EMERGING ORGANIC CONTAMINANTS: WHAT ARE THEY AND SHOULD WE BE CONCERNED?

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ABSTRACT

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Emerging organic contaminants (EOCs) are gaining increasing attention across the globe. But what are they and should we be concerned?

What are they?

EOCs are a diverse range of compounds that are found in water and wastewater and stormwater that can adversely affect the environment and/or people. These chemicals come from a range of sources, such as pharmaceuticals, flame retardants, surfactants, preservatives, pesticides, plasticisers, and more. The most commonly recognised are the perfluorocarbons (PFCs), flame retardant chemicals that have been used in firefighting and are now being found in groundwater at airports and other firefighting sites.

This paper describes the New Zealand context and how work done around the world can be used to inform the risk of EOCs the environment and people in New Zealand. It also describes the treatment of selected EOCs using common wastewater treatment technologies employed in New Zealand drawing on various large scale, international, peer reviewed research from Europe and North America. The paper describes how EOCs vary between catchments, as well as over time (diurnally, weekly, and seasonally).

Should we be concerned?

EOCs are complex molecules, capably of undergoing different chemical reactions depending on the environmental conditions. This increases the complexity of understanding EOCs and the risk they pose to the environment and people. The potential for the formation of intermediate compounds, which may be more or less hazardous than the original EOC chemical requires consideration.

A key challenge for New Zealand is identifying and agreeing a robust set of EOCs that can be used as indicators and allow direct comparisons between studies as well as an underpinning benchmark for regulations. This paper discusses what guidance is currently available in current New Zealand regulations and proposes the process for establishing a consistent framework for EOC management in New Zealand.

KEYWORDS

Emerging organic contaminants, EOC

PRESENTER PROFILE

Becky is a chartered engineer and a Fellow of IChemE. She is currently on the Technical and Programme Committees for this Water NZ Conference and is Chair for the Chemeca 2018 conference. She was recently elected Deputy Chair of IChemE in New Zealand. Becky is a chemical engineer and a designer of wastewater treatment plants and has been the design lead for many wastewater treatment projects across New Zealand, including Christchurch, Motueka, Woodend, Blenheim, Havelock, Kaikoura, Tekapo, Twizel, and Timaru, wastewater treatment plants.

1 INTRODUCTION

Emerging organic contaminants (EOCs) are a large and diverse group of chemical compounds that come from a range of domestic, industrial and commercial sources[i]. EOCs are gaining increasing attention across the globe as environmental legislation becomes increasingly interested in the fate of chemicals in the environment[ii].

It is generally accepted that one of the main sources of EOC's in the environment is from wastewater treatment plants (WWTPs)[iii]. WWTPs have been traditionally designed to remove nitrogen compounds, reduce biological oxygen demand, and more recently reduce microorganisms. Traditional treatment processes have not been designed to remove EOCs. Studies show that the effectiveness of WWTPs to remove EOC is variable, some compounds are effectively treated and removed, others pass through with little or no treatment, and others are converted to other compounds that are also toxic [iii]. This is due to the varying chemical properties of the individual compounds, which also lead to some compounds being associated treated in the liquid phase, whereas others attach to the solid phase (i.e. the sewage sludge).

This paper describes how work done around the world can be used to inform the risk of EOCs the environment and people in New Zealand. It also describes the treatment of selected EOCs using common wastewater treatment technologies employed in New Zealand drawing on various large scale, international, peer reviewed research from Europe and North America. The paper describes how EOCs vary between catchments, as well as over time (diurnally, weekly, and seasonally).

2 WHAT ARE THEY AND SHOULD BE CONCERNED?

The US Geological Survey (USGS) defines EOCs as:

> *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 chemicals …. 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 emerging contaminants.* [iv]

EOC of concern are those that are considered may pose harm to either the environment or human health. Many of these are being or have been used in a wide range of everyday applications as summarised in Table 1.

Of key concern is the consequence of EOCs in the human food chain. For example, a key motivation for the study of the fate of antibiotics in WWTPs is whether the discharge of these into the environment contributes antibiotic resistance in the wider population [v]. A study in Europe in 2005 found that a number of common antibiotics pass through a WWTP relatively untreated, appearing in the sewage sludge (solid phase) [v]. However, it is important to note that the likelihood of this is considered low [vi].

Plasticisers are used in a wide range of plastics manufacturing applications, such as coatings, paints, paper, packaging etc, indeed most man-made materials contain plasticisers of some type. Plasticers are a subset of antioxidant compounds. A common plasticiser, Bisphenol A has been well studied. This chemical comprised two aromatic alcohol rings connected via a propane. Bisphenol A by has been shown to have endocrine disruption activity, which mean that it can can interfere natural hormone systems in living things, including humans. Study show that Bisphenol A is well treated in WWTPs, reported removal rates of up to 99% [vii].

Table 1: Examples of common EOC Categories

Category	Examples
Antibiotics	Amoxicillin Erthromycin Metrinidazole
Fire retardants	Perflorinated chemicals (PCFs, PFOS, PFAS etc) Polybrominated diphenyl ethers (PBDEs)
Prescription and non-prescription drugs	Gabapentin (antiepileptic) Sildenafil (erectile disfunction) Oxycodone (painkiller) Ketamine (anaesthetic) Theophylline (bronchodilator)
Personal Care Products	Quarternary ammonium compounds (QAC) musks
Pesticides	Monobutylin Dibutylin trubutylin
Plasticisers	Phthalate esters (PAEs, DEHP etc) Bisphenol A
Steroids and hormones	Oestradiol Oestriol
Preservatives	Triclosan (TCS) Troclocarbon (TCC) Parabens
Sunscreens	oxybenzone, octisalate, homosalate

Another class of plasticisers are the phthalate esters (PHEs), which are widely used in personal care products (PCPs), medical devices and household chemicals as a softener that does not chemically react with the product chemical. There is very little information on the fate of PAEs in WWTPS, however whilst they are relatively insoluble, become readily form increasingly water-soluble compounds as they undergo biological degradation [v].

Fire retardant chemicals (PFCs and PBDE's) have become a focus for many recent studies. These chemicals are used in a wide variety of applications that require flame or heat resistance, such as textiles, cookware, and firefighting foams. PFCs and PBDE's are of concern as they are reported to be endocrine disruptors that lead to neurodevelopmental defects, as well as being carcinogen compounds [v]. PFCs and PBDE's have very different chemical structures. PFCs are long chain, polymers, similar to a lipid, with fluorine replacing the hydrogen atoms along the chain. At one or both ends of the chain is a polar active group. PBDE's on the other hand comprise two brominated aromatic rings connected via an oxygen atom. Globally, the use of these chemicals is being increasing regulated and it is expected that concentrations these chemicals in wastewater will decrease over time.

Quaternary ammonium compounds (QAC's) are a group of cationic compounds with surface active properties (surfactant). They are structurally similar to an ammonium molecule, with the hydrogen atoms replaced with various alkyl or aryl functional groups. QACs are widely used for a variety of applications such as disinfectants, wetting agents, emulsifiers, PCPs, essentially anywhere a surface-active function is required. Due to their cationic surfactant properties, QACs have been shown to strongly associated with the surface of particles it is estimated that over 90% of QACs entering a WWTP pass through with the solids phase (sludge) [v].

Steroids and hormones are commonly found in wastewater entering WWTPs, mainly from domestic wastewater. Generally the treatment of steroids and hormones in WWTPs is reported as high, ranging from 64% to 99.9%. However, some studies suggest that excreted oestrogen compounds undergo either chemical or biological reaction in WWTPs are reform as oestrogen compounds [viii].

Antimicrobials such as triclosan (TCS) and troclocarban (TCC) are used in a wide variety of PCPs and other consumer products as they provide broad spectrum antimicrobial activity (bacteria, yeast, and virus). Studies show that TCC entering a WWTP associates with the solids phase and up to 75% of the TCC can be found in the treated sludge.

3 HOW EFFECTIVE IS TREATMENT?

3.1 VARIABILITY

The concentration EOCs varies over time, hour to hour, day to day, week to week and season to season. Concentrations also vary with location. These variations are in an important consideration when collecting data on EOC's and when considering treatment options. This is described in Table 2 below:

Table 2: EOC Variability

Category	Variability	Explanation
Pharmaceuticals: Antibiotics Steroids Hormones	Hourly	Waking up in the morning, people shower and toilet. Antibiotics accumulate in the urine during sleep and are excreted, leading to an increase in antibiotics in the 'first flush'
Fire retardants	Location	PFCs and PBDEs are often found where firefighting foams have been used. PFCs and PBDEs are also found in industrial areas where flame retardant chemical are used, such as textile and plastics manufacturing
Non-prescription (recreational) drugs	Weekly	Recreational drugs and their metabolites, such as cocaine and MDMA are found in wastewater higher concentration on the weekend. Short term spike of these drugs have also been found following events such as festivals or concerts.

Hospital dispensed drugs	Hourly	Drugs such as those used in cancer are found in wastewater higher concentration during the working week, due to these treatments generally being administered during the working week in new Zealand hospitals
Personal Care Products Preservatives	Hourly	Waking up in the morning, people shower and toilet. Surfactants and preservatives are used in a range of PCPs and this leads to an increase in concentration in wastewater the morning
Pesticides and insect repellents	Seasonal	Insects follow seal patterns, generally being more prolific during warmer summer months in New Zealand
Plasticisers	Little variability	Plasticisers are found in industrial areas where flame retardant chemical are used, such as textile and plastics manufacturing
Sunscreens	Seasonal	Sunscreens are used during warm weather when people are out in the sun, leading the significantly higher concentrations during summer in New Zealand.

3.2 REMOVAL EFFECTIVENESS

There is very little data on the fate of EOCs as they pass through a WWTP and the effectiveness of the various unit operations. Table 3 summarises some published data on the effectiveness of wastewater treatment to remove EOCs.

Table 3 Removal of EOCs with Different WWTP Technology [ix]

WWTP Technology	Removal Efficiency
Constructed wetland	42%
Aeration basin	62%
Rotating biological contactor	63%
Waste stabilisation pond	82%

Furthermore, EOCs incorporate a diverse range of compounds with a wide range of chemistries and it is these differing chemistries that makes treating EOCs in a WWTP a complex task with variating results and this is shown in Table 4. Thus, treatment technologies need to be tailored for each chemical can include involving physical, chemical and/or biological. Fortunately, modern WWTPs combine several unit processes that involve different treatment mechanisms.

As Table 4 shows, the concentration of some contaminants increases in wastewater as it undergoes treatment. This is likely due a range of factors. Measurement and sampling errors can result in poor characterisation of the wastewater, especially when concentration varies considerably over time. Another factor is metabolites of some EOCs may not be measured in the influent. However, during treatment these metabolites react and reform the original EOC (e.g. oestrogens are known to do this).

Table 4 Removal of Different EOCs[x]

EOC	Removal Efficiency %
Clotrimazole (antifungal)	-55
Dextropropoxyphene (pain killer)	107
Diclofenac (NSAID)	-71
Erthromycin (antibiotic)	79
Ibuprofen (NSAID)	-89
Mefenamic acid (NSAID)	67
Paracetamol (pain killer)	100
Propanodol (betablocker)	334
Tamoxifen (cancer drug)	30
Trimethoprim (antibiotic)	3

3.3 THE NEW ZEALAND SITUATION

The information presented in tables 3 and 4 is summarised from studies in Europe. There is very little published information on the fate of EOCs in New Zealand WWTPs. Of the studies undertaken in New Zealand, most are focused on the environmental effects of EOCs in WWTP effluent, not the effectiveness of the WWTP processes to treat the EOCs.

One recent study on the Gisborne WWTP has reported data on the effectiveness of that treatment plant to treat EOCs [xi]. The Gisbourne WWTP comprises screening and grit removal followed by a biological tricking filter (BTF) some of the soluble compounds are converted to the solid phase. The treated wastewater is then discharged via an ocean outfall. It is important to note that the BTF solids are not separate prior to disposal. Hence any reduction in EOC concentrations is due to the removal of screening and grit removal, or conversion to other chemical through BTF (i.e. chemical reaction). Table 5 summarises some of the removal efficiencies reported in this study and shows that the range of removal of EOCs is widely variable, even between chemicals with similar functionality. For example the removal of different phthalate esters varied from 5.8% to 98.5%.

Table 5 EOCs Reported at the Gisborne WWTP [xi]

EOC	Removal Efficiency %
Antimicrobials *Used in a variety of PCPs and other household chemicals*	46.8 – 97.3
Parabens *A group of chemically commonly used as preservatives*	>98.5
Alkylphenols *Chemical precursor for a variety of industrial speciality chemicals such as surfactants, lubricants and resins*	33.3 – 100
Alkylphosphates *A group of chemicals used as flame retardant in a side range of plastic polymer products*	4.1 – 77.6
Insect repellents	19 – 94
Pharmaceuticals	
Diclofenac	39.5
Ibuprofen	96.9
Phthalate esters (PAEs, DEHP etc) *A group of chemicals used as plasticisers*	5.8 – 98.8
Steroids and hormones	54.6 – 100

3.4 GUIDANCE FOR DESIGN IN NEW ZEALAND

Currently there is very little guidance in New Zealand on how to design for EOC treatment. The current biosolids guidelines are being revised and draft guidelines have been developed[xii,xiii]. The latest draft of these guidelines provides guideline values for the concentration of only five EOCs in treated biosolids; two musks, two surfactants and a plasticiser:

- Musks – tonalide
- Musk – galaxolid
- Plasticers – Phthalate ester – DEHP
- Surfactant – nonyl phenol and ethoxylates (in the form of NP/NPE equivalents)
- Surfactant – alkylbenzene sulphonate (LAS)

4 WHAT IS A DESIGN ENGINEER TO DO?

Most research has focused on the fate of EOCs in the environment. Designers need guidance on the effectiveness of treatment process on EOC concentrations. Data clearly shows that different EOCs behave differently when subjected to different treatment processes. Data also shows that the different treatment process have different treatment efficiencies. Some EOCs are associated with the solid phase, others with the liquid phase. So treatment needs include both liquid treatment and sewage sludge treatment

So as a design engineer, my wish list is:

- Data from a wide range of EOCs would provide insight to the design process and allow designers to make informed decisions on the treatment or EOCs
- A consistent set of 'indicator' EOCs that provide a snapshot of the would be helpful, akin to indictor organisms use for microbiological compliance
- A consistent set of 'indicator' EOCs that cover a range of EOC categories and chemistries
- A set f cost effective analytical techniques that allow consistent comparison of results between WWTPs
- Understand the position of iwi and the role wish to take on managing the discharge of EOCs into the environment

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