By far the largest number of ECs are man-made chemicals. They include new classes of halogenated persistent organic pollutants, pharmaceuticals, chemicals in personal care products, and natural steroid hormones.

Emerging contaminants are differentiated from traditional persistent organic pollutants like polychlorinated biphenyls and organochlorine pesticides (DDT for example) by their bioactive properties. Many of the chemicals classified as ECs are manufactured to provide a specific biological mode of action, for example, pharmaceuticals which are designed to treat specific medical conditions.

[1] http://toxics.usgs.gov/regional/emc/

This review focuses on chemicals that are typically of an organic, rather than inorganic, nature. These chemicals are collectively referred to as 'emerging organic contaminants' (EOCs), so ECs such as nanoparticles, are not considered. Research on bulk nanoparticles (carbon black, titanium dioxide, iron oxides) suggest various adverse effects, and the toxicity of these materials is poorly understood (Borm *et al*. 2006). A recent United Kingdom study focussed on silver and nanosilver products, which are key nanoparticles entering sewage treatment plants (STPs). This study concluded that the risks of particulate and nanosilver in the environment may be less than expected (Johnson *et al*. 2014)

2.1.3. Groups of emerging organic contaminants

Emerging organic contaminants are components or active ingredients in products that are commonly and frequently used by humans. The major groups of EOCs include pharmaceuticals and personal care products (PPCP), veterinary medicines, fire retardants and other industrial products, and new generation pesticides. Endocrine disrupting chemicals (EDCs) are also often defined in a category of their own. However, they refer more to a mechanism of toxicity and so EOCs from the above-mentioned groups may demonstrate endocrine disrupting activity. In comparison to industrial chemicals, EOCs are sourced from products that are used in relatively small amounts. However, because they are used by many individuals on multiple occasions daily, the total amounts released to the environment can be significant.

2.1.4. Molecular structure of emerging organic contaminants

Emerging organic contaminants include a vast range of molecules like new generation organic compounds containing bromine and fluorine. Polybrominated diphenyl ethers are used as flame retardants in plastic, electrical goods and in many components of electronic circuit boards. Perfluoroctanoic acid is used to produce non-stick coatings on frying pans and other household items. Perfluorooctanesulfonic acid was the ingredient in 3M's Scotch Guard™ protective fabric coating that was voluntarily withdrawn from the market due to concerns regarding its environmental impact and bioaccumulation in humans. These new generation organic compounds have similar properties to other persistent organic pollutants—they can be bioaccumulative, persistent in the environment and toxic. Some of these chemicals have already been identified as substances to control and are being considered for inclusion under the Stockholm Convention[2].

Pharmaceuticals and personal care products (PPCPs) include a wide variety of chemicals used as medicines, disinfectants, fragrances, insect repellents, surfactants

[2] The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment.

and other chemical components in personal care products like shampoos, body washes, and cosmetics.

2.1.5. Environmental fate research and concerns

The persistence and toxicity of some EOCs is similar to harmful man-made agricultural and industrial chemicals that have been banned by numerous countries. The quantity of EOCs produced each year is similar to some intensively used agricultural pesticides but there is limited information on their environmental fate and potential long-term impact (Luo *et al*. 2014).

As analytical instrumentation becomes more sensitive and new methods of analysis continue to be developed the number of identified EOCs and knowledge of their fate and effects in the environment will increase.

2.2. Sources of emerging organic contaminants

The main sources of EOCs to the environment include industrial discharges, effluents from wastewater treatment plants, landfill leachates, land application of biosolids, septic treatment systems, animal manures and oxidation pond effluent, animal processing plants and aquaculture.

Apart from chemical industry discharges, the major input of EOCs released into the environment is from wastewater treatment plant effluents (Pal *et al*. 2010). Municipal wastewater systems collect human waste, greywater (from showers and washing) and industrial discharges (through trade waste permits). This waste is then treated and discharged, either to aquatic environments, or on land. A wide variety of EOCs are collected with this waste and most are not fully degraded and/or removed from the waste stream by traditional primary and secondary wastewater treatment systems (Ternes *et al.* 2004; Liu *et al.* 2009). Municipal wastewater treatment plant (WWTP) effluent and biosolids have been identified as main sources for the release of EOCs into the environment, particularly EDCs and PPCPs (Gottschall *et al*. 2012; Ternes *et al*. 2004).

The number of EOCs identified in WWTP effluents will continue to increase in the future. This is in response to the growth in consumption of chemical products used in households, increasing prescription of medications, and the rapid introduction of new chemicals into the marketplace. It is also due to the introduction of new and more sensitive methods to analyse them.

2.3. Fate of emerging organic contaminants during wastewater treatment

Full removal of EOCs from domestic and industrial wastewaters by primary and secondary wastewater treatment processes is not possible and can only be achieved by advanced chemical oxidative (ozonolysis) and membrane filtration (reverse osmosis *etc*.) treatments (Luo *et al*. 2014).

Currently used primary and secondary wastewater treatment processes are designed to reduce nutrient, biological organic demand (BOD) and pathogen loadings to concentrations that are considered environmentally acceptable. This includes removing and reducing the load derived from residues of particulate and organic matter associated with:

- faecal residues.
- dissolved organic carbon within the influent.
- cellular residues of the active biomass within the WWTP.

Traditional WWTP processes were designed to degrade and reduce labile and biodegradable organic matter derived from natural sources. Degradation of man-made chemicals is coincidental to the predominant processes of natural organic matter transformation and degradation.

Municipal WWTPs typically use secondary treatment (*i.e.* activated sludge) to reduce BOD and total suspended solids (TSS). Most also disinfect final effluents and inactivate and/or remove pathogens, and use advanced treatment systems to remove other pollutants, most notably nutrients. These plants are not designed to specifically remove EOCs from their wastewater.

The fate of EOCs in WWTPs is controlled by a range of 'internal factors' and 'external factors' (Luo *et al*. 2014). Internal factors are chemical-related and modulated by the hydrophobicity, biodegradability, and volatility of a chemical. In general, polar and non-volatile compounds are more likely to escape wastewater treatment processes (*e.g.* polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyl [PCBs], carbamazepine, diclofenac and metoprolol). External factors are WWTP-specific and include the treatment conditions of wastewater treatment processes, composition and size of the microbial biomass, the mixture of micro-pollutants that can act as competitors, and properties of the wastewater stream (pH and temperature). Sludge retention time (SRT) controls the size and diversity of the microbial biomass. Enhanced elimination of micro-pollutants can be achieved if the treatment processes have extended SRTs, which facilitates the build-up of slow-growing bacteria such as nitrifying bacteria. Nitrifying biomass has been found to improve the removal of a range of micro-pollutants such as ibuprofen, galaxolide, ethinylestradiol, bisphenol-A

and nonylphenol. However, it should be noted that high SRT does not necessarily mean better removal performance and conventional waste water treatment processes have been reported to achieve inadequate removal of many EOCs (Luo *et al*. 2014).

The biologically-activated sludge process is the predominant form of secondary treatment for biological nutrient removal in WWTPs. Although much is known about the various processes involved, their ability to remove EOCs is poorly understood. The combination of biological degradation and chemical oxidation occurring within treatment, processes can degrade contaminants to carbon dioxide and water. Contaminants can also be transformed to metabolites, and their risks are often unknown.

Some EOCs, in particular many pharmaceuticals, are excreted as inactivated conjugated metabolites of the parent compound. Deconjugation of these metabolites commonly occurs during wastewater treatment. This can result in the discharge of higher concentrations of residual active pharmaceuticals in the effluent, compared to the influent of the WWTP. The transformation of EOCs during wastewater treatment can produce metabolites that are more persistent than the original parent compound, *e.g.* clofibric acid *versus* clofibrate, and/or bioaccumulative, *e.g.* methyl-triclosan *versus* triclosan.

Table 1 (Roberts & Thomas, 2006) shows the change in the median concentration of selected pharmaceuticals passing through a 3-stage pilot treatment process incorporating:

- sequential screening
- primary clarification
- trickling filter
- activated sludge
- ultra-violet (UV) treatment

This data aptly demonstrates:

- the significant differences in the ability of wastewater treatment processes to degrade and remove different classes of pharmaceuticals.
- the significant differences in removal that occur for individual compounds within a specific class, as exemplified by the range in percentage change achieved for individual pain killers and non-steroidal anti-inflammatory drugs.
- the increase in concentration of some pharmaceuticals following wastewater treatment.

Table 1. Percentage change in the concentration of pharmaceutical residues following wastewater treatment.

Compound	Class/description	% change (±)
Clofibric acid	Metabolite of clofibrate[1]	-91
Clotrimazole	Antifungal	-55
Dextropropoxyphene	Analgesic/pain killer	107
Diclofenac	NSAID[2]	-71
Erthromycin	Macrolide antibiotic	79
Ibuprofen	NSAID	-89
Mefenamic acid	NSAID	67
Paracetamol	Pain killer	-100
Propranolol	Beta-blocker	334
Tamoxifen	Breast cancer drug	30
Trimethoprim	Bacteriostatic antibiotic	3

Source: (Roberts & Thomas, 2006)
[1] Clofibrate is a lipid regulating drug
[2] Non-steroidal anti-inflammatory drug/painkiller

Very few WWTPs are specifically designed to degrade and fully remove all EOCs. These man-made chemicals, many of which possess anti-microbial properties, display levels of recalcitrance and persistence that may result in their effective concentration during wastewater treatment processes. The effective concentration of anti-microbial compounds during wastewater treatment has the potential to negatively impact the efficacy of the wastewater treatment process by inhibiting the activity of the microbial biomass.

A number of significant studies have investigated the removal efficacy of various EOCs during full-scale wastewater treatment processes, or by specific unit processes employed for advanced wastewater and/or drinking water treatment. The wide range of EOCs present in WWTP effluent streams, combined with the complexities and expense of analysis, preclude the analysis of every individual chemical. As a consequence, it is common for studies of this type to select a limited number of individual chemicals whose physico-chemical properties represent a wider range of relevant chemical classes.

A study funded by the American Water Works Association (AWWA) Research Foundation investigated the efficacy of various drinking water and reuse treatment processes to remove a range of representative selected EOCs from natural waters (Snyder *et al*. 2007). The removal of EOCs was assessed by physical, chemical and biological water treatment modes in bench-scale batch mode and/or pilot-scale flow-through mode.

The study concluded that the removal of EOC using magnetic ion-exchange resin and UV irradiation at disinfection rates was ineffective. However, removal of EOCs using UV-advanced oxidation with hydrogen peroxide was highly effective for most of the contaminants that were studied. The use of coagulation, flocculation and filtration techniques to remove EOCs was ineffective. However, the use of disinfection using oxidised free chlorine removed approximately half of the target EOCs, including all phenolic steroid hormones. In comparison, sorption using both powdered and granular forms of activated carbon was highly effective. However, removal efficacy was a function of carbon type, contact time, water quality, and contaminant structure. Ozonolysis was capable of removing most target analytes to below detection limits and nanofiltration and reverse osmosis both provided high rates of contaminant removal, while microfiltration and ultrafiltration offered only limited contaminant removal.

Another study Stephenson and Oppenheimer (2007) assessed the removal of 20 PPCPs commonly found in wastewater treatment plant influents. This study concluded that an increase in SRT during activated sludge treatment, enhanced the removal of the majority of the PPCPs. However, the SRT required to consistently remove > 80% of individual PPCPs, was compound-specific. But it seemed that a significant number of PPCPs were removed during the activated sludge treatment when the SRTs were from 5 to 15 days. Notably, extending SRTs beyond 30 days were necessary to remove > 80% of the synthetic fragrances, Galaxolide and musk ketone, and the alkylphosphate flame-retardant, Tris (2-chloroethyl) phosphate. This study found that, while activated sludge treatment could be effective in PPCP removal, it was necessary to incorporate a second barrier treatment, *e.g.* membrane bioreactors or reverse osmosis, to achieve effective removal of most of the target compounds.

Similarly, a major study Salveson *et al*. (2012) investigated the removal of 22 selected EOCs during conventional wastewater treatment. This study found that long SRTs generally obtained higher removal efficiencies for EOCs that are amenable to biotransformation, than shorter SRTs It indicated there was a relationship between the removal of EOCs and nitrification in wastewater treatment plants operating a high level of secondary treatment to meet low ammonia limits. Similar to observations from other related studies, the authors concluded conventional secondary treatment did not effectively remove EOCs exhibiting slow rates of biotransformation and low sorption potential to sludge (Table 2). The removal of these EOCs required advanced treatment processes subsequent to conventional wastewater treatment.

Table 2. Sludge retention time (SRT) values necessary to achieve at least 80% removal of emerging organic contaminants (EOCs).

Compound	SRT (days)
Acetaminophen	2
Caffeine	2
Ibuprofen	5
Naproxen	5
Bisphenol-A	10
Triclosan	10
DEET	15
Gemfibrozil	15
Atenolol	15
Butylated hydroxyl anisole	15
Iopromide	15
Cimetidine	15
Diphenylhydramine	20
Benzophenone	20
Trimethoprim	30

Source: (Salveson *et al*. 2012)

Another study assessing the removal of EDCs by wastewater treatment investigated the removal of testosterone, four estrogenic hormones, and four phenolic compounds (bisphenol-A and alkylphenol degradation products, 4-nonylphenol, 4-(tert-Octyl) phenol and 4-octylphenol) from 11 treatment plants in the USA. The WWTPs employed various combinations of treatment, including: activated sludge, media filtration, chlorine disinfection, UV disinfection, reverse osmosis, membrane bioreactors, and soil-aquifer treatment. The study found conventional secondary treatment provided substantial removal of the EDCs, but there was no significant improvement in removal when the SRT was between 2 and 10 days. Advanced treatment processes, such as activated carbon, reverse osmosis membranes, and soil-aquifer treatment provided additional removal (Drews *et al*. 2006).

The European Union-funded POSEIDON Project, assessed the removal of a range of EOCs including pharmaceuticals, polycyclic musk fragrances, hormones, bisphenol-A, and nine alkylphenols and alkylphenol ethoxylates from nine pilot and full-scale wastewater treatment systems. They included six full-scale activated sludge wastewater treatment systems with varying SRTs, and three membrane bioreactor pilot systems with varying SRTs.

- Some compounds,*e.g.* the anti-epileptic drug carbamazepine, were not removed in any of the sampled treatment facilities.
- The removal of other compounds, *e.g.* diclofenac and 17α-ethinylestradiol, was variable.
- Other compounds,*e.g.* bisphenol-A and ibuprofen, were nearly completely removed

Researchers found a strong correlation between achievable effluent concentrations and SRT for bisphenol-A, ibuprofen, bezafibrate and the natural estrogens. For these compounds, they found a critical SRT of approximately 10 days, which corresponds to the SRT for nitrogen removal (nitrification and denitrification). There was no significant difference between removal of target compounds by membrane bioreactors and activated sludge treatment, indicating the ultra-filtration membranes used in the bioreactors, did not improve removal of target compounds (Clara *et al*. 2005b).

A note of caution is required when assessing the removal of EOCs from wastewater effluent streams and treatment processes reported in these studies. Municipal wastewater is one the most complex and challenging sample matrices to analyse for EOCs. As a consequence liquid effluents are commonly pre-filtered and the filtered dissolved phase selectively extracted and analysed. This procedure selectively removes the suspended solids/particulate fraction, onto which numerous EOCs will be absorbed, from the whole effluent sample. Therefore, EOCs removal efficacy could be under-estimated when considering this pre-treatment of whole effluent samples.

To summarise, the critical factor for the effective removal of EOCs by conventional secondary waste water treatment processes is the SRT, but this alone will not result in full removal of all EOCs from the wastewater stream. The efficacy of secondary waste water treatment processes to remove EOCs can be highly variable and appears to be plant dependent. SRTs in the order of 10–15 days are required to effectively remove many EOCs but more persistent and recalcitrant chemicals require considerably longer SRTs (*i.e.* up to 30 days) to achieve 80% removal.

Full removal of EOCs from wastewater treatment plant effluent streams can only be achieved by the introduction of tertiary treatment such as advanced oxidation (ozonolysis), sorption to activated carbon, or nanofiltration and reverse osmosis/ membrane filtration processes.

2.4. Selection of indicator/model emerging organic contaminants for determining their removal during wastewater treatment and fate in the environment

The significant number of individual EOCs present in WWTP effluent combined with the high cost of analysis, means it is impossible to identify and analyse all of the individual chemicals that will be present. Instead researchers have either focused on analysing specific classes of EOCs, for example, EDCs, or individual compounds that are representative of specific classes of chemicals. Many studies have prioritised the selection of model, or indicator compounds, based on their potential high risk to exposed organisms at relatively low concentrations (parts per trillion).

Various subclasses of EOCs have been ranked on the basis of their predominance in municipal wastewater, toxicity, unique and specific biological activity, and persistence and bioacccumulative properties. On this basis EOCs can generally be divided into three main groups (Tremblay *et al*. 2011):

1. Endocrine disrupting compounds (EDCs)
2. Pharmaceuticals and personal care products (PPCPs)
3. Fire retardants and other industrial chemicals

These three groups of chemicals represent a very large number of EOCs that are components within a range of products commonly found and used in households. For instance, many natural and man-made chemicals are classified as EDCs, including natural estrogenic and androgenic steroid hormones, pharmaceuticals (contraceptive and hormone replacement therapies), industrial chemicals (bisphenol-A and nonylphenols) and pesticides (DDT and vinclozolin) (Hotchkiss *et al*. 2008). Human urine and faeces can also contribute EOCs to household waste streams as they can contain residues of pharmaceuticals, naturally occurring steroid hormones, and EOCs sourced from food and air.

Indicator compounds are chemicals that occur at quantifiable concentrations and have physico-chemical properties and biodegradation characteristics that are representative of wider classes of EOCs with respect to their fate during wastewater treatment, and within receiving environments. Physico-chemical and biological properties are most often the important factors determining the fate of EOCs during wastewater treatment and upon their release into the environment. Selecting multiple indicator compounds representing a broad range of properties enables the extrapolation of outcomes to chemicals not previously identified and to new chemicals entering wastewater streams and the environment.

Another significant factor affecting the selection of indicator compounds is the availability of advanced instrumentation and appropriate methods for their analysis.

This practicality is often a major influence on the selection of indicator compounds. This can introduce bias , the sheer number of individual EOCs present in WWTP effluent means there is considerable scope to ensure representative indicator compounds can be selected.

Various approaches and criteria have been used to assist the selection of indicator chemicals that are suitable for assessing the removal of EOCs during wastewater treatment processes and their fate upon release to the environment.
An early Water Environment Research Foundation (WERF) study assessed the fate of personal care chemicals during wastewater treatment. These chemicals were selected (Table 3) because they frequently occur in municipal WWTP effluents and are able to be analysed by gas chromatography mass-spectrometry.

Table 3. Target analytes frequently detected in wastewater treatment plant (WWTP) effluents.

Target compound	**Use**
Galaxolide	Fragrance
Ethyl-3-phenylpropionate	Fragrance
Methyl-3-phenylpropionate	Fragrance
Musk ketone	Fragrance
3-Phenylpropionate	Fragrance
Benzophenone	UV filter
Octylmethoxycinnamate	UV filter
Oxybenzone	UV filter
Benzyl salicylate	UV filter
Ibuprofen	Non-steroidal anti-inflammatory drug
Caffeine	Stimulant/medicine
Triclosan	Anti-microbial
Chloroxylenol	Anti-microbial
Tri(chloroethyl)phosphate (TCEP)	Flame retardant
Triphenylphosphate	Flame retardant
Methylparaben	Preservative
BHA (butylated hydroxyanisole)	Anti-oxidant
Butylbenzylphthalate	Plasticiser
Bis(2-ethylhexyl)phthalate	Plasticiser
DEET	Insect repellent
Octylphenol	Detergent/lubricant

Source: Stephenson and Oppenheimer, 2007

Another WERF study used a different approach to identify indicator chemicals by comprehensively reviewing over 100 peer-reviewed journal articles. This review identified chemicals present in secondary and tertiary treated wastewater effluents, and for which viable methods of analysis were available (Drews *et al*. 2008). This comprehensive list of indicator chemicals was reduced by determining the detection ratio of the chemicals, defined as the ratio of the median reported concentration and limit of quantitation of the chemical. Compounds demonstrating a detection ratio greater than five were accepted. While this approach has certain limitations it effectively eliminates compounds that are not ubiquitously present in WWTP effluents, and/or those for which adequately sensitive detection techniques are not available.

Using this assessment criteria a total of 33 chemicals with detection ratios greater than five were identified from those reported to occur in both European and North American studies (Table 4).

Table 4. Indicator compounds reported to occur in European and North American studies displaying detection ratios greater than 5.

Indicator compound	**Uses**
Triclosan	Anti-microbial
Clarithromycin	Antibiotic
Erythromycin	Antibiotic
Sulfamethoxazole	Antibiotic
Acetyl cedrene	Fragrance
AHTN	Polycyclic fragrance
Benzyl acetate	Fragrance/aroma
Benzyl salicylate	Fragrance/ UV filter
g-Methyl ionine	Fragrance/aroma
Hexyl salicylate	Fragrance/aroma
Hexylcinnamaldehyde	Fragrance/aroma
HHCB	Polycyclic fragrance
Isobornyl acetate	Fragrance/aroma
Methyl dihydrojasmonate	Fragrance/aroma
Methyl salicylate	Fragrance/aroma /analgesic
Musk ketone	Nitromusk fragrance
Musk xylene	Nitromusk fragrance
OTNE (iso-E-super)	Fragrance/aroma
p-t-Bucinal	Fragrance/aroma
Terpineol	Fragrance/aroma

Indicator compound	Uses
Estrone	Steroid hormone
Estradiol	Steroid hormone
EDTA	Preservative/chelation medicine
NTA (nitrilotriacetic acid)	Chelating agent/water softener
Carbamazepine	Anticonvulsant/mood stabiliser
Clofibric acid	Metabolite of clofibrate
Diclofenac	Non-steroidal anti-inflammatory drug
Gemfibrozil	Lipid lowering medicine
Ibuprofen	Non-steroidal anti-inflammatory drug
Ketoprofen	Non-steroidal anti-inflammatory drug
Naproxen	Non-steroidal anti-inflammatory drug
Salicylic acid	Anti-inflammatory/food preservative
Nonylphenol	Detergent/emulsifier/solubilizer

Source: Drews *et al*, 2008

Many consumer product chemicals are classified as high-production-volume chemicals by the United States Environmental Protection Agency (USEPA). These chemicals include those manufactured in, or imported into, the United States in amounts equal to (or greater than) 0.5 million kg per year. Similar products containing high-production-volume chemicals are also imported, produced and used in New Zealand.

A WERF study selected household chemicals from a total list of 720 high-production-volume compounds within eight main domestic activities: auto products, inside the home, pesticides, home maintenance, personal care/use, pet care, arts and crafts, and landscape/yard (Drews *et al*. 2009). From the extensive list of high-production-volume chemicals, a 2-tiered ranking approach based on production volumes, environmental relevance, and feasibility for analytical quantification was developed. The shortlist of 11 Tier 1 chemicals was classified as high-production-volume consumer products, which are likely to be present in domestic wastewater due to their physico-chemical properties and reported environmental fate. The 13 Tier 2 chemicals included chemicals below the high-production-volume threshold but frequently used in household products, likely to be present in domestic wastewater due to their physico-chemical properties and reported environmental fate (Drews *et al*. 2009). Triclocarban was added to the compound list as a model compound representing emerging contaminants for which limited information is available, and linear alkylbenzene

sulphonates were included as a model for complex multi-component mixtures. The selected indicator compounds are summarised in Table 5.

Table 5. Major emerging organic contaminants (EOCs) associated with household waste: Tier 1 and Tier 2 and model compounds.

Tier 1 household chemicals	
Compound	**Applications**
2,6-Di-tert-butyl-p-cresol (BHT)	Antioxidant, food additive, skin care products, hobby supplies
Dibutyl phthalate	Plasticiser, additive in adhesives and printing inks, nail care
Atrazine	Herbicide
Bisphenol-A	Plasticiser, additive in epoxy resins and glues
Benzophenone	UV stabiliser in perfumes and soaps, polymer packaging and clear plastics
Oxybenzone (Benzophenone-3)	UV stabiliser in sunscreens, hair sprays, and cosmetics, nail polishes, synthetic resins and food packaging
Triclosan	Anti-microbial in detergents, soaps, lotions, toothpaste and toys
Vanillan	Fragrance and flavouring agent in foods, beverages, and pharmaceuticals
o-Phenylphenol	Biocide, preservative and agricultural fungicide.
Phenoxyethanol	Preservative and bactericide in skin cream, cosmetics and sunscreen
Hexabromocyclododecane	Flame retardant
Tier 2 household chemicals	
Simazine	Herbicide and biocide
N,N-Diethyl-m-toluamide (DEET)	Insect repellent
Hydrocortisone (cortisol)	Anti-itch, anti-inflammation medication
Butylated hydroxyanisole	Antioxidant, various
3-Indolebutyric acid	Plant rooting compound
Camphor	Fragrance, various
Menthol	Fragrance, various
2-Methylresorcinol	Hair colourants and cosmetics
Isobutylparaben	Preservative, cosmetics and pharmaceuticals, various
Acriflavine	Topical antiseptic, antifungal agent in aquariums
Trifluralin	Herbicide
2,3,4,5-Bis(2-butylene)tetrahydro-2-furaldehyde	Insect repellent in pet shampoos
Propylparaben	Preservative, cosmetics, pharmaceuticals and food
Selected model compounds	
Triclocarban	Anti-bacterial in soaps, lotions, deodorants
Linear alkylbenzene sulphonates	Surfactant, detergents, laundry powders

A set of specific indicator pharmaceutical chemicals was also selected on the basis that they had been previously studied in WWTP effluents (Table 6).

Table 6. Model emerging organic contaminants (EOCs) associated with household waste used as model and indicator compounds.

Model compounds	**Application**
Triclocarban	Anti-bacterial, soap, deodorant
Linear alkylbenzene sulfonate (LAS)	Surfactant, various

Indicator compounds	
Primidone	Anti-epileptic drug
Phenacetine	Anti-inflammatory drug
Carbamazepine	Anti-epileptic drug
2-Naphthol	Industrial chemical
Fenofibrate	Blood lipid regulator
Gemfibrozil	Blood lipid regulator
Propyphenazone	Anti-inflammatory drug
Sulfamethoxazole	Antibiotic drug
Ibuprofen	Anti-inflammatory drug
Naproxen	Anti-inflammatory drug
Diclofenac	Anti-inflammatory drug

Table 7 lists the EOCs included in a 2009 USEPA study[3] that measured the concentrations of a range of indicator PPCPs in WWTP influent and effluent. The WWTPs included in this study comprised a range of treatment technologies and SRTs servicing catchments with populations with various age distribution, and influents with varying levels of industrial input. All of the indicator pharmaceuticals are available as prescription medications or over-the-counter in New Zealand and are likely to be present in local WWTP effluents.

[3] USEPA 2009. Occurrence of Contaminants of Emerging Concern in Wastewater From Nine Publicly-Owned Treatment Works. EPA-821-R-09-009. 85 p.

Table 7. Selected pharmaceuticals present in the influent and effluent from nine publicly-owned wastewater treatment plants (WWTPs) in the United States from 2005–2008, and their prescribed names in New Zealand.

Pharmaceutical/personal care products	Type	Form prescribed in NZ
Chlorotetracycline	Antibiotic	
Doxycycline	Antibiotic	Doxine
Tetracycline	Antibiotic	-
Sulfamerazine	Antibiotic	-
Sulfadiazine	Antibiotic	-
Sulfamethoxazole	Antibiotic	Trisul
Sulfathiazole	Antibiotic	-
Ciprofloxacin	Antibiotic	Ciproxin
Clarithromycin	Antibiotic	Klamycin
Erythromycin	Antibiotic	E-mycin
Ofloxacin	Antibiotic	-
Lincomycin	Antibiotic	Lincomysin
Acetaminophen	Analgesic	Paracetamol
Cotinine	Tobacco metabolite	-
Fluoxetine	Anti-depressant	Fluox
Carbamazepine	Anti-epileptic	Tegratol
Gemfibrozil	Lipid regulator	Lopid
Ibuprofen	Anti-inflammatory	Nurofen
Naproxen	Anti-inflammatory	Naprogesic
Triclocarban	Disinfectant	Tricloram
Triclosan	In toothpaste	Triclosan
Albuterol	Anti-asthmatic	Salbutamol
Cimetidine	Anti-ulcer	Apocimetidine
Metformin	Anti-diabetic	Metomin
Ranitidine	Anti-ulcer	Zantac
Progesterone	Hormone	Naturally-occurring
Testosterone	Hormone	Naturally-occurring

The target compounds selected for investigation in a study assessing the attenuation of PPCPs in WWTP effluent recycled to golf courses was based on their likelihood of being present in recycled water (McCullough 2012). This included a total of 14 pharmaceuticals and the anti-microbial chemical, triclosan. The list of target

compounds (Table 8) was subsequently investigated in laboratory, plot-scale and field studies.

Table 8. Indicator compounds selected for investigating the attenuation of pharmaceuticals and personal care products (PPCPs) in recycled water applied to golf courses.

Target/indicator compound	Use
Atenolol	Beta-blocker, hypertension
Atorvastatin	Blood pressure regulator
Carbamazepine	Anti-convulsant
Diazepam	Sedative and anti-convulsant
Diclofenac	Non-steroidal anti-inflammatory drug
Dilantin	Anti-convulsant and seizure treatment
Fluoxetine	Anti-depressant
Gemfibrozil	Lipid regulator
Ibuprofen	Non-steroidal anti-inflammatory drug
Meprobamate	Tranquiliser
Naproxen	Non-steroidal anti-inflammatory drug
Primidone	Anti-convulsant and seizure treatment
Sulfamethoxazole	Antibiotic
Triclosan	Anti-microbial
Trimethoprim	Antibiotic

Source: McCullough, 2012.

In summary, various criteria have been applied to identify and select indicator compounds for use in studies assessing the removal of EOCs during wastewater treatment and their fate in receiving environments. There is no specific recommended list of EOC indicator compounds to use in such assessments and the final selection is often based on the availability of appropriate analytical instrumentation and methods of analysis. Despite the different criteria applied to select indicator compounds a number of chemicals are commonly identified and ultimately selected. These include triclosan and other anti-microbial chemicals, parabens, fragrances, steroid hormones, anti-inflammatory drugs, lipid regulating drugs and antibiotics.

2.5. Risk assessment of emerging organic contaminants

There is global concern that the presence of EOCs in the environment may lead to adverse human and ecological health effects. There is also an increasing requirement to provide estimates of the potential risk of EOCs within consenting processes in New Zealand. As most EOCs are not currently monitored they could be considered as added stressors to more traditional environmental contaminants such as metals and

semi-volatile organic contaminants (*i.e.* PAHs). There is a significant absence of fate and effects data to assess the environmental risk of EOCs. Of the 15,000 high-production-volume chemicals in commercial use in the USA and the European Union only 25% have been subjected to basic toxicity testing (Drews *et al*. 2009).

Scientists have enough information on EOCs to know they are widely released into the environment wherever humans live. What remains unclear is the risk EOCs pose to environmental and human health. Unlike agricultural and industrial chemicals, most EOCs have not undergone screening to determine whether or not they will have an adverse environmental effect. The standardised test methods used to assess the impact of chemicals in the environment assess acute effects, or the amount of chemical resulting in the death of test organisms. The amount of an EOC needed to cause the death of an organism is very high, and for this reason they have previously been considered safe.

Many EOCs degrade in the environment and this has previously led to them being considered non-persistent, and therefore environmentally safe. But the real situation is more complicated than it first appears. While many EOCs degrade in the environment, within a matter of days, they are constantly replenished by fresh inputs, *e.g.* from WWTP continually releasing treated effluent and therefore any residual EOCs into the aquatic environment. This continuous replenishment means there is always a source of un-degraded EOCs being introduced into the environment to effectively replace the fraction being degraded within the receiving environment. This leads to what is described as ‘pseudo persistence’ (Daughton & Ternes 1999).

2.5.1. Direct toxicity assessment

A direct toxicity assessment (DTA) approach is commonly used to assess the potential impacts of a substance or complex mixture such as treated WWTP effluent. The tests are conducted with species from various phylogenetic levels likely to be present in the receiving environment. In New Zealand, those species often include algae, an invertebrate like an amphipod and the larvae of the blue mussel that show a range of sensitivities to complex mixtures. Those tests assess the baseline toxicity but don’t provide information at the mechanistic level. For instance, receptor-mediated and reactive mechanism studies can provide information specific to the contaminants to derive general principles and understand differences in species sensitivity (Schwarzenbach *et al*. 2006). However, when it comes to assessing the risk of EOCs to exposed organisms those standard tests and other more sophisticated approaches always involve a level of uncertainty due to inherent variability and complexity of both environmental and biological systems (Schwarzenbach *et al*. 2006).

The majority of risk assessment frameworks for organic contaminants were developed in response to the need to regulate organic chemicals that are persistent, bioaccumulative and toxic. Representative persistent, bioaccumulative and toxic

organic contaminants include dibenzodioxins and furans, polychlorinated biphenyls and organochlorine pesticides, and many other agrichemical pesticides and industrial chemicals. The primary endpoint of effect measure in first generation persistent, bioaccumulative and toxic-based risk frameworks is acute toxicity, as determined by the EC_{50} of a chemical (*i.e.* the concentration of a substance or material resulting in a specific response in 50% of the test organisms), or the concentration resulting in 50% mortality of a test organism. Various modifications of these risk frameworks incorporated higher levels of protection to exposed organisms by the adopting reduced degrees of mortality by introducing EC_{20} and EC_{10} (*i.e.* the concentration of a substance or material resulting in a specific response in 20% and 10% of the test organisms, respectively) values.

As knowledge of the effects of persistent, bioaccumulative and toxic organic chemicals grew other measures of organism exposure and effect were introduced into risk frameworks. These resulted in the introduction of the Lowest Observable Effects Level (LOEL) and No Observable Effects Level (NOEL) concepts in ecotoxicology. Nowadays LOEL and NOEL based concentration limits are well established within risk assessment protocols favouring a precautionary approach.

2.5.2. Endocrine disrupting chemicals

There is much uncertainty and significant gaps in data to enable the accurate assessment of the risk and potential biological effects of EOCs. Of all the EOCs, EDCs have been the subject of extensive research over past decades due to their potential to disrupt endocrine functions in wildlife, invertebrates, fish, and human populations.

Endocrine disruptor chemicals that mimic or interfere with the functions of natural estrogenic steroids have been extensively studied. This is because estrogens regulate a wide variety of biological functions in vertebrates, such as: growth, metabolism, cell growth and proliferation, cell function and differentiation, sexual development and behaviour, and development of the immune system in both sexes (Leusch *et al*. 2010). The pharmaceuticals that have endocrine activity include potent, long-lasting estrogens, antibiotics, β-blockers, anti-epileptics, androgenic steroids, lipid regulating agents, phenolic xenoestrogens, and plasticisers (BPA and phthalate esters). Some of those EOCs have been linked to significant effects in wildlife, including near extinction of species of vultures in Asia and sex reversal and infertility in several species of fish (Hotchkiss *et al*. 2008).

In spite of a vast amount of literature on EDC research, it is still very challenging to suitably assess their risk within receiving environments (Hotchkiss *et al*. 2008). There is extensive information on the risk of contaminants with estrogenic activity. Predicted-no-effect concentrations (PNECs) have been derived at 2 and 0.1 ng/L (parts per trillion) for the two key EDCs 17β-estradiol and 17α-ethinylestradiol (Caldwell *et al*.

2012). The European Union has derived PNECs of 0.33, 0.10 and 1.50 µg/L respectively for the three EDCs tert-nonylphenol, triclosan (WFD-UKTAG, 2009), and bisphenol-A (EU, 2008). Predicted-no-effect concentrations of 1.60 and 0.175 µg/L have been derived for bisphenol-A (BPA) in Japan and Canada, respectively (AIST 2007; Canada 2008). A weight of evidence assessment of data from 61 studies assessed the effects of BPA upon aquatic organisms. This study concluded that existing PNECs did not provide adequate protection for exposed organisms and instead proposed a much lower PNEC of 0.06 µg/L (Wright-Walters *et al*. 2011). The PNEC values for these EDCs are in the parts-per-trillion concentration range, reflecting the potency of these biologically-active chemicals.

A study investigating the effects of combinations of 17α-ethinylestradiol with the pharmaceuticals carbamazepine, diclofenac and metoprolol demonstrated they induce multi-generational effects in the progeny of exposed organisms (Dietrich *et al*. 2010). The ecotoxicology of pharmaceuticals remains poorly understood and there is a paucity of information on their fate in the environment to characterise the long-term risk of individual and mixtures of EOCs (Fent *et al*. 2006; Pal *et al*. 2010). Overall, there is limited information resulting in a high level of uncertainty around the risk of PPCPs in receiving environments.

2.5.3. Pharmaceuticals

Most EOCs have been produced for human use and those that have been subjected to ecotoxicological assessment have been assessed for their potential effects on humans and other mammals. Pharmaceuticals provide an useful example. Some common antibiotics used to treat humans are also used as veterinary medicines for the treatment of sick animals. But, scientists have little knowledge of the effect of these chemicals on non-mammalian species such as insects, fish, and birds which can potentially be exposed to them when they are released into the wider environment.

For example the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin have been identified as chemicals of particular concern in aquatic environments by scientists around the world (Johnson *et al*. 2015). The concern regarding these specific antibiotics derives from their rates of consumption and discharge to aquatic environments, persistence and toxicity. Predicted concentrations of these antibiotics in European rivers were within the range of previously reported measurements (Johnson *et al*. 2015). The mean predicted concentrations of the four antibiotics in river water ranged from between two to six orders of magnitude lower than concentrations known to be toxic to fish, *Daphnia magna*, duckweed and cyanobacteria or green algae. A risk assessment of the four antibiotics of concern concluded it unlikely they were causing acute toxicity to wildlife within European rivers on their own (Johnson *et al*. 2015). However, their ability to exert longer term chronic effects was not assessed.

2.5.4. Current state of knowledge about the risk of emerging organic contaminants

The assessment of human and ecotoxicological risks caused by the release of EOCs into the environment is difficult to quantify. Our knowledge of the nature and degree of natural attenuation of EOCs is poor, it is therefore difficult to predict the fate of EOCs in receiving environments and therefore the concentrations at which organisms are exposed to them (Pal *et al*. 2010). The effects of EOCs can be more subtle and potentially cause chronic or long-term effects on organisms that are more difficult to assess, but are no less dangerous. New test methods are currently being developed to measure the long-term effects of EOCs on exposed organisms. For instance, the trans-generational effects of chemical exposure can be assessed through epigenetic mechanisms modulating gene expression (Vandegehuchte & Janssen 2014). An analysis of epigenetic changes following exposure to multiple stressors, constitutes a promising area for research assessing the risks of EOCs.

Cutting-edge research is showing that the effects of EOCs upon exposed organisms (for example the zebrafish) are subtle and may be profound. Many EOCs have been produced to impart a specific mode of biological action and treat medical conditions in humans. A good example is selective serotonin re-uptake inhibitors (SSRIs) such as the anti-depressant, Prozac (*i.e.* fluoxetine). These have proven to accumulate in fatty tissue in freshwater fish, specifically in the brain. There is mounting evidence that the presence of these chemicals in fish is having an effect on their behaviour. They exhibit anxiety and anti-social and aggressive behaviours that are not conducive for the breeding success of fish and maintenance of thriving populations.

Some of the most commonly used organophosphate flame retardants have recently been demonstrated to affect estrogenic and thyroid hormone concentrations in zebrafish (Kim *et al*. 2015; Wang *et al*. 2015). Clofibric acid, the active metabolite of the blood-lipid lowering drug clofibrate induced chronic mutigenerational effects in a zebrafish population including reduced growth, reduced triglyceride muscle content, impact on male gonad development and increase in embryo abnormalities in the offspring of exposed fish (Coimbra *et al*. 2015).

It is recognised that managing EOCs is challenging and there is continuing effort to develop comprehensive ranking systems to help rank EOCs for monitoring and treatment purposes. For instance, a ranking system was developed for surface and finished drinking waters[4] based on criteria including:

- occurrence
- treatment in drinking water utilities
- ecological effects

[4] 'Surface' is water that systems pump and treat from sources open to the atmosphere, such as rivers, lakes, and reservoirs. 'Finished water' has been treated and is ready to be delivered to customers.

- health effects for stream water/source water and finished drinking water (Kumar & Xagoraraki 2010).

Finished drinking water is the final product from a drinking water treatment plant. Recently a risk framework was proposed to assist regulators develop ecological screening and monitoring programmes for EOCs using a hazard-based approach (Diamond *et al.* 2011). Emerging organic contaminants were ranked on the basis of their bioaccumulative potential or persistence in the environment, and preference was given to chemicals that were rarely included in aquatic pollutant monitoring programmes. This process identified 11 high-priority chemicals that are commonly present in treated wastewater released into waterways and were recommended for inclusion in future aquatic monitoring programmes (Table 9). This could improve the generation of data on the distribution and concentration of these chemicals in aquatic waterways and subsequently provide the necessary baseline data to incorporate into future risk assessments of these chemicals.

Table 9. High priority organic wastewater contaminants rarely included in aquatic monitoring programmes.

Chemical	Application
3-Methylcholanthrene	Polycyclic aromatic hydrocarbons
4-Nonylphenol mono/di ethoxycarboxylate	Surfactant
Acetyl cedrene	Fragrance
Benfluralin	Herbicide
Celestolide	Fragrance
Clotrimazole	Pharma-anti-fungal
Di-N-octyl phthalate	Plasticiser
Musk xylene	Fragrance
Novobiocin	Pharma-antibiotic
Oryzalin	Herbicide
Octahydro-tetramethyl-naphthalenylethanone	Fragrance

Source: Diamond *et al.* 2011

2.5.5. Risk of mixtures

Another important aspect on the risk assessment of EOCs is that once released in the environment, they combine with other pollutants and environmental stressors and their potential combined or synergistic effects remain unknown. This is particularly the case in estuarine environments receiving EOCs from WWTP discharges that combine

with other contaminant sources from the whole catchment. As a consequence, in the environment, organisms (including humans) are rarely exposed to isolated micro-pollutants but to complex chemical mixtures, the individual components of which might be present at concentrations too low to raise concern. There is limited information to estimate whether additive or even synergistic effects can render those mixtures more potent (Schwarzenbach *et al*. 2006).

The top-ranked question, regarding the hazards, exposure assessment, and environmental and health risks of PPCPs in the natural environment, identified in a review summarising the outcomes from a series of workshops involving participants from academia, industry and government agencies was: "How important are PPCPs, relative to other chemicals and non-chemical stressors, in terms of biological impacts in the natural environment?" (Boxall *et al*. 2012). This important point was also highlighted in the emerging organic contaminants Envirolink report regarding the ranking of issues related to environmental contaminants, *e.g.* EOCs versus traditional persistent organic pollutants (Tremblay *et al*. 2011). Currently, this question cannot be definitively answered. For example, a recent review confirmed that many questions remain unanswered regarding our understanding of environmental hazards and risks from pharmaceuticals and other contaminants. However, current investigations such as those focussing on the impacts of anti-depressants in urban aquatic systems will continue to provide useful information to manage the uncertainty (Brooks 2014).

In conclusion, there is mounting evidence that EOCs exert multiple effects upon exposed organisms within receiving environments. These effects are much more subtle than the traditionally accepted acute ecotoxicity endpoints and instead impart chronic and/or multi-generational effects. Current accepted standard ecotoxicity methods are not optimised to discern chronic or multi-generational effects imparted by many EOCs and new test paradigms are required before the true impact of EOCs released into the environment can be fully understood. This is confirming the earlier predictions of Dr Christian Daughton (USEPA Office of Research and Development) and Professor Thomas Ternes (German Federal Institute of Hydrology), that '*Subtle effects from low concentrations of bioactive PPCPs, whose continual expression over long periods of time in certain nontarget populations, could lead to cumulative, insidious, adverse impacts that would otherwise be attributed to natural change/adaptation or ecologic succession.'* (Daughton & Ternes 1999). There is a research need for the development of robust risk assessments and exposure limits. The group of EOCs for which realistic effect level limits have been derived are the ones with endocrine disrupting activity.

3. EMERGING ORGANIC CONTAMINANTS IN THE NEW ZEALAND ENVIRONMENT

3.1.1. Studies on endocrine disrupting chemicals

There is limited information about the levels of emerging organic contaminants (EOCs) in the New Zealand environment. Most of the data to date has been focussed on compounds with endocrine disrupting potential. The levels of estrogenic and androgenic activity in treated municipal wastewater from Canterbury were below those reported by researchers in the United Kingdom (Leusch *et al.* 2006). Another study measured the concentration of selected estrogens in the final effluents of three wastewater treatment plants (WWTPs) in the Waikato region. The concentration of the estrogenic steroid, 17β-estradiol, and its principal, metabolite estrone, was measured in the final effluents from three WWTPs. Levels varied from trace to a maximum of 100 ng/L. The total estrogenic activity measured by bioassays, ranged from below the quantification limit to a maximum of 32 estradiol equivalents (Sarmah *et al.* 2006). The efficacy of a newly-commissioned Beachlands/Maraetai WWTP to remove estrogenic and androgenic activity over a period of a year was evaluated using bioassays[5]. The Bardenpho process and clarification treatment was used at this plant. This treatment was then followed by disk filtration and ultra-violet (UV) disinfection before passage through a riparian wetland and discharge into a small stream. Androgenic activity was not detected in the effluent samples. Estrogenic activity was only measured at the relatively low concentration of 10 ng/L estradiol equivalents in a sample collected in October. The results suggest the absence of industrial inputs into the WWTP, in combination with the multi-phase treatment system, effectively reduced endocrine activity in the final treated effluent to non-detectable or relatively low levels. A similar study was conducted at the Rotorua WWTP. The concentration of endocrine disrupting chemicals (EDCs) detected in the membrane bioreactor and Bardenpho treatment stage effluents were below the predicted-no-effect concentrations (PNECs) for aquatic organisms (Tremblay *et al*. 2013).

Another study completed for the Waikato Regional Council (WRC) assessed the endocrine disruption potential of eight water samples collected from the Waikato River between Taupo and Tuakau. The results obtained from this assessment of EDCs in the Waikato River demonstrated that when specific contaminants were present it was at low concentrations that posed negligible risks to aquatic biota (Tremblay & Northcott 2013). However, it is important to acknowledge the samples analysed in this study were obtained as one-off grab samples and the results must therefore be interpreted with caution with regards to temporal levels and potential long-term effects.

[5] Tremblay *et al.* 2010 Water NZ

3.1.2. Studies on emerging organic contaminants

Two studies assessing EOCs in WWTP effluents are currently in progress in New Zealand. A PhD student project (Jason Strong, unpublished) is investigating the concentration of EOCs in WWTP effluents released into aquatic receiving environments, their partitioning into sediment, and potential to bioaccumulate in sediment biota. The EOCs under investigation in this project were selected to represent those most likely to persist in sediment and bioaccumulate in exposed biota. The initial phase of this project analysed the selected EOCs within the influent and treated effluent of WWTPs in New Zealand. A total of 13 WWTPs were identified and selected to represent a range of different catchment sizes (metropolitan, urban, semi-rural), wastewater sources (domestic or domestic/industrial), wastewater treatment processes (primary, secondary, advanced secondary/tertiary, oxidation pond *etc*.), and points of discharge (including stream, river, estuarine, marine outfall).

The classes of EOCs being analysed in this study include alkylphosphate flame retardants, musk fragrances, anti-microbial chemicals, paraben preservatives, phenolic xenoestrogens, and an insect repellent, DEET. A full list of the 42 individual EOCs under investigation is provided in Table 10.

Table 10. Classes and individual emerging organic contaminants (EOCs) being investigated in the influent and effluent of New Zealand wastewater treatment plants (WWTPs).

Flame retardants (FRs)	**Musks/fragrances**	**Anti-microbials**	**Preservatives**	**Phenolic xenoestrogens**	**Others**
Alkylphosphate FRs	**Nitro-musks**	Chloroxylenol	Methyl paraben	Bisphenol-A	**Insect repellent**
Tri-isobutyl-phosphate (TiBP)	Musk ambrette	o-phenylphenol	Ethyl paraben	4-tert-amylphenol	DEET
Tri-n-butyl-phospahte (TBP)	Musk ketone	Chlorphene	Propyl paraben	4-n-amylphenol	
Tris-(2-chloroethyl)phospahte (TCEP)	Musk mosken	Triclosan	Butyl paraben	4-tert-nonylphenol	
Tris-(2-chloroisopropyl)phosphate (TCPP)	Musk tibetene	Methyl triclosan	Benzyl paraben	4-n-nonylphenol	
Tris-(2-chloro-1-(chloromethyl)ethyl)-phosphate (TDCP)	Musk xylene	2,4,5,6-tetrabromo-cresol		4-tert-octylphenol	
Tiphenyl phosphate (TPP)	**Polycyclic musks**	Benzyl benzoate		4-n-octylphenol	
Tris-(butoxyethyl)-phosphate (TBEP)	Cashmeran			4-tert-heptyphenol	
Tris-(2-ethylhexyl)-phosphate (TEHP)	Celestolide			Technical nonylphenol equivalents	
Tri -ortho-cresyl-phosphate (ToCP)	Galaxolide				
Tri-meta-cresyl-phosphate (TmCP)	Phantolide				
Tri-para-cresyl-phosphate (TpCP)	Traseolide				
Tetrabromo-bisphenol-A					

Samples of influent and effluent were obtained from the 13 representative New Zealand WWTPs on two separate sampling occasions and analysed for the 42 EOCs (Table 10). An assessment of this data has demonstrated not all of the individual EOCs within a particular class are detected in the WWTP effluent samples. For example, four of the 11 alkylphosphate flame retardants were not detected in influent and effluent of the WWTPs, two were frequently detected at relatively low concentrations, and five were frequently detected at relatively high concentrations.

Similarly, the profile of musk fragrance EOCs was dominated by contributions from the polycyclic musks galaxolide and tonalide and many nitro-musks were either consistently not detected or detected at low concentrations.

Preliminary results reporting the concentrations of anti-microbial agents and the plasticiser bisphenol-A in wastewater entering and discharged from WWTPs in New Zealand are summarised in Table 11. The frequency of detection of the individual chemicals within influent and effluent from the 13 plants was high, and most often 100%.

Table 11. Anti-microbial agents including triclosan and parabens measured in municipal effluents from 13 New Zealand wastewater treatment plants (Strong *et al*. unpublished).

Compound	% Detected		Median concentration (ng/L)
	Influent	Effluent	
Methyl paraben	100	96	14.1
Butyl paraben	92	62	294
Chloroxylenol	100	100	68.6
Triclosan	100	100	30.5
Bisphenol-A	100	92	7.5

The EOC concentrations detected in treated effluent discharging from New Zealand WWTPs are comparable to those reported for European and North American WWTPs (Northcott *et al*. 2013). The method used to analyse EOCs incorporated filtration of the whole effluent sample followed by analysis of EOCs in the filtered or dissolved phase of the effluent samples. This is standard practice for the analysis of EOCs in WWTP effluents and allows/provides direct comparison against overseas data obtained using the same sample pre-treatment. However, the removal of particulate matter to which many EOCs will adsorb to, from the samples prior to extraction and analysis, under-estimates the concentration and mass load of EOCs in WWTP effluent streams.

The second ongoing study is assessing the ability of the biological trickling filter operating at the Gisborne City WWTP to remove EOCs from the wastewater stream. This study is investigating the EOCs listed in Table 6 together with six estrogenic, four androgenic, hydrocortisone (a glucocorticoid steroid hormone) and two progestogenic steroid hormones, benzophenone (a UV filter chemical), Picaridin (insect repellent), eight phthalate esters, five non-steroidal anti-inflammatory drugs (acetylsalicylic acid (aspirin), diclofenac, naproxen, paracetamol, ibuprofen) and bioassay analyses of total estrogenicity and androgenicity.

The Gisborne City biological trickling filter study is the most extensive assessment to date of EOCs in WWTP effluent in New Zealand. Preliminary data is confirming the conclusion of the aforementioned PhD project that the concentration of EOCs in New Zealand WWTPs' effluents is comparable to that measured overseas (Northcott, unpublished). A significant point of difference of this Gisborne City study is EOCs are being analysed in both the dissolved and particulate phases of the wastewater effluent stream. Preliminary data demonstrates the common practice of filtering WWTP effluents and only analysing the dissolved filtered phase significantly under-estimates the total load of EOCs entering and exiting WWTPs. The practice of excluding EOCs associated with the particulate phase within the effluent stream will therefore have a significant impact on the calculated removal rates for many EOCs, and particularly those exhibiting medium to high levels of sorption affinity to residual suspended solids and colloidal organic matter in effluent.

Further information will become available as these two studies progress to completion and the forthcoming data and project outcomes will provide valuable knowledge for understanding the fate of EOCs within WWTPs in New Zealand and the range, concentration and mass flux of EOCs entering the New Zealand environment via discharges of effluent.

Once the concentration and flux of EOCs entering the environment have been quantified the next critical step is to determine their fate within receiving environments, and ultimately, their effect. Studies completed to date demonstrate pharmaceuticals and personal care products (PPCPs) entering New Zealand's estuarine and coastal environment persist in sediment. For example, the concentration of pharmaceutical residues detected in harbour and estuarine sediments within the Auckland region are similar to those reported in Europe and the USA (Figure 1) (Stewart *et al.* 2014; Luo *et al*. 2014).

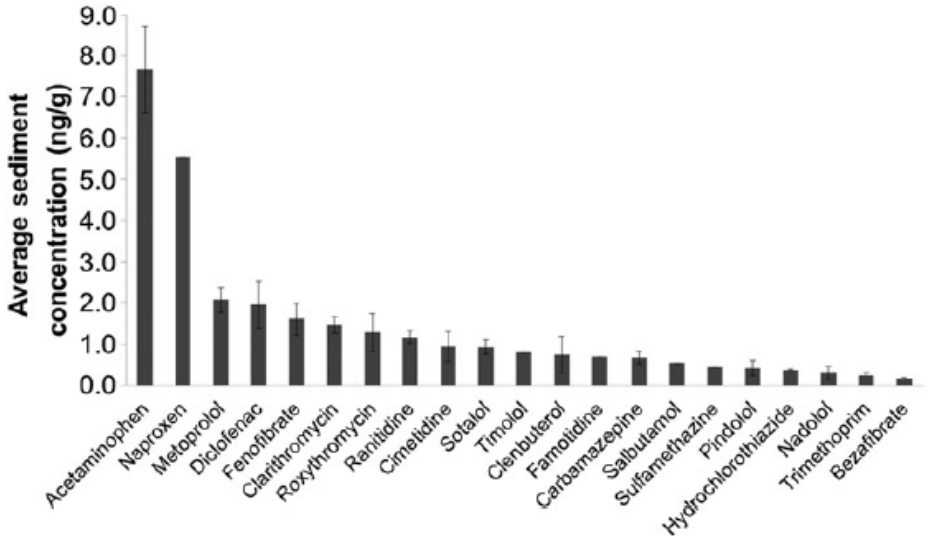


Figure 1. Average concentration of pharmaceuticals measured in estuarine sediments collected around the Auckland region. Source: Stewart *et al.* 2014.

In summary, the data to date, demonstrate the concentration of EOCs/PPCPs in New Zealand WWTP effluents are comparable to those in Europe and the USA. This results from the same broad volume of water use per day/per person in the Western world, and a similar rate of consumption of chemical products. What is different is the total mass of chemicals being released to the New Zealand environment and those in Europe and the USA. This is dependent upon the volume/flow characteristics of the plant, therefore larger municipalities servicing larger populations have larger WWTPs to deal with larger flows. So while these have a similar measured concentration of EOCs/PPCPs the total mass per unit of time is much higher.

3.2. The risk of Omaha treatment plant treated wastewater

Omaha and Warkworth wastewater treatment plants incorporate biological treatment and UV disinfection of the final effluent. The Algies Bay/Snells Beach WWTP uses an ocean outfall. The three WWTPs service relatively low population catchments with limited industrial input. The effluent discharge volumes range from 300–4,100 m^3/d from the three plants.

3.2.1. Land application options

Treated effluent from the Omaha WWTP is irrigated onto a golf course and eucalyptus plantation. A proportion of the irrigated treated effluent applied to the golf course infiltrates the predominately sandy soil to the relatively shallow groundwater beneath the golf course. This groundwater flows westwards towards Whangateau Harbour—eventually flowing through the sand/soil into the harbour itself. Surface water features

(*i.e.* small streams) are present within the kahikatea forest (between the golf course and the harbour) and some groundwater will also emerge in these streams, which also flow into the harbour. The geology through which the groundwater flows comprises sandy material below the golf course with lenses/discrete layers of silty or peaty material, highly organic silty material below the kahikatea forest, and a mix of silty and sandy material beneath the harbour.

Similarly, the shallow groundwater beneath the eucalyptus plantation flows east towards Whangateau Harbour, eventually flowing through sand/soil into the harbour itself. The shallow geology comprises a high organic silty layer with peat deposits, underlain by sandy material. It can be expected that the natural bio-filtration function and capacity of soils overlying the golf course and eucalyptus plantation will provide additional attenuation of EOCs in irrigated effluent. However, this does not ensure that residues of EOCs in the irrigated effluent will not leach into groundwater or be transported by overland flow events or groundwater infiltration into the harbour. It is reasonable to assume the concentration of EOCs irrigated onto soil will be attenuated to some degree but numerous factors influence the degradation and retention of EOCs in soil and ideally these should be assessed on an individual site basis.

The scarcity of water resources in many parts of the world is leading to an increase in the practice of irrigating turfgrass with treated wastewater. While this practice prevents unnecessary use of potable water supplies and may be cost-effective there are concerns that residues of EOCs in the irrigated wastewater can leach and contaminate groundwater, and/or migrate off the site of application into nearby waterways.

A number of studies have investigated the presence of EOCs in soil irrigated with recycled wastewater or receiving infiltration of treated wastewater via pond systems Soils irrigated with reclaimed wastewater have been demonstrated to contain and accumulate residues of wastewater derived pharmaceuticals (Kinney *et al*. 2006). Of a total of 19 pharmaceuticals the four most commonly detected in soil irrigated with reclaimed water were erythromycin, carbamazepine, fluoxetine and diphenyldramine. The authors concluded some of the pharmaceuticals may have sufficient mobility to migrate through the top 30 cm of soil and into deeper soil layers and that some pharmaceuticals can persist in soil for months after irrigation. The study identified soil organic matter as a significant factor in the retention of pharmaceuticals in soil.

A total of 151 organic micro-pollutants, including numerous EOCs, were identified in groundwater underlying a wastewater infiltration site in Berlin (Germany; Wode *et al*. 2015). Two groups of organic micro-pollutants were identified in groundwater samples:

- those sourced from treated wastewater infiltrating the site since 2005 (‘current’)
- those sourced from the infiltration of untreated wastewater prior to 1985 (‘legacy’).

The elimination/reduction of organic micro-pollutants during infiltration displayed a strong dependence upon the properties of the chemicals. Infiltration removed 85% of cationic chemicals and 50% of non-ionic chemicals, but this was reduced to 17% (2 out of 12) for anionic chemicals. This study demonstrated that once organic micro-pollutants and EOCs leach through the soil profile into groundwater they can persist unaltered for decades.

3.2.2. Effluent application to land

A Water Environment Research Foundation (WERF) study investigated the fate and transport of EOCs in turfgrass/soil systems irrigated with recycled water. This extensive programme of study incorporated laboratory-based bench-top, meso- and field-scale experiments assessing the fate and transport of the same suite of selected PPCPs. The specific PPCPs under investigation represented those most frequently occurring in recycled water originating from wastewater treatment (Table 8).

Laboratory-based sorption and degradation tests using a sand and loam soil, showed most of the PPCPs exhibited low to moderate sorption in the soils. Only a few of the PPCPs were susceptible to degradation under aerobic conditions (diclofenac, ibuprofen and sulfmethoxazole) while other compounds were relatively persistent with half-lives exceeding 100 days. The combined low sorption and extended half-lives of most of the PPCPs suggested they would have high mobility in sandy soils commonly found on golf courses, and therefore present a risk for groundwater contamination from the irrigation of recycled water.

The long persistence of PPCPs observed in the lab experiments may be due to the low organic carbon content of the soils. This differs from golf courses where the soil is overlaid by a thatch layer (grasses and plants) which encourage microbial diversity and activity and provides an enriched layer of organic matter within the upper surface soil layer. These processes combined with the effect of sunlight (photolytic degradation) will increase the retention and degradation of PPCPs, therefore decreasing their leaching potential.

Field-based leaching assessments of the selected PPCPs conducted using monolithic soil lysimeters (61 cm diameter × 120 cm depth) with and without turfgrass cover showed most of the PPCPs were not mobile. Nine of the PPCPs were detected in drainage water after 745 days of irrigation with recycled water. Only three of these exhibited a consistent pattern that correlated with the number of unsaturated pore volumes displaced from the soil lysimeters, namely primidone, sulfamethoxazole and carbamazepine. The relative mobility of these three compounds compared to chloride was 37% for primidone and only 1–3% for sulfamethoxazole and carbamazepine.

Significantly higher leaching losses of PPCPs were observed with the loamy sand soil and with higher leaching fractions on uncovered soil. However, this combination of

experimental factors was considered a worst-case scenario that would be unlikely to occur under normal irrigation practices. The key soil, plant and water factors affecting the leaching of the PPCPs were identified to be:

- unsaturated pore volumes
- evapotranspiration
- irrigation rate
- turf cover
- % sand of the soil
- microbial biomass
- average redox potential
- organic matter content

The conclusion of the soil lysimeter experiments was that only small amounts of PPCPs would leach under typical golf course conditions. However, until the biological effect of these losses can be quantified they deserve greater attention by the scientific community.

3.2.3. Field-scale experiments

Field-scale experiments were conducted on active golf courses where turfgrass plots were irrigated with recycled water for over six months at elevated irrigation rates. With the exception of a few compounds most PPCPs did not appear in the drainage leachate (90 cm depth) under the conditions used in the experiment. While trimethoprim and primidone were frequently detected in drainage water under the irrigated plots their mass removal was > 80%. The conditions used in this field-scale experiment represented a 'worst-case scenario' for recycled water irrigation. The irrigation rates were selected to be high compared to normal practices, the soil texture was very sandy and the collection of drainage water at 90 cm depth represents an extremely shallow groundwater aquifer. Under normal irrigation regimes on operating golf courses the mass flux of PPCPs leaching would be considerably reduced as the compounds would have extended contact time in the soil during which they can be sorbed and degraded as they migrate down the soil profile. Despite the persistence of the selected PPCPs and the weak sorption capacity of the soil at the study sites it was demonstrated that turfgrass/soil systems effectively filtered out most PPCPs from irrigated recycled water under normal field conditions.

A recent study assessing the leaching of EOCs from recycled water irrigated on four golf courses in the south-western USA showed a major reduction in pharmaceutical residues in collected drainage water compared to the irrigated recycled water (Young *et al*. 2014). Carbamazepine, meprobamate, and sulfamethoxazole were the most commonly detected pharmaceuticals in drainage water collected 0.8 m below the

turfgrass surface. The overall results demonstrated the mass fluxes of the studied pharmaceuticals in drainage water were substantially reduced following vertical transport through only 60 cm of soil. The study concluded that while increased time frames are needed to assess the long-term effects of irrigation with recycled wastewater, the turfgrass/soil system showed much potential to retard and reduce the concentration of target EOCs leaching through the soil profile after irrigation.

Any environmental and human impacts of PPCPs and other EOCs in irrigated recycled wastewater will be minimised if drainage water remains on site following penetration below the root zone. Therefore, it is vital to maintain robust water management and irrigation practices on sites being irrigated with recycled wastewater.

It is important to note the aforementioned studies didn't address the challenging issue of spatial variability of soil properties and conditions that are recognised to exist at the field scale. The transport of irrigated water and associated contaminants can be dominated by preferential flow processes within soils that can be prevalent in real field situations.

The outcomes of the studies mentioned above, suggest there is a very low risk of EOCs in irrigated WWTP effluent leaching into underlying groundwater, if robust irrigation practices are followed. While the risk of EOCs leaching into groundwater is very low the possibility of this occurring cannot be totally excluded. The WERF/McCullough study concluded closer monitoring of irrigation of recycled water on golf courses and other field sites should be undertaken to better understand the leaching risk of PPCPs/EOCs. Furthermore, the leaching behaviour of EOCs will vary with site and management specific conditions so future studies should address the effects of soil type and texture, the depth of groundwater tables, and different irrigation management practices.

3.2.4. Options for Omaha wastewater catchment

In the absence of specific data demonstrating the ability of soils at the Omaha irrigation sites to retain and/or degrade EOCs it is pertinent to adopt a precautionary approach and assume over time there will be a degree of contaminant breakthrough and leakage into the underlying groundwater aquifers. Similar to the situation regarding irrigation of dairy effluents to land the key limiting factors are the inherent properties of the soil (particularly permeability, infiltration, water retention characteristics), nature of subsurface layers (*e.g*. an underlying impervious layer of clay), and the rate and timing of irrigation application.

As the population within the Omaha wastewater catchment grows the volume of effluent and mass of residual EOCs being irrigated onto the golf course and forest will increase unless other means of disposal are forthcoming. If irrigation continues to be

the preferred choice for effluent disposal in the future there will be an increased risk of EOCs leaching to groundwater and migrating into the Whangateau Harbour as the capacity of overlying soils to attenuate EOCs is exceeded.

The absence of appropriate data makes it impossible to exclude the risk that EOCs may leach into groundwater and/or migrate into the Whangateau Harbour from the irrigation application sites.

Relevant information necessary to better quantify this risk includes assessing the following.

- Range and concentration of EOCs present in the final treated effluent stored and used for irrigation.
- Physical and chemical properties of soils underlying the golf course and plantation forest.
- Water permeability and mass transport properties of soils underlying the golf course and plantation forest.
- Ability of soils underlying the effluent irrigation zones to both degrade and retain EOCs present in the irrigated recycled effluent.

Data obtained from these assessments can be incorporated into a combined water transport and environmental fate model for EOCs that predicts outcomes based on the concentration of EOCs in the irrigated effluent and effluent irrigation application scenarios. Alternatively, surface and groundwater samples collected between the golf course and Whangateau Harbour could be analysed for select EOCs.

4. CONCLUSIONS

Emerging organic contaminants (EOCs) represent a wide range of chemical classes, and the number of identified EOCs will continue to increase with advancements in analytical technologies and the development of new methods of analysis.

Effluent from wastewater treatment plants (WWTPs) is the main source of EOCs released into the environment. It is likely that the number of EOCs identified in WWTP effluents will continue to increase in future in response to the growth in consumption of chemical products used in households, increasing prescription of medications and the rapid introduction of new chemicals into the marketplace.

The critical factor for the effective removal of EOCs by conventional secondary waste water treatment processes is sludge retention time, but this alone will not result in full removal of all EOCs from the wastewater stream. The ability of secondary waste water treatment processes to remove EOCs can be highly variable and is ultimately plant dependent.

There is no standardised list of EOC indicator chemicals to use in studies determining the efficacy of wastewater treatment to remove or reduce them, or assess their fate and effects in receiving environments. However, various individual EOCs are consistently identified as indicator compounds regardless of differences in the criteria applied for selection. These EOCs are useful model compounds to include in future assessments as the results can be directly compared to those obtained in other studies.

Currently there is a paucity of data to assess the risk EOCs pose to the environment and wildlife. The risk assessments completed to date for EOCs using current accepted ecotoxicological test methods, and mainly acute toxicity endpoints, suggest these EOCs pose negligible risk to the environment and wildlife. However, there is general agreement in the research community that the combined effects of EOCs will be seemingly harmless but profound.

Predicted-no-effect concentration values derived for selected endocrine disrupting chemicals (EDCs) reflect the biological potency and specific mode of action of these chemicals and are significantly lower than other EOCs. As such EDCs present the greatest level of risk to organisms exposed to EOCs originating from treated wastewater effluent. It is important to acknowledge that as understanding of the range of biological effects induced by other bioactive EOCs grows (*e.g.* pharmaceuticals) we can expect their predicted-no-effect concentrations (PNECs) to reduce to concentrations (parts per trillion) similar to those of EDCs.

Studies of EOCs in New Zealand demonstrate they are present in WWTP effluents at similar concentrations to those found overseas, they are present in receiving

environments, and some persist and accumulate in receiving environments. Emerging organic contaminants will likely exert the same range of effects upon native species as those observed overseas.

Previous studies assessing the leaching and transport of EOCs in WWTP effluent irrigated onto soil indicate significant removal of EOCs can be achieved in soil covered by turf grass. However, these studies have been carried out under controlled conditions and have not considered the impact of preferential flow processes or the highly variable nature of soil at the field scale. These factors will have a considerable impact on the migration and transport of effluent within the irrigation zone and the fate and behaviour of associated EOCs.

The risk that EOCs within Omaha WWTP effluent will leach from irrigation application sites into underlying groundwater and/or migrate into the Whangateau Harbour is low but the possibility of this occurring cannot be excluded. A robust assessment of this risk can only be made by assessing the range and concentration of EOCs in the irrigated effluent and conducting assessments of their fate and transport within the soils underlying the irrigation application sites.

Current knowledge of the fate and effects of EOCs suggests residues of EDCs within the irrigated wastewater effluent present the highest risk to the health of organisms within Whangateau Harbour. In real terms this risk remains very low. The concentration of EDCs within irrigated wastewater effluent will be reduced during passage through the overlying grass sward and soil at the irrigation application sites, and during subsequent passage through solid substrates within the groundwater aquifer. As a consequence the concentration of any residues of EDCs ultimately transported to Whangateau Harbour via ground water flows will be significantly reduced.

If EOCs leach within soils at the effluent irrigation sites and migrate with groundwater flow and/or migrate off-site and are transported into Whangateau Harbour, their ultimate fate will be determined by another range of chemical, biological and physical processes. These include sorption and retention by estuarine sediments, abiotic and biotic degradation, and dilution and transport by tidal flow. The relative importance of these removal processes will be determined by the predominating physical characteristics at the point(s) of entry into the Whangateau Harbour.

There are solutions to further manage the introduction of potentially problematic chemicals into the environment. It is a priority to operate the sewage treatment plants (STPs) at optimum treatment conditions and to assess the efficacy of post-WWTP treatment like disposal of treated effluent to turfgrass/soil and wet land systems to reduce contaminant loading. Many EOCs are found in commonly used household products that are discharged into the wastewater systems. Therefore, all individuals share some responsibility for the range of household products they use, the chemicals

they contain, and their release into the environment (Tremblay *et al*. 2013). Tools like eco-labelling of pharmaceuticals and personal care products (PPCPs) and more eco-friendly products should help communities make better product choices that would result in less harmful compounds entering the waste stream (Goldsmith *et al*. 2014).

There is concern that delaying the management of potentially harmful EOCs could lead to undesirable effects being realised in the future. However, the task for regional councils of characterising the risk of EOCs and dealing with their consequences can be a significant undertaking. The aim of achieving safe and reliable water is possible through extensive treatment and rigorous monitoring to detect and correct any drift from expected performance but it is important to look at ways to harmonise efforts and resources across interested groups (Snyder 2014). Hence any approach to address this can be resource intensive and should be staged to maximise resources. For instance, any requirement to significantly reduce the concentrations of potentially harmful EOCs detected in WWTP effluent in the region may require large investments in additional or upgraded treatment plant infrastructure, for example microfiltration.

5. RECOMMENDATIONS

The management of the risk of emerging organic contaminants (EOCs) is a challenging task. There is a need to generate local information on EOCs of relevance to the Auckland region and to characterise the efficacy of the various methods of effluent treatments and disposal. In light of the above conclusions the following recommendations are made:

1. **Assess the composition and concentration of emerging organic contaminants in wastewater treatment plant effluents**

   Because the ability of wastewater treatment plants (WWTPs) to remove and reduce EOCs is so variable, effort should be made to characterise a range of representative EOCs within the final effluents of plants operating at or near optimum treatment conditions.

   The EOCs analysed in the final effluents of the three WWTPs should include the same chemicals being investigated in the Gisborne City biological trickling filter project. This would provide a direct comparison with residue data previously obtained for 13 other WWTPs in New Zealand, together with a wider range of EOCs being assessed in the Gisborne study. These include alkylphosphate flame retardants; nitro and polycyclic musks; phenolic anti-microbials; parabens; industrial alkylphenols; the insect repellents DEET and Piccaridin; estrogenic, androgenic and progestogenic steroid hormones; phenolic anti-microbial chemicals, ultra-violet (UV) filter chemicals, and phthalate esters, and non-steroidal anti-inflammatory drugs. Because they represent the highest level of risk to organisms, special attention should be given to characterising the profile of individual endocrine disrupting chemicals (EDCs) and total endocrine activity in the influents and treated effluents through a combined approach of trace chemical and bioassay analyses. Bioassay analyses (*e.g.* reporter gene assays) should be used to determine estrogenic, androgenic and dioxin-like activities of the samples.

2. **Determine the risk of emerging organic contaminants in wastewater treatment plant effluent discharged into waterways**

   The results obtained for concentration of EOCs analysed in WWTP effluent should be combined with appropriate hydrological data to estimate the concentrations that organisms within relevant waterways are likely to be exposed to. The estimated exposure concentrations can be combined with predicted-no-effect concentrations (PNEC) to derive exposure quotients that provide a measure of the risk EOCs pose to various types of organisms residing within those waterways.

3. **Monitor emerging organic contaminants within the irrigation application sites**

   Numerous uncertainties were highlighted in this report regarding the risk of EOCs in irrigated wastewater effluent leaching through soil and into underlying groundwater.

These risks can only be quantified and mitigated, if the necessary data is available. Completing a full assessment of the fate and transport of EOCs in soil within the irrigation application fields is complex and expensive. Alternatively we recommend adopting a tiered approach comprising:

- Characterisation of EOCs in WWTP effluent as outlined above.
- Analysing soil cores from the wastewater irrigation sites for residual EOCs following three years of continued wastewater irrigation.
- Consider further on-site monitoring assessments if soil cores show any evidence of downward migration of EOCs, for example, installing porewater/groundwater sampling devices to sample and monitor the leaching and migration of EOCs.

6. REFERENCES

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

Borm PJA, Robbins D, Haubold S, Kuhlbusch T, Fissan H, Donaldson K, Schins R, Stone V, Kreyling W, Lademann J, Krutmann J, Warheit D, Oberdorster E 2006. The potential risks of nanomaterials: a review carried out for ECETOC. Particle and Fibre Toxicology 3:11.

Boxall ABA, Rudd MA, Brooks BW, Caldwell DJ, Choi K *et al*. 2012. Pharmaceuticals and Personal Care Products in the Environment: What Are the Big Questions? Environmental Health Perspectives 120, 1221-1229.

Brooks BW 2014. Fish on Prozac (and Zoloft): Ten years later. Aquatic Toxicology 151(0): 61–67.

Caldwell DJ, Mastrocco F, Anderson PD, Lange R, Sumpter JP 2012. Predicted-no-effect concentrations for the steroid estrogens estrone, 17 beta-estradiol, estriol, and 17 alpha-ethinylestradiol. Environmental Toxicology and Chemistry 31(6): 1396–1406.

Clara M, Kreuzingera N, Strenna B, Gans O, Kroissa H 2005a. The Solids Retention Time--A Suitable Design Parameter to Evaluate the Capacity of Wastewater Treatment Plants to Remove Micro-pollutants. Water Research. 39: 97-106

Clara M, Strenn B, Gans O, Martinez E, Kreutzinger N, Kroiss H 2005b. Removal of Selected Pharmaceuticals, Fragrances and Endocrine Disrupting Compounds in a Membrane Bioreactor and Conventional Wastewater Treatment Plants. Water Research 39: 4797-4807.

Coimbra AM, Peixoto MJ, Coelho I, Lacerda R, Carvalho AP, Gesto M, Lyssimachou A, Lima D, Soares J, Andre A, Capitao A, Castro LF, Santos MM 2015. Chronic effects of clofibric acid n zebrafish (*Danio rerio*): a multi-generational study. Aquatic Toxicology. 160: 76-86.

Daughton CG and Ternes TA 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environmental Health Perspectives. 1999 Dec;107 Suppl 6:907-38.

Diamond JM, Latimer HA, Munkittrick KR, Thornton KW, Bartell SM, Kidd KA 2011. Prioritizing Contaminants of Emerging Concern for Ecological Screening Assessments. Environmental Toxicology and Chemistry 30(11): 2385–2394.

Dietrich S, Ploessl F, Bracher F, Laforsch C 2010. Single and combined toxicity of pharmaceuticals at environmentally relevant concentrations in Daphnia magna - A multi-generational study. Chemosphere 79(1): 60-66.

Drewes JE, Hemming JDC, Schauer JJ, Sonsogni WC 2006.Removal of Endocrine Disrupting Compounds in Water Reclamation Processes. Water Environment Research Foundation (WERF) and IWA Publishing. Report 01-HHE-20T.

Drewes JE, Sedlak D, Snyder S, Dickenson E 2008. Development of indicators and surrogates for chemical contaminant removal during wastewater treatment and reclamation. Water Reuse Foundation and Water Environment Research Foundation (WERF) .

Drewes JE, Dickenson E, Snyder S 2009. Contributions of household chemicals to sewage and their relevance to municipal wastewater systems and the environment. Water Environment Research Foundation (WERF) and IWA Publishing.

Environment 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

European Union (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.

Fent K, Weston AA, Caminada D 2006. Ecotoxicology of human pharmaceuticals. Aquatic Toxicology 76(2): 122-159.

Goldsmith MR, Grulke CM, Brooks RD, Transue TR, Tan YM, Frame A, Egeghy PP, Edwards R, Chang DT, Tornero-Velez R, Isaacs K, Wang A, Johnson J, Holm K, Reich M, Mitchell J, Vallero DA, Phillips L, Phillips M, Wambaugh JF, Judson RS, Buckley TJ, Dary CC 2014. Development of a consumer product ingredient database for chemical exposure screening and prioritization. Food and Chemical Toxicology 65: 269–279.

Gottschall N, Topp E, M*etc*alfe C, Edwards M, Payne M, Kleywegt S, Russell P, Lapen DR 2012. Pharmaceutical and personal care products in groundwater, subsurface drainage, soil, and wheat grain, following a high single application of municipal biosolids to a field. Chemosphere 87: 194-203.

Hotchkiss AK, Rider CV, Blystone CR, Wilson VS, Hartig PC, Ankley GT, Foster PM, Gray CL, Gray LE 2008. Fifteen years after "Wingspread" - Environmental endocrine disrupters and human and wildlife health: Where we are today and where we need to go. Toxicological Sciences 105(2): 235–259.

Johnson AC, Jurgens MD, Lawlor AJ, Cisowska I, Williams RJ 2014. Particulate and colloidal silver in sewage effluent and sludge discharged from British wastewater treatment plants. Chemosphere 112, 49-55.

Johnson AC, Keller V, Dumont E, Sumpter JP. 2015. Assessing the concentations and risks of toxicity from the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin in European rivers. Science of the Total Environment. 511: 747-755.

Kim S, Jung J, Lee I, Jung D, Youn H, Choi K. 2015. Thyroid disruption by triphenyl phosphate, an organophosphate flame retardant in zebrafish (danio rerio) embryos/larvae, and in GH3 and FRTL-5 cell lines. Aquatic Toxicology. 160: 188-196.

Kinney CA, Furlong ET, Werner SL, Cahill JD 2006. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environmental Toxicology and Chemistry. 25: 317-326.

Kumar A, Xagoraraki I 2010. Pharmaceuticals, personal care products and endocrine-disrupting chemicals in U.S. surface and finished drinking waters: A proposed ranking system. Science of the Total Environment 408, 5972-5989.

Leusch FDL, Chapman HF, van den Heuvel MR, Tan BLL, Gooneratne SR, Tremblay LA 2006. Bioassay-derived androgenic and estrogenic activity in municipal sewage in Australia and New Zealand. Ecotoxicology and Environmental Safety 65(3): 403–411.

Leusch FDL, De Jager C, Levi Y, Lim R, Puijker L, Sacher F, Tremblay LA, Wilson VS, Chapman HF 2010. Comparison of Five in Vitro Bioassays to Measure Estrogenic Activity in Environmental Waters. Environmental Science & Technology 44(10): 3853–3860.

Liu ZH, Kanjo Y, Mizutani S 2009. Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment - physical means, biodegradation, and chemical advanced oxidation: A review. Science of the Total Environment 407(2): 731–748.

Luo YL, Guo WS, Ngo HH, Nghiem LD, Hai FI, Zhang J, Liang S, Wang XCC 2014. A review on the occurrence of micro-pollutants in the aquatic environment and their fate and removal during wastewater treatment. Science of the Total Environment 473, 619-641.

McCullough MD 2012. Attenuation of PPCPs through golf courses using recycled water. Water Environment Research Foundation (WERF) and IWA Publishing. Report WERF1C08.

Northcott GL, Strong JMS, Tremblay L, Wilkins AL. 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.

Pal A, Gin KYH, Lin AYC, Reinhard M 2010. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. Science of the Total Environment 408, 6062-6069.

Roberts PH. and Thomas KV. 2006. The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment. Science of The Total Environment 356, 143-153.

Rorije E, Aldenberg T, Peijnenburg W 2013. Read-across Estimates of aquatic toxicity for selected fragrances. Atla-Alternatives to Laboratory Animals 41, 77-90.

Salveson A, Rauch-Williams T, Dickenson E, Drewes JE, Drury D, McAvoy D, Snyder S. 2012. Trace organic compound indicator removal during conventional wastewater treatment. Water Environment Research Foundation (WERF) and IWA Publishing. Report CEC4R08.

Sarmah AK, Northcott GL, Leusch FDL, Tremblay LA 2006. A survey of endocrine disrupting chemicals (EDCs) in municipal sewage and animal waste effluents in the Waikato region of New Zealand. Science of the Total Environment 355(1-3): 135–144.

Schwarzenbach RP, Escher BI, Fenner K, Hofstetter TB, Johnson CA, von Gunten U, Wehrli B 2006. The challenge of micro-pollutants in aquatic systems. Science 313, 1072-1077.

Snyder S, Wert EC, Lei H, Westerhoff P, Yoon Y 2007. Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes. American Water Works Association Research Foundation (AwwaRF) and IWA Publishing.

Stephenson R and Oppenheimer J 2007. Fate of Pharmaceuticals and Personal Care Products through Municipal Wastewater Treatment Processes. Water Environment Research Foundation (WERF) and IWA Publishing. Report 03-CTS-22UR.

Stewart M, Olsen G, Hickey CW, Ferreira B, Jelic A, Petrovic M, Barcelo D 2014. A survey of emerging contaminants in the estuarine receiving environment around Auckland, New Zealand. Science of the Total Environment 468: 202-210.

Ternes TA, Joss A, Siegrist H 2004. Scrutinizing pharmaceuticals and personal care products in wastewater treatment. Environmental Science & Technology 38(20): 392A–399A.

Tremblay LA, Challenger I, Ataria JM, Horswell J, Baker V 2013. Up-the-pipe Solutions — a best practice protocol. CIBR Report No 8. 14 p.

Tremblay LA, Northcott GL 2013. Analysis of Waikato River Water Samples for Selected Endocrine Disruptor Chemicals and Hormonal Activity. Prepared for Waikato Regional Council. Cawthron Report No. 2422. 15 p.

Tremblay LA, Leusch FDL, Prochazka E, Northcott GL 2013. Analysis of Hormonal Activity and Selected Endocrine-disrupting Chemicals in Rotorua District Council Sewage Treatment Plant Wastewater and Stream Water Samples. Prepared for Rotorua District Council. Cawthron Report No. 2363. 15 p.

Tremblay LA, Stewart M, Peake BM, Gadd JB, Northcott GL 2011. Review of the Risks of Emerging Organic Contaminants and Potential Impacts to Hawke's Bay. Prepared for Hawke’s Bay Regional Council. 39 p

Vandegehuchte MB, Janssen CR 2014. Epigenetics in an ecotoxicological context. Mutation Research-Genetic Toxicology and Environmental Mutagenesis 764, 36-45.

Wang Q, Lam JCW, Han J, Wang X, Guo Y, Lam PKS, Zhou B. 2015. Developmental exposure to the organophosphate flame retardant tris(1,3-dichloro-2-propyl)phosphate: Estrogenic activity, endocrine disruption and reproductive effects on zebrafish. Aquatic Toxicology. 160: 163-171.

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 Agenecy and the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER).

Wode F, van Baar P, Dunnbier U, Hecht F, Taute T, Jekel M, Reemtsma T 2015. Search for over 2000 current and legacy micro-pollutants on a wastewater infiltration site with a UPLC-high resolution MS target screening method. Water Research. 69: 274-283.

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, 676-685.

Young MH, Green RL, Conkle JL, McCullough M, Devitt DA, Wright L, Vanderford BJ, Snyder SA 2014. Field-Scale Monitoring of Pharmaceutical Compounds Applied to Active Golf Courses by Recycled Water. Journal of Environmental Quality 43, 658-670.