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Review of the Risks of Emerging Organic Contaminants and Potential Impacts to Hawke's Bay

RESEARCH BASED SOLUTIONS

Review of the Risks of Emerging Organic Contaminants and Potential Impacts to Hawke's Bay

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EXECUTIVE SUMMARY

Emerging Organic Contaminants (EOCs) are naturally occurring or anthropogenic chemicals that are not commonly monitored in the environment but have potential to enter the environment and cause adverse ecological and (or) human health effects. EOCs of major concern include endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs), but are not restricted to these two. Recent technological advances in analytical instrumentation have led to the detection of increasing numbers of EOCs in different environmental compartments (soil, air and the freshwater and marine environments) around the world. The main sources have been found to include municipal sewage treatment plant (STP) effluent and biosolids, landfill leachate, urban stormwater and agricultural and horticultural runoff. There is increasing global concern that the presence of EOCs in the environment may lead to adverse human and ecological health effects. EOCs are likely to accumulate in receiving environments and cause impacts. There is also concern about EOCs in drinking water and potential associated safety issues, which will only be exacerbated by the increased pressures on water resources worldwide. As EOCs are not currently monitored they could be considered as added stressors to current environmental contaminants.

Much information on environmental levels and fate of EOCs has been generated in the past two decades, mainly in the United States of America and the European Union. This information has been predominantly around those that are thought to affect the endocrine system but many knowledge gaps remain for a range of EOCs. The Hawke's Bay Regional Council (HBRC) has recognised that the knowledge gap around the risk and management of EOCs can present challenges to territorial authorities. There is growing negative public perception of the potential fate and effects of EOCs in their region. HBRC is concerned about a range of EOCs that are potentially released from sewage outfalls and runoff from urban, industrial, and agricultural activities including PPCPs, pesticides/herbicides, and anti-fouling agents. There is some information on levels of EOCs in the New Zealand aquatic environment. This data is sparse and real or potential ecological effects are largely unknown. These issues are likely to be specific to our range of volcanic soils, non-point source contamination from agriculture activities and our unique ecosystems.

The international and national literature on EOCs research was reviewed and confirmed that they are released in the environment from a range of sources. The main research groups have recognised that the continued introduction of EOCs into the environment requires ongoing research and monitoring to ensure the sustainability of a range of land-use activities. For the HBRC and New Zealand, the first step is to remain up-to-date with research and policy activities of the main international groups. Because of limited resources, it is important to focus on the most efficient steps to address the knowledge gaps about the fate and potential effects of EOCs on our unique ecosystems in New Zealand to enable policy-makers to rank the real or potential risks arising from EOCs relative to other stressors.We suggest a tiered approach to address the following questions:

1. What is the fate of EOCs in the receiving environment?
2. What are the effects of EOCs on our unique ecosystems?
3. What are the cumulative impacts (complex mixtures/multiple stressors) of EOCs?

There is a trend in the scientific community for the need to better coordinate resources and establish partnerships between the research, policy and industry groups. Some groups even call for a global coordination of research efforts to assess the risk posed by EOCs. We recommend the development of a national strategy to build a knowledge base, capability, policies, and management practices appropriate to evaluate, protect and manage the risk of EOCs to the New Zealand environment. The strategy would require a lead agency such as the Ministry for the Environment (MfE) that would coordinate the partnership needed including relevant multi-expertise research capability, policy, and industry key participants. The strategy would also ensure that New Zealand participates in any global research programme aimed at better management of the environmental risks posed by EOCs.

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ABBREVIATIONS

BDE	Brominated diphenylether.
BPA	Bisphenol A.
CEC	Contaminant of emerging concern.
CREEC	Consortium for Research and Education on Emerging Contaminants.
EC	Emerging contaminant.
EDC	Endocrine disrupting chemical.
EOC	Emerging organic contaminant.
EU	European Union.
HBRC	Hawke's Bay Regional Council.
MAV	Minimum acceptable value.
MfE	Ministry for the Environment.
MIW SIG	Micropollutants in Water Special Interest Group.
PAH	Polycyclic aromatic hydrocarbon.
PNEC	Predicted no effect concentration.
PFOA	Perfluorooctanoic acid.
PFOS	Perfluorooctane sulfonate.
PhACs	Pharmaceutical active compounds.
PPCPs	Pharmaceuticals and personal care products.
RMA	Resource Management Act.
SAICM	Strategic Approach to International Chemicals Management.
SETAC-AU	Australasian Society for Ecotoxicology.
STP	Sewage treatment plant.
UNEP	United Nations Environment Programme.
US EPA	United States Environmental Protection Association.
USGS	United States Geological Survey.
WHO	World Health Organization.
WQC	Water quality criteria.
WWTP	Wastewater treatment plant.

1. INTRODUCTION

1.1. What are emerging contaminants?

Most human activities of living, eating, working and dying involve the use of chemicals and generate waste (Tammemagi 1999). Unfortunately, much of this waste contains contaminants that are resilient to degradation and hence can accumulate in the different environmental compartments where they can potentially lead to environmental and human health issues. The world population is also rapidly expanding and the effects of globalisation are becoming significant issues on important resources such as potable water and food availability. Countries such as China and India provide a good indication of the effects of the increased rate of industrialisation compounded with population growth and the significant impacts on environmental and water qualities (Liu & Diamond 2005). This global increase in production and release of industrial and municipal wastewaters in the environment is in addition to agricultural run-offs of fertilisers, pesticides and manure causing a range of effects particularly in estuarine environments where contaminants accumulate (Matthiessen & Law 2002; Lotze *et al.* 2006; Murray *et al.* 2010). With the improvement of analytical methodologies a wider range of contaminants of industrial and agricultural origin and from household activities can now be detected, such as endocrine disrupting chemicals (EDCs), pharmaceutically active compounds (PhACs) and personal care products (PPCPs) along with other traditional chemicals found in treated wastewater (Kolpin *et al.* 2002; Ternes *et al.* 2004). In particular, the environmental effects associated with the manufacture and use of PhACs is of increasing global concern (Kummerer 2009; 2010), 2010). Indeed it has been claimed by Schwarzenbach *et al.* (2006) that the increasing accumulation of both natural and industrial chemical contaminants in freshwater is one of the key environmental problems facing humanity.

The US Geological Survey has been a leader in this field with their "Emerging Contaminants Project". They define an emerging contaminant (EC) 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 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 emerging contaminants" (US Geological Survey 2011). Most of the attention so far has focussed on EDCs, PhACs, PPCPs and a range of chemicals associated with agricultural activities that are biologically active (Pal *et al.* 2010). All these chemicals are typically of an organic rather than inorganic nature and so they are collectively referred to as *Emerging Organic Contaminants* (EOCs; (Kumar & Xagoraraki 2010; Pal *et al.* 2010)).

As the definition of emerging organic contaminants covers a wide range of compounds, they are often grouped into classes depending on their chemical group, their use, or their mode of action (for example, estrogenic compounds). We have used a mixture of these different classes in this report following the way these contaminants are described internationally.

The major groups of EOCs that are reviewed and discussed in this report include:

- Endocrine disrupting compounds
- Pharmaceuticals and personal care products
- Veterinary medicines
- Fire retardants and other industrial products
- New generation pesticides

This report does not cover toxins from freshwater or marine algal blooms nor pollutants that have been well studied and regulated, such as metals, organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) dioxins and furans and heavy metals. Nanoparticles and emerging/evolving microorganisms were considered outside the scope of this project.

1.2. Background to this report

The release into the environment of an increasing range of EOCs is of growing international concern. In New Zealand, there is a dearth of information on the levels of EOCs in the environment and their potential effects on our ecosystems. To address this issue, a series of Envirolink – Small Advice Grant workshops have been conducted in recent years and attended by scientists, environmental managers and policy makers to identify a pragmatic way forward – a strategy – for building a knowledge base, capability, policies, and management practices appropriate to evaluating, protecting and managing the risk of EOCs to the New Zealand environment.

The two main outcomes from these workshops have been the development of:

1. A FutureWatch Trend policy paper on emerging contaminants by staff from the former MoRST. However, it is unclear at this stage (June 2011) whether the report will be used by the new Ministry of Science and Innovation (MSI).
2. The present Envirolink medium size advice project in partnership with the Hawke's Bay Regional Council (HBRC).

The knowledge gap concerning the environmental risk of EOCs can present challenges to territorial authorities and this has been acknowledged by the HBRC. They realize that there is a growing negative public perception of the potential fate and undesirable effects of such chemicals on their environment. The concentrations of the limited EOCs that have been measured in the New Zealand environment are similar to those reported from overseas studies. It is likely that EOCs that have not yet been investigated will be present at levels similar to other developed countries and exert similar impacts/pressures on the New Zealand environment.

Discussions with HBRC staff identified some of the key issues that would also be relevant to other regional councils. They are concerned about a range of EOCs - including PPCPs, pesticides-herbicides, and anti-fouling agents (*e.g.* tributyltin (TBT) and diuron) - that are potentially released from major sources in their region, such as sewage outfalls and runoffs from urban, industrial, and agricultural activities. As EOCs are likely to be present with other environmental stressors, there are also concerns about the effects of multiple or synergistic effects, particularly in estuarine environments which receive EOCs and other contaminants from whole catchments. A further real concern is that any delay at management level to deal with potentially harmful EOCs could lead to undesirable effects further into the future. However the HBRC is also conscious that characterising the risk of EOCs and dealing with the consequences is a significant undertaking and hence any approach to address this matter must be staged to minimise eventual costs. For instance, any requirement to significantly reduce the concentrations of potentially harmful EOCs detected in sewage effluent from the sewage treatment plants in the region may require large investments in additional treatment plant infrastructure such as microfiltration and UV irradiation.

To better assess the risk of EOCs, HBRC identified the main knowledge gaps as data on actual EOC levels in surface/ground waters, hot spots, links between land use/activities and relevant contaminants, and effects on our native fauna in terrestrial, freshwater, estuarine, and marine environments.

If the presence of EOCs in the environment is associated with potential risk, there is a need to explore management options. To address a problem of this size, there will also be a need for public engagement, encompassing social and cultural aspects, to develop "up-the-pipe" solutions. Consumer education such as green labelling is also likely to play a significant role alongside any practical solutions derived from life cycle analysis. Industry will need to incorporate aspects of EOC minimisation in their best management practices.

The aims of this report are to:

- Provide a brief review of the relevant international and national literature on the fate, effects and risk characterisation of EOCs,
- Review international policy and regulations to manage the risks of EOCs,
- Provide recommendations to the HBRC to assist them in their assessment of the potential risk of emerging contaminants to their region and that can also be used to assist other regional councils,
- Identify key steps in the development of a national research strategy to address the issue of EOCs in New Zealand.

This report is not intended to be an ecological risk assessment of EOCs. The term "risk" is used in this context to describe potential risk of EOCs associated with their source, fate and potential effects.

1.3. Background to the Hawke's Bay region

The Hawke's Bay region is representative of other New Zealand provinces in terms of its level of urbanisation and range of agricultural and other land-based activities. The population of the region is approximately 148,000, with more than 60% living within the two cities of Napier City (population 55,500) and Hastings (population 38,500, (Statistics NZ 2006)). Smaller urban areas in the region include the towns of Havelock North (population 10,000), Wairoa (population 4,300), Waipukurau (population 4,000) and Waipawa (population 1,900).

The region governed by the Hawke's Bay Regional Council (HRBC) is 1.4 million hectares, of which 472,000 ha (33%) is in native vegetation, 717,000 ha (51%) is agricultural land, 158,000 ha (11%) is forestry, 29,000 ha (2%) is horticultural land (including vineyards), and 7600 ha (<1%) is urban (Ministry for the Environment 2002).

Drinking water for Napier and Hastings is sourced from the Heretaunga Plains artesian aquifer. Groundwater is also the source of the drinking water for many of the other rural towns and for individual houses and farms. The town of Wairoa takes water from the Waiau River for drinking water.

Wastewater from the cities of Napier and Hastings is only treated to primary level before being discharged into the coastal environment. There are planned upgrades to both the Hastings and Napier wastewater treatment plants to incorporate secondary treatment using biological trickling filter systems. In rural areas most households use on-site wastewater disposal (septic tanks) to treat and dispose of wastewater.

While the region does not have an extensive industrial base, there are several large industrial sites located within Hawke's Bay (Logan Stone 2002). These are predominantly associated with processing of primary production, such as forestry and wood processing, wool processing/scouring, dairy processing and meat processing (Logan Stone 2002). There is also some industry associated with the Napier Port (Logan Stone 2002).

Agriculture is a major land use in the Hawke's Bay region, with sheep farming the major livestock (>3,400,000 sheep at June 2010), followed by beef (450,000 beef cattle) and dairy (110,000 dairy cattle (Statistics NZ 2010)). Dairy cattle numbers have increased over the past 15 years and can be expected to increase further due to the current high prices for milk solids. Horticultural land use is primarily apple (5,400 ha), grapes (5,300 ha) and squash (4,200 ha)(Statistics NZ 2009), with a small proportion of the total horticultural land certified as organic horticulture (860 ha or 3%)(Statistics NZ 2002).

2. OVERVIEW OF THE PROBLEM

2.1. International situation concerning EOCs

Research into the sources, fate and effects of emerging contaminants around the world has taken an exponential upturn over the last 10 years. Figure 1 shows the number of research publications per year by each calendar year as determined from a search of the Web of Science® database (search term: "emerging contaminants"). This research has been largely driven by research groups in the United States of America and European Union.

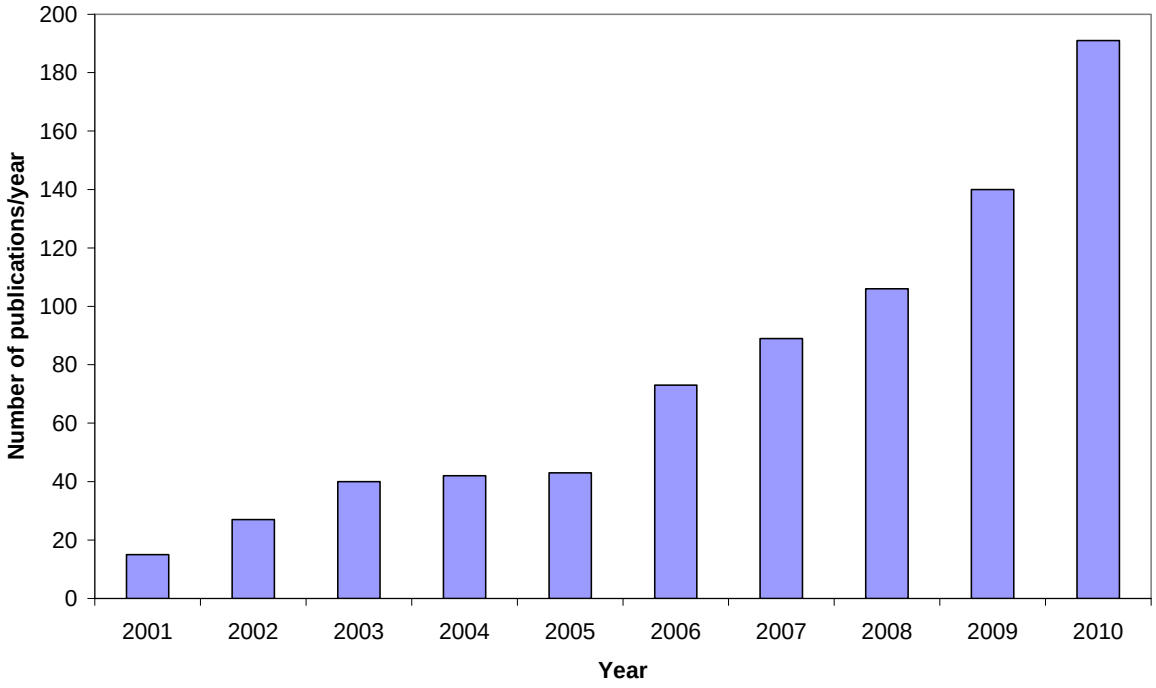


Figure 1. Number of research publications per year by each calendar year from a search of the Web of Science® database (search term "emerging contaminants").

2.2. Effects and ecotoxicology of EOCs

In general, the mechanisms of toxicity of the major families of toxic contaminants have been well studied and characterised but there is still a lack of knowledge to fully characterise the risk of most individual chemicals. For instance, ligands of the cytochrome p450 (CYPs) enzymes involved in the detoxification of a range of traditional environmental contaminants such as polycyclic aromatic hydrocarbons (PAHs), have been strongly correlated with the incidence of cancer (Wogan *et al.* 2004). However, there are still new mechanisms of toxicity that have been described for PAHs making it challenging to establish protective management approaches (Billiard *et al.* 2008).

In the case of EOCs, there is even more uncertainty and data gaps as to their potential biological effects. Of all the EOCs, EDCs have generated the most research over past decades due to their potential to disrupt endocrine functions in wildlife, invertebrates, fish, and human populations. There is a vast literature on this EDC research and, to date, it is still very challenging to suitably assess their risk (Sumpter & Johnson 2005; Hotchkiss *et al.* 2008). There are also new concerns about the potential effects of mixtures of EOCs (Hotchkiss *et al.* 2008). With the heavy legacy of the adverse environmental effects caused by antifouling agents, it has been well established that tributyltin (TBT) and triphenyltin (TPT) are potent inducers of imposex in molluscs (Nishikawa *et al.* 2004). Imposex, short for imposed sexual organs, is an irreversible syndrome resulting from a superimposition of male genital tracts, such as penis and vas deferens, on female reproductive organs (Nishikawa *et al.* 2004). Several hypotheses have been tested to explain the mechanism of toxicity leading to imposex including various interactions with reproductive processes. However, there is still much uncertainty over the exact mechanism(s) leading to this undesirable condition. There is limited information on the levels of environmental exposure to TBT and the resulting effects on humans but experiments on surrogate animal models suggest that TBT could lead to a wide range of effects involving different systems (Antizar-Ladislao 2008).

An extended review of the ecotoxicology of pharmaceuticals has highlighted the lack of information required to assess the environmental risk of these contaminants (Fent *et al.* 2006). A recent study investigated the multi-generational effects of combinations of pharmaceuticals including carbamazepine, diclofenac, 17α-ethinylestradiol and metoprolol in daphnia (Dietrich *et al.* 2010). The results demonstrated that multi-generational effects are likely and that it is important to use such an approach to characterise the risk of individual and mixtures of EOCs.

There is very limited information on the effects of EOCs on New Zealand native species. However a recent study assessed the acute effects of Tamiflu on a native copepod (Tong *et al.* 2011a).

2.3. Major sources of EOCs

As EOCs cover a wide variety of chemicals, with differing uses, there is a wide range of different sources of EOCs into the environment (US Geological Survey 2011). These include wastewater discharges, stormwater discharges, landfill leachate, incineration, agricultural wastes, solid waste disposal and atmospheric deposition. However, there are several sources that have been identified in literature as the major sources: municipal wastewater discharges and agricultural wastes (US Geological Survey 2011).

Municipal wastewater systems (or sewage) collect human wastes, grey water (from showers and washing) and industrial discharges (through trade waste permits), treat the waste and then discharge it, either to aquatic environments or on land. A wide variety of EOCs are collected with this waste and most are not completely removed in treatment systems Ternes

et al. 2004; Liu Z –H *et al.* 2009). Human urine and faeces contain pharmaceuticals and naturally occurring steroid hormones. Grey waste contains personal care products such as antimicrobials and perfumes found in soaps, shampoos and toothpastes. Industrial discharges can contain any number of different compounds depending on the activities undertaken, but may include industrial surfactants such as nonylphenol ethoxylates, flame retardants and plasticisers.

Agricultural wastes have similarly been identified as a major source of EOCs to receiving environments (Hanselman *et al.* 2003; Hansen *et al.* 2009). These include poultry litter, pig and cattle manures, and dairy shed effluents. As with human wastes, agricultural wastes contain naturally occurring steroid hormones and veterinary medicines such as antibiotics and pesticides (Hanselman *et al.* 2003; Hansen *et al.* 2009). As these wastes are typically applied to land, this can affect soil microorganisms, or contaminants may leach into groundwater, or runoff may transport contaminants into surface waters.

Horticultural land is also a potential source of some EOCs, specifically pesticides. Insecticides and herbicides can be transported from land into waterways through leaching or runoff. Pesticide residues have been found in streams and groundwater both internationally and in New Zealand (Gaw *et al.* 2008; US Geological Survey 2011).

2.4. Internationally reported concentrations of EOCs

Endocrine disrupting chemicals

Much of the early research on EOCs focused on compounds that specifically interfere with the normal functions of the endocrine system. These are termed endocrine disrupting chemicals (EDCs) and there have been numerous international studies measuring these compounds in river water, estuarine waters, sediments, wastewater treatment plant (WWTP) influents and effluents and agricultural effluents. There have been several comprehensive reviews of their occurrence in different environmental compartments (see (Gomes & Lester 2003; Liu *et al.* 2009) and some of the relevant data is presented in Table 1 (environmental waters) and Table 2 (WWTP influent and effluent)).

Table 1. Examples of EDCs and their concentrations measured in the influent and effluent of international wastewater treatment plants (WWTPs) (Gomes & Lester 2003).

Compound	Water concentration (ng/L)	Reference
Estrone	<DL [a] - 56	Gomes & Lester (2003)
17β-estradiol	<DL – 5.5	Gomes & Lester (2003)
EE2	<DL-15	Gomes & Lester (2003)
Nonylphenol	<DL – 180,000	Gomes & Lester (2003)
Octylphenol	<DL – 84	Gomes & Lester (2003)

[a] <DL= Concentration was below detection limit of analytical method.

Table 2. Examples of EDCs measured internationally in WWTP influents and effluents.

Compound	Influent (ng/L)	Effluent (ng/L)	Reference
Estrone	4 – 670	<0.3 – 96	Liu *et al.* (2009)
17β-estradiol	2.4 – 162	<DL [a] – 30	Liu *et al.* (2009)
EE2	ND – 14	<0.3 - 5	Liu *et al.* (2009)
Testosterone	ND – 143	<DL– 4.9	Liu *et al.* (2009)
Androstenedione	21-164	<DL-5.3	Liu *et al.* (2009)
Epiandrosterone	626-1261	<DL	Chang *et al.* (2008)
Androsterone	1102-1441	<DL	Chang *et al.* (2008)
Progesterone	ND – 14	<DL-0.37	Liu *et al.* (2009)
17α-hydroxyprogesterone	2.1	0.25	Chang *et al.* (2008)
17α,20β-dihydroxy4-pregnene-3-one	1.7-2.2	1.0-1.4	Chang *et al.* (2008)
6α-methyl-hydroxyprogesterone		0.24-1.6	Chang *et al.* (2008)
Medroxyprogesterone acetate	0.21-2.42	0.03-0.42	Chang *et al.* (2008)
Genistein	9 – 384	2–22	Liu *et al.* (2009)
Bisphenol A	250 – 5600	6–4090	Liu *et al.* (2009)
Nonylphenol	240 – 27,000	300–2200	Liu *et al.* (2009)
Octylphenol	ND – 13,000	<DL–1300	Liu *et al.* (2009)
Diethylphthalate	<1000 – 74,000	<DL-4000	Marttinen *et al.* (2003)
Bis(2-ethylhexyl) phthalate (DEHP)	28,000 – 122,000	2000–8000	Barnabe *et al.* (2008); Marttinen *et al.* (2003)
Benzyl butyl phthalate	<1000 – 5000	<DL	Marttinen *et al.* (2003)
Triclosan	280-9000	23-1100	Gatidou *et al.* (2007); Ying & Kookana (2007)
Polycyclic musk HHCB	1300-3000	490-1300	Zhou *et al.* (2009)
Polycyclic musk AHTN	110-290	47-89	Zhou *et al.* (2009)

[a] <DL= Concentration was below detection limit of analytical method.

Pharmaceuticals and personal care products (PPCPs)

PPCPs are a source of contaminants that are increasing dramatically especially throughout the western world, both in the amounts used and the numbers of new products. Research has shown that PPCPs are often not completely removed by wastewater treatment plant (WWTP) processes (e.g., Ternes *et al.* 2004). With continual and increasing input, this situation can create a source of these contaminants to the environment, especially if solid WWTP biosolids are disposed to a landfill and the effluent into the aquatic environment.

A good example of the levels of a range of PPCPs that have been detected in sewage, is provided by a 2009 US EPA study report of measurements made over the 2005 – 2008 period of the influent and effluent sampled from nine publicly owned sewage treatment plants (see Table 3) (US EPA 2009). There is clearly a wide variation in the ranges of concentrations

reported for these compounds and this was attributed to many factors including the time of day and season when the sampling was undertaken, the ongoing development and refinement of the analytical techniques during the 4-year course of the study, the different treatment processes in each plant, variations in the lower concentration limit of detection (DL) reported by different analytical companies analysing samples at different times, and the different types of domestic and industrial sources of the sewage influent. The report also cautions using any measurable decrease between influent and effluent levels of a compound as an indication of the removal efficiency for that compound in the sewage plants. However, there is clearly a broad indication of a general decrease in the detectable levels of most compounds with sewage treatment.

Table 3. US EPA 2009 determination of levels of selected pharmaceuticals and personal care products in the influent and effluent from nine publicly owned sewerage treatment plants in the United States of America.

Pharmaceutical / Personal Care Product	**Type**	**Form Prescribed in New Zealand**	**Concentration (ng/L)**	
			Influent	Effluent
chlorotetracycline	antibiotic	`	434	<DL
doxycycline	antibiotic	Doxine	2,970 - 176	<DL
tetracycline	antibiotic	-	490 - 231	568
sulfamerazine	antibiotic	-	15.3 – 12.5	<DL
sulfadiazine	antibiotic	-	31.1	<DL
sulfamethoxazole	antibiotic	Trisul	2,625 – 1,500	1,490 – 9.54
sulfathiazole	antibiotic	-	212	<DL
ciprofloxacin	antibiotic	Ciproxin	1,530 - 591	161 – 36.7
clarithromycin	antibiotic	Klamycin	748 - 292	89.7 – 23.9
erythromycin	antibiotic	E-mycin	586 - 119	418 – 91.8
ofloxacin	antibiotic	-	3,240 - 147	162
lincomycin	antibiotic	Lincomysin	19.1	<DL
acetaminophen	analgesic	Paracetamol	340,00-79,300	<DL
cotinine	tabacco metabolite	-	2,980 - 535	<DL
fluoxetine	antidepressant	Fluox	58.7 – 24.7	24.7 – 14.7
carbamazepine	antiepileptic	Tegratol	163	598 - 487
gemfibrozil	lipid regulator	Lopid	6,630 - 539	259 – 18.9
ibuprofen	anti-inflammatory	Nurofen	20,500 – 7,360	<DL
naproxen	anti-inflammatory	Naprogesic	18,800 – 11,300	75.3
triclocarban	disinfectant	Tricloram	13,700 - 187	154 – 40.6
triclosan	in toothpaste	Toothpaste	4,110 - 996	<DL
albuterol	anti-asthmatic	Salbutamol	75.6 – 22.5	<DL
cimetidine	anti-ulcer	Apocimetidine	11,700 – 73.1	<DL
metformin	anti-diabetic	Metomin	248,000 – 11,100	5,420 – 1,250
ranitidine	anti-ulcer	Zantac	16,800 - 496	7.22
progesterone	hormone	Naturally-occurring	118	< DL
testosterone	hormone	Naturally-occurring	2,650 - 831	< DL

<DL = less than limit of detection

Veterinary medicines

A significant quantity of pharmaceuticals are also used in agriculture and these include antibiotics, parasiticides and in some cases hormone growth promotants. Parasiticides include endo- and ectoparasiticides such as ivermectin and abamectin. Residues arising from this use have been detected in overseas studies of pasture soils and in some cases, nearby surface or groundwater (Boxall *et al.* 2005; Kemper 2008; Khan *et al.* 2008). The presence of antibiotic and antimicrobial residues in pasture is of particular concern as this may lead to antibiotic resistant bacteria. Residues have also been associated with decreased decomposition rates for other contaminants, due to diminished microbial communities (Boxall *et al.* 2005; Kemper 2008; Snow *et al.* 2008).

Perfluorinated surfactants

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are EOCs used as polymerisation agents during cookware, carpet and clothing manufacture and deserve specific mention. They are ubiquitous, bio-persistent and bioaccumulative contaminants that have possible toxic effects such as endocrine disruption, thyroid and liver carcinogenicity and developmental alteration (Negri *et al.* 2008). Detection of these fluorinated contaminants is complicated by their ubiquitous nature and the need for their analysis in specialised laboratories equipped with Teflon-free instrumentation.

2.4.1. International research networks

Several international networks have been established around the world specifically to address the impending problems of EOCs. The networks all acknowledge that a multi-disciplinary approach is required to adequately assess how EOCs might affect the state of the environment. Recently, the establishment of a National (U.S.) Research Programme to Elucidate the Potential Risks to Human Health and the Environment Posed by EOCs was suggested (Novak *et al.* 2011a).

United States Geological Survey (USGS)

The USGS Toxic Substances Hydrology Program has a research project to evaluate the threat to environmental and human health by EOCs (US Geological Survey 2011), with the aims to:

1. Develop analytical methods to measure chemicals and microorganisms or their genes in a variety of matrices (*e.g.* water, sediment, waste) down to trace levels,
2. Determine the environmental occurrence of these potential contaminants,
3. Characterise the myriad of sources and source pathways that determine contaminant release to the environment,
4. Define and quantify processes that determine their transport and fate through the environment,
5. Identify potential ecological effects from exposure to these chemicals or microorganisms.

United States Environmental Protection Agency (US EPA)

Risk associated with previously unknown, unrecognised, unanticipated, or unsuspected chemical pollutants in the environment have long been a major concern of environmental scientists. The importance of identifying such emerging risks is reflected in one of the top five goals of the Strategic Plan for the US EPA's Office of Research and Development (US EPA 2001).

US EPA PPCP research is focussing on seven core topics:

- Sources
- Introduction to Environment: Fate and Transport
- Exposure Pathway: Human
- Exposure Pathway: Ecological
- Monitoring and Detection Tools
- Assessment of Potential Ecological Effects
- Assessment of Potential Human Health Effects

Numerous studies demonstrate PPCPs are entering and persisting in water bodies of the United States of America and further research suggests that certain drugs may cause ecological harm. The US EPA is committed to investigating this topic and developing strategies to help protect the health of both the environment and the public. To date, scientists have found no evidence of adverse human health effects from PPCPs in the environment.

A primary goal of the US EPA's Office of Research and Development is to identify and foster investigation of potential environmental issues/concerns before they become critical ecological or human health problems. Pollution prevention (*e.g.* source elimination or minimisation) is preferable to remediation or restoration to minimise both public cost and human/ecological exposure.

Consortium for Research and Education on Emerging Contaminants (CREEC)

CREEC (CREEC 2011) state they are a "non-profit organisation comprised of world-class scientists and stakeholders with a shared interest in the source, fate, and physiological effects of contaminants of emerging concern. This consortium is made up from not only scientists at the local, university, state, and federal level, but also has active participation from regulators, policy makers, public health workers, drinking water providers, wastewater treatment providers, and concerned citizens. CREEC has access to broad expertise in hydrology, aquatic biology, environmental geochemistry, analytical chemistry, wastewater- and drinking-water treatment technology, wildlife toxicology, environmental policy and regulation, public education and outreach, and water system engineering."

European Union

The Norman Network was established in 2005 with European Union funding and is now "a permanent self-sustaining network, of reference laboratories, research centres and related organisations for the monitoring and biomonitoring of emerging environmental substances" (Norman Network 2011).

Japan

The United Kingdom - Japan joint research on endocrine disruptors (UK-J 2011) involves eight scientists from the United Kingdom and 14 from Japan and has a mission statement "To build strong and productive collaborations and facilitate the exchange of information relating to research into endocrine disruption between Japan and the United Kingdom".

While the initial collaboration was based on EDCs the core projects include assessing the fate of other EOCs such as some pharmaceuticals and nanoparticles as well as advancing bioassay test methods for all kinds of EOCs.

Australia

The Australasian Society for Ecotoxicology (now SETAC-AU) has a Micropollutants in Water Special Interest Group (MIW SIG) in acknowledgement that there will be significant future pressures on freshwater. With increasing needs for water recycling, it will be necessary to characterise the effects of micropollutants.

One outcome of this Australasian group has been the "Black Mountain Declaration" on Endocrine Disrupting Chemicals in Australian waters (Blockwell *et al.* 2007). This consensus statement, signed by 32 participants of the November 2007 CSIRO-Canberra workshop, summarises the environmental and human health implications of EDCs in Australian waters and outlines future research priorities (Land & Water Australia 2008).

United Kingdom/Australia/New Zealand

A collaboration between the United Kingdom, Australia and New Zealand has been set up under the auspices of MIW SIG (ASE 2009). This involves increased dialogue between these countries with scientists from the United Kingdom visiting both Australia and New Zealand to share research findings and discuss future priorities. Currently New Zealand is only an observer in this partnership, but the scheme offers the opportunity to develop a more active collaboration among research groups in the three countries.

2.5. New Zealand situation concerning EOCs

In comparison with the situation in many overseas countries (as reviewed above), little is known about the nature and levels of EOCs in much of the New Zealand environment. To a large extent this situation has arisen from the historical image of New Zealand being 'clean and green' and the lack of appreciation that many of the sources of EOCs which have been identified in these overseas studies, are in fact also present in New Zealand such as:

- **Rural**: agricultural (especially dairy activities), horticultural (wineries, fruit and vegetables), including the use of veterinary medicines, septic tank overflows
- **Urban**: stormwater, raw and treated sewage from households and hospitals
- **Industrial**: waste water arising from specific processes *e.g.* wool scouring activities

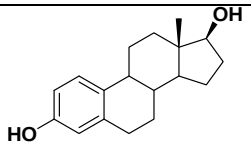
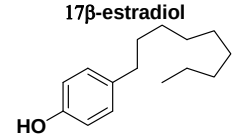
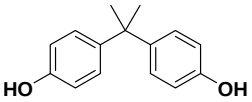
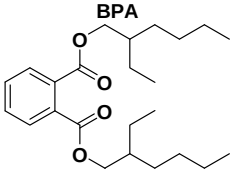
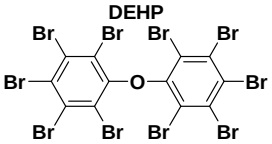
The following sections review at least some of the areas of EOC research that have been undertaken to date in New Zealand.

2.5.1. Endocrine Disrupting Chemicals (EDCs)

Scoping Report

A report by Sarmah *et al.* (2005) for Environment Waikato reviewed the international literature on EDCs and strove to set a New Zealand perspective including some New Zealand literature at that time on biosolids and wastewater treatment plant WWTP effluents. The report was concerned primarily with EDCs and scored each class from high to low concern using criteria such as source, potency, environmental concentrations, persistency, mobility, bioaccumulative potential and removal during treatment. A representative of each class of EDC addressed is presented in Table 4, ranked by the total score for priority as EDCs, as described by Sarmah *et al.* (2005).

Table 4. EDCs of highest priority to New Zealand (Sarmah *et al.* 2005).

Class of EDC	Representative	EDC priority score[a]
Steroid Estrogens	 17β-estradiol	15
Alkylphenol ethoxylates and metabolites	 4-nonylphenol	14
Bisphenol A	 BPA	10
Phthalates	 DEHP	10
Brominated Flame Retardants	 BDE-209	9-11
Heavy Metals	Cd, As, Pb, Hg	7

[a] Sarmah *et al.* 2005

Steroid estrogens from dairy/municipal waste

Following this 2005 scoping study, there was a further survey undertaken to assess the occurrence and concentrations of natural estrogens in animal wastes and sewage treatment plant effluents in the Waikato region (Sarmah *et al.* 2006). The survey showed high levels of natural estrogens from dairy effluent (up to 1360 ng/L and 3123 ng/L for estradiol (both α and β epimers) and estrone, respectively. Much lower concentrations of these estrogens were measured in pig and goat effluent. The synthetic estrogen 17α-ethynylestradiol was detected in trace amounts in effluent samples collected from one of three municipal sewage treatment plants using primary and secondary treatment.

Gadd *et al.* (2010b) undertook a much larger study of dairy farms (18 farms) and analysed steroid estrogens and their conjugates, as well as estrogenic activity using the E-Screen bioassay. This study highlighted the importance of measuring conjugates and 17α-estradiol (the dominant form of estrogen excreted by cattle). Concentrations of steroid estrogens were elevated in dairy shed effluents with potential to cause environmental effects if discharged directly to the aquatic environment with minimal dilution. The study also suggested that

when disposed of on land, there is a possibility for water-soluble conjugated steroids to leach through soils to the aquatic environment and pose a problem if hydrolysed at a later time.

Gadd *et al.* (2010a) also assessed the reduction of estrogens from dairy effluent using the two pond system and advanced pond system treatment options. The results suggested a 50-100% decrease in total steroid concentrations and 62-100% decrease in estrogenic activity. However it was noted that estrogenic activity of the effluent at times exceeded suggested guideline values for protection of freshwater fish (Young *et al.* 2002) and therefore dilution is required.

Biological methods were developed in New Zealand to determine estrogenic and androgenic activity from sewage treatment plant effluents (Leusch *et al.* 2006b). These methods were applied to raw sewage from Australia (Leusch *et al.* 2006b) and both raw and treated sewage from South Queensland and Canterbury, with results suggesting that the particular treatment processes were efficient in removing most estrogenic and androgenic activity (Leusch *et al.* 2006a).

The findings from two New Zealand laboratory studies into the sorption and degradation of estrogens and their conjugates suggested that soil type was important in determining the fate of these chemicals. Sarmah *et al.* (2008) suggested that dissolved organic carbon facilitated transport of these hormones and needs to be considered when assessing the leaching risk for these compounds in the environment. Microcosm laboratory experiments were conducted in three pasture soils from New Zealand to study the aerobic degradation and metabolite formation kinetics of estrogen sulfate conjugates, which are excreted by livestock in urine (Scherr *et al.* 2009). Again it was suggested that soil type was important as degradation was shown to be different between the three soils.

Field and modelling studies have been undertaken to characterise the transport of estrogens through representative soils in New Zealand following land application of animal waste. Results confirmed that estrogens were transported mainly via preferential/macropore flow and also via an enhanced transport, probably mediated by colloids (Steiner *et al.* 2010).

2.5.2. Urban contaminants

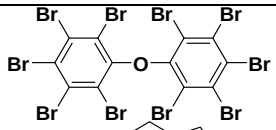
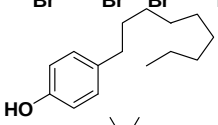
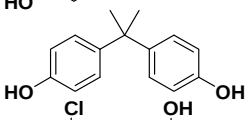
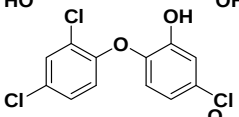
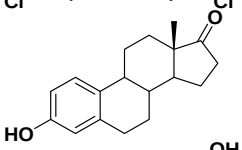
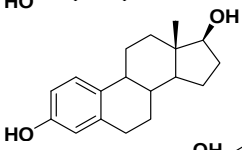
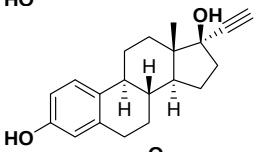
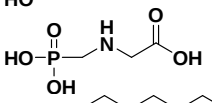
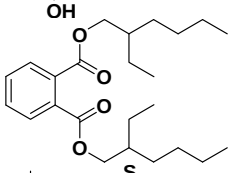
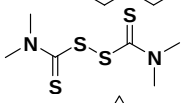
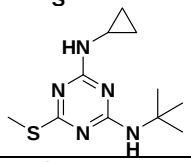
With prior research into emerging contaminants within New Zealand based largely around EDCs and agricultural practices, a knowledge gap concerning the nature and levels of detectable EOCs in the urban environment has been partially addressed by two projects in the Auckland region. A comprehensive literature review by Ahrens (2008) was carried out in a similar manner to that of Sarmah *et al.* (2005), classing EOCs into hazard risk categories using toxicity, persistence and bioaccumulation properties. The review included EDCs as well as chemicals that are not currently regulated such as PPCPs, and some pesticides and antifouling agents.

The report suggested that urban environments with the greatest likelihood of receiving emerging contaminants include:

- Marinas (antifouling agents),
- Nearshore settling zones receiving agricultural and residential land run-off containing pesticides, hormones and antibiotics,
- Water bodies receiving water from catchments with decommissioned landfill sites producing leachates containing solvents, plasticisers, pharmaceuticals, pesticides and petroleum products,
- Urban streams downstream of combined wastewater and stormwater overflows which would receive wastewater containing EDCs such as hormones, surfactants, pesticides and plastic additives.

A follow-up field analysis of emerging contaminants in the aquatic receiving environment around Auckland was undertaken (Stewart *et al.* 2009), which included sites that covered a range of land uses receiving various inputs such as sewage, and material from landfill marina, industrial and agricultural activities. Analysis was undertaken of sediment samples collected from these sites for a subset of EOCs which were considered from the review of Ahrens (2008) to be likely to be of high use and/or relevance, and for which commercial analyses could be undertaken within New Zealand or Australia. This study highlighted hotspots of contamination around the region and suggested that ranges of concentrations in sediments were not dissimilar to those observed in other parts of the world for these particular compounds (see Table5). This dataset was subsequently expanded to include pharmaceuticals (see next section).

Table 5. Concentrations of EOCs in Auckland estuarine sediments in comparison with overseas values.

Compound	Class	Chemical Structure	Reported environmental concentrations (ng/g)	
			Auckland	World-wide[a]
BDE-209	major PBDE flame retardant		0.5 - 570	0.03 - 1650
Nonylphenol (multiple isomers)	Alkylphenol breakdown product		100 - 36,000	<0.1 - 21,000
Bisphenol A	plastic additive		<50 - 160	0.6 - 191
Triclosan	cosmetic disinfectant		<100	0.27 - 130.7
Estrone	estradiol breakdown product		<0.58 - 2.8	<0.05 - 3.5
17β-estradiol	natural estrogen		<0.43 - 1.2	0.22 - 2.48[b]
17α-ethynylestradiol	synthetic estrogen		<1.8	<0.05 - 41
Glyphosate	herbicide		<40 - 1,000	No data[d]
DEHP	plasticiser		<0.6 - 12	0.04 - 24
Dithiocarbamates[c]	fungicide		20 - 110	No value[c]
Irgarol	antifouling co-biocide		<10	<0.016 - 690

[a] ranges are indicative (see Stewart *et al.* (2009)); [b] both epimers; [c] the method used for detection of dithiocarbamates does not differentiate between individual compounds, thiram shown; [d] direct comparisons could not be established for glyphosate estuarine sediment levels.

Organonitrogen and phosphorous pesticides (suite of 90) were all below detection limits (10 to 300 µg/L). Previously reported environmental sediment levels of most pesticides (see Stewart *et al.* 2009) are in the µg/L range, but vary widely.

2.5.3. Pharmaceuticals and personal care products (PPCPs)

Many of the PPCP compounds found in wastewaters in the United States of America (Table 3) are not commonly prescribed (if at all) in New Zealand and hence are unlikely to be detected in wastewater influent from urban sources. However at least large quantities of acetaminophen (paracetomol) are routinely prescribed or purchased over-the–counter in New Zealand and so the levels reported in this table for at least this compound might be a guide to what would be measured in the New Zealand municipal wastewater. Combined with the 2010 Pharmac list of the other most commonly prescribed pharmaceuticals in New Zealand (Pharmac 2010) (Table 6) some of which were also analysed in the US EPA study, these results do provide some indication of what compounds could be analysed for in the influent and effluent of typical New Zealand wastewater of urban origin and hence in samples collected from the Hawke's Bay wastewater treatment plants.

Table 6. Ranking by number of prescriptions of the top 20 pharmaceuticals used in New Zealand in 2010 (Pharmac 2010).

Rank	Common Chemical name	Treatment Condition
1	Paracetamol	Analgesic / Antipyretic
2	Aspirin	Analgesic / Anti-platelet
3	Simvastatin	Cholesterol and cardiovascular control
4	Omeprazole	Dyspepsia, peptic ulcer disease
5	Amoxycillin	Broad spectrum antibiotic
6	Metoprolol succinate	β- blocker for blood pressure control
7	Amoxycillin clauvulanate	Broad spectrum antibiotic
8	Salbutamol	Asthma (inhaled)
9	Diclofenac sodium	Analgesic/ Anti-inflammatory
10	Cilazapril	ACE inhibitor
11	Zopiclone	Hypnotic
12	Ibuprofen	Analgesic
13	Prednisone	Steroid
14	Flucloxacillin	Antibiotic
15	Quinapril	ACE inhibitor
16	Bendrofluazide	Diuretic
17	Feldopine	Calcium channel blocker
18	Alendronate sodium	Osteoporosis
19	Metformin	Type II diabetes
20	Fluticasone	Asthma (inhaled)

Some New Zealand research has been undertaken into the presence of PPCPs in wastewaters and environmental matrices. A PhD study at the University of Canterbury (Gielen 2007) assessed 12 PhACs in sewage effluent, biosolids, soils and pore water. Removal efficiencies of three treatment options; activated sludge, composting and land application were assessed. PhACs were detected in all environmental compartments but at the concentrations detected were not acutely toxic to soil organisms or in lettuce seed germination tests. Studies showed

that PhACs had both short- and long-term effect on soil microbial communities. Short-term microbial stresses were replaced by longer term (12 years) adaptation to three of these PhACs, namely paracetamol (acetaminophen), tetracycline and aspirin.

Archived sediment samples from Auckland (Stewart *et al.* 2009) and biosolids from five WWTPs around New Zealand were analysed for a suite of 46 Phacs (sediments) and 68 Phacs (biosolids) in a collaboration between the National Institute of Water & Atmospheric Research (NIWA) and Dr Mira Petrović in Barcelona, Spain. The biosolids data were highly variable but showed PhACs concentrations of over 3000 ng/g in some instances, from the larger WWTP and up to 780 ng/g from a WWTP of with similar catchment area to Hawke's Bay. The sediment data showed that many PhACs were entering the marine receiving environment around Auckland, with concentrations up to 10.8 ng/g observed (Stewart *et al.* unpublished).

Researchers from the School of Pharmacy and Chemistry Departments at Otago University are actively involved in research into disposal practices for PhACs both in New Zealand (Braund *et al.* 2009; Peake & Braund 2009) and around the world (Tong *et al.* 2011b). The analytical procedures required to measure levels of commonly-prescribed PhACs in New Zealand according to Pharmac records are being developed and will be applied to typical urban New Zealand sewage before and after different levels of wastewater treatment. Research is also being undertaken into advanced oxidation processes (AOPs) involving the generation of hydroxyl radicals and their degradation of specific PhACs. For example, the rate and chemical mechanism of UV-induced degradation of Tamiflu in aqueous solution has been investigated (Tong *et al.* 2011a).

Researchers at Plant & Food Research have developed methods to analyse a wide range of emerging contaminants including polycyclic- and nitro- musks, alkylphosphate flame retardants, phenolic antimicrobials including parabens, nonylphenols and octylphenol and insect repellents. A current PhD project will measure these contaminants in municipal wastewater discharges and assess their presence in marine sediments (Strong, pers. comm.). This research is being undertaken in the Hawke's Bay region, focussing on the Hastings District Council wastewater discharge and its coastal marine receiving environment (Strong, pers. comm.).

2.5.4. Pesticides

As stated in Section 2.5.2, the analysis of 90 organonitrogen and phosphorous (ONP) pesticides in urban sediments around Auckland indicated that the environmental concentrations of all these compounds were below their respective detection limits.

The fifth national survey of pesticides in groundwater in New Zealand was undertaken in 2006 (Gaw *et al.* 2008). Most pesticides were detected at concentrations less than 6% of the minimum acceptable value (MAV) as specified in the Drinking-water Standards for New Zealand 2005 (Ministry of Health 2005) and none were detected in any groundwater samples

collected from the Hawke's Bay region. Many of the pesticides will concentrate in sediments and there is a paucity of New Zealand data on pesticides in sediments from agricultural catchments. In addition, most monitoring programmes only look for the active ingredient and not the primary and secondary metabolites which often provide the only evidence of the use of pesticides.

2.5.5. Veterinary medicines

Veterinary medicines are widely used in New Zealand agriculture (Table 7), including those identified overseas as being of potential concern to soil microorganisms. Soil scientists at Landcare Research are currently undertaking research into the occurrence and fate of veterinary antibiotics in New Zealand but any findings are yet to be published.

Table 7. Total antibiotic sales in 2008-09 by antibiotic family and animal group (kg/year) (Ministry of Agriculture and Forestry 2010).

Antibiotic family	Cattle	Pigs/ Poultry	Companion	Multiple	Other	Total
Aminoglycosides	171.8	62.7	6.8	995.6	0.0	1,217
Bacitran		18,818.6	0.7	0.4		21,733
Cephalosporins	1,019.2		353.7	154.7		1,528
Clavulanic Acid	20.8		163.9	27.9		213
Fluoroquinolones	0.1		19.1	22.0		41
Fusidic Acid			1.7			2
Macrolides/ Lincosamides	53.3	1,093.2	28.9	4,156.6		5,439
Nitrofurans		16.8		0.5	1.5	6
Nitro-imidazoles		95.4	11.0		1.0	49
Novobiocin	0.6					1
Other		326.3	0.2	9.7		336
Penicillins	7,115.9	65.6	470.9	7,863.1	111.6	15,552
Sulphonamides/ Trimethoprim	150.5	7.0	0.0	2,680.4	2,059.7	5,187
Tetracyclines	28.7	440.0	25.2	3,622.1	2.2	4,492
Virginiamycin		0.0			12.4	14
Total	**8,560.8**	**21,070.5**	**1,082.1**	**19,533.0**	**2,189.1**	**55,809**

2.6. Legislation

2.6.1. Existing legislation for controlling levels of ECs

As EOCs are not commonly monitored in the environment, there has been no legislation to limit their levels in environmental systems. However, the recent research emphasis and public interest has resulted in regulation of some individual compounds. For example, nonylphenol and nonylphenol ethoxylates, previously used as surfactants in many products including industrial detergents, are now banned from such use in the United Kingdom and in Europe (Directive 76/769/EEC). Bisphenol A, a plasticiser with estrogenic properties, is no longer permitted for use in baby bottles in many European countries and Canada. Despite the international regulatory action on these chemicals, there has been no regulation of them in New Zealand and their use continues in this country.

For veterinary medicines there was previously no recognition of animal excretion as a source of pharmaceuticals to the environment and no environmental assessment was required for veterinary medicines in the European Union. A 2004 European Union parliament directive now requires environmental risk assessment of all new veterinary medicines to establish their likelihood for persistence, fate and adverse effects in the environment once excreted by animals. However such environmental risk assessments are **not** required for approval of veterinary medicines in New Zealand.

Internationally, there are also no drinking water standards for EOCs. In the United States of America, there is some movement towards regulation through inclusion of some EDCs in the "Contaminant Candidate List 3". This is a list of contaminants that are not currently regulated in drinking water, but are known to, or anticipated to occur in drinking water sources and therefore may need regulation under the Safe Drinking Water Act (USEPA 2009). EOCs on the list include estrogenic steroid hormones, new generation pesticides and chemicals used as flame retardants and in fire fighting.

In New Zealand the most recent standards for drinking water released in 2005 by the Ministry of Health (Ministry of Health 2005) specify maximum acceptable levels (MAVs) of a range of pesticides, cyanotoxins, trihalomethanes (often arising from chlorination of natural waters) in New Zealand drinking water (see Appendix 1). However there are no MAVs given for EOCs such as PPCPs which could potentially be also present in sources of drinking water within New Zealand.

Water quality guidelines are used for many chemical contaminants to minimise the risks of adverse effects on biota. These guidelines are developed from laboratory studies relating chemical concentration to toxicity (usually acute and/or chronic), in a range of species, covering a number of different phyla (usually including algae, invertebrates and vertebrates). Guidelines are available for metals, common pesticides and priority pollutants (ANZECC 2000; USEPA 2006; CCME 2007)), however a large dataset is usually required to develop these guidelines and this is not yet available for most EOCs. There have been suggestions for water quality guidelines based on predicted no effect concentrations (PNECs, Table 8

(Young *et al.* 2002; Caldwell *et al.* 2008)), but these proposed guidelines have no regulatory standing. It should be noted that if a guideline were to be derived or adopted by ANZECC (2000), it would also have no regulatory standing in New Zealand.

Table 8. Proposed PNECs for steroid estrogens.

Compound	Proposed PNECs for freshwater and saltwater (ng/L)	
Reference	Young *et al.* (2002)	Caldwell *et al.* (2008)
17α-ethynylestradiol (EE2)	0.1 [a]	0.35
17β-estradiol	1 [b]	-
Estrone	3-5 [c]	-

[a]. Tentative value for saltwater; [b]. Tentative value for freshwater and saltwater; [c]. Provisional value, based on potency of estrone 3-5 times lower than 17β-estradiol.

2.6.2. Possible future legislation in New Zealand for controlling concentrations of EOCs

The Strategic Approach to International Chemicals Management (SAICM) is a policy framework to promote chemical safety around the world endorsed by the United Nations Environment Programme (UNEP) and the World Health Organization (WHO). The aim of this policy is to achieve the sound management of chemicals throughout their life cycle so that, by 2020, chemicals are produced and used in ways that minimise significant adverse impacts on human health and the environment. New Zealand adopted the SAICM at the 2006 Dubai Declaration when it was established (UNEP & WHO 2006). Although it is not legally binding, SAICM could provide an umbrella to address EOC issues. However, the development of any regional or national legislation specifying maximum environmental levels for a range of EOCs in New Zealand environmental systems is still some way off. This is because even a list of EOCs that should be routinely monitored let alone any specification of an appropriate maximum level in a given environmental system, has not yet been established in any overseas country. As has often happened in the past, the appropriate national authorities in New Zealand such as the Ministry of Health and Ministry for the Environment will rely on the results of overseas research on EOCs such as that being undertaken by the United States Environmental Protection Agency (US EPA) and United States Geological Survey (USGS). Until those organisations report the relevant research data and enact appropriate legislation to control the levels of EOCs in the environmental systems in their own countries, New Zealand is unlikely to develop any of its own.

However the RMA (1990) does have provision for at least monitoring some EOCs in the New Zealand environment. For example, aspects of EOCs have been included as part of resource consent conditions for two recently approved discharge consents for municipal wastewater.

Environment Southland in renewing the consent for the Milford Sound Development Authority to discharge treated wastewater into Milford Sound (RMA Consent M186-005) in October 2008, specified (Condition 9):
"By 1 November 2018, the consent holder shall provide a report to the Council's Compliance Manager on the potential effects on the receiving environment at Deepwater Basin, Milford Sound of anthropogenic chemicals such as endocrine disruptors, pharmaceuticals and personal care products likely to be present in the effluent from the Milford Sound wastewater treatment plant. The report shall include an assessment of whether there is the feasibility, including financial feasibility, to measure such chemicals in the treated effluent and/or receiving waters, and if so, what concentrations are considered to have an adverse effect and whether the chemicals are having an adverse effect on the receiving environment."

Although not specifying any particular class of EOCs that need to be assessed, this requirement did at least formally signal that this was an emerging issue for which much more information is likely to available by 2018. At that time, Environment Southland can review the present consent conditions to require both additional monitoring and/or additional waste water treatment.

One of the conditions of the Hamilton City Council's consent for discharge of treated wastewater into the Waikato River, specifies:
"Additional Investigations: Viral and Organic Chemicals
14.The consent holder shall in 2012 and thereafter on a five yearly basis undertake an investigation into the likelihood of viral pathogens and organic chemicals (including but not limited to endocrine disrupting chemicals and steroidal hormones) entering the river water from the discharge. An analysis of the likely removal of viral pathogens and substances within each stage of the treatment system (including bypasses) shall be made and based on actual results. The results of this investigation shall be compared with any relevant literature on the subject on removal of viral pathogens and organic chemicals within treated wastewater and their environmental fate/public health risk. A copy of the investigation and comparison shall be supplied to the Waikato Regional Council by 1 December each year the investigation is required to be undertaken."

Inclusion of similar consent conditions could also be considered for inclusion in any future resource consents granted by other regional councils in New Zealand including the Hawke's Bay Regional Council.

2.7. Research needed to assess the risks of EOCs within New Zealand

Because of the high level of uncertainty, there is a growing perception of risk associated with the presence of EOCs in the environment and the potential adverse effects on wildlife and humans. There is not sufficient scientific information on EOCs exposure, effects, and interactions to fully assess their risks (Novak *et al.* 2011a). For the HBRC and New Zealand, the first step is to remain up-to-date with research and policy activities of the main international groups. Because of limited resources, it is important to focus on the most efficient steps to address the knowledge gaps about the fate and potential effects of EOCs on our unique ecosystems in New Zealand to enable policy-makers to rank the real or potential risks arising from EOCs relative to other stressors.

We recommend a tiered approach to assess the risk of EOCs to the New Zealand environment. The research questions needing to be addressed are:

- What is the fate of EOCs in the receiving environment?

Combine available international and national data with land-use types in Hawke's Bay to identify the EOCs most likely to be present. The approach could involve the development of a ranking of analytes to focus the resources as recently proposed (Kumar & Xagoraraki 2010, Appendix 2). HBRC should characterise EOCs from the main sources and assess seasonal variations (*e.g.* WWTP effluent, industrial canning effluent, horticulture (especially wineries), urban and agricultural runoffs). When available, carry out effects-based assays (*e.g.* particularly for EDCs) to complement analytical chemistry approaches. Preliminary New Zealand results suggest that EOCs are likely to be found in surface waters and so undertaking a survey of "hot spot" areas would be advisable to determine whether there is a requirement for biological testing.

- What are the effects of EOCs on our unique ecosystems?

If EOCs are found in the environment at significant levels, it becomes a priority to determine whether they are having adverse effects on our unique biota, particularly on taonga species as it could potentially have human health implications.

- What are the cumulative impacts (complex mixtures/multiple stressors) of EOCs on the receiving environments and the long-term multi-generational effects?

As EOCs will be present as mixtures rather than individual compounds, there will be a need to assess the potential interactive effects with other contaminants and non-chemical stressors. In the larger context there will be a need to use an evolutionary toxicology approach to assess the effects of EOCs on genetic structure of exposed populations.

- What are the social and cultural concerns/values around EOCs?

This is a societal issue and there is a need to involve the general public and iwi in the debate to develop solutions.

3. IMPLICATIONS FOR FUTURE RESEARCH INTO EOCs IN NEW ZEALAND

Research conducted to date in New Zealand would indicate that at least some EOCs are finding their way into parts of our environment. There is also a perceived risk in New Zealand about the environmental fate and consequences of EOCs as exemplified by the HBRC seeking guidance about how it should be dealing with this issue. This situation could impact the primary industry if the New Zealand clean and green image was tarnished. A science-based approach to characterise an issue of this magnitude will require to be underpinned by a national strategy to coordinate the resources. Recently United States of America scientists have proposed a call for the government, the public, non-governmental organisations, and industry leaders to join the scientists in meeting this challenge (Novak *et al.* 2011a). The same group went further and called for an urgent need for a globally coordinated research programme to evaluate the risks to human health and the environment posed by what are termed "contaminants of emerging concern" (CECs) (Novak *et al.* 2011b). New Zealand is well positioned to participate in such a research venture as there are many examples of multi-stakeholders/expertise teams successfully working in collaboration/partnerships. A similar approach can be developed to assess the impacts of EOCs.

3.1. Proposed national strategy on EOCs

The strategic objective would be to build a knowledge base, capability, policies, and management practices appropriate to evaluate, protect and manage the risk of EOCs to the New Zealand environment. The strategy vision vision/outcome statement should cover:

- Ensuring sustainable use of chemicals
- Ranking of issues (*e.g.* EOCs versus traditional persistent organic pollutants (POPs))
- Protection of our native species
- Maintain soil function and ecosystem services
- Ensure sustainable productivity of New Zealand primary industry and address potential trade barriers
- Underpin the three goals of the New Zealand Waste Strategy (MfE 2007):
    - lower waste's costs and risks to society
    - reduce environmental damage from generation and disposal of waste
    - increase economic benefit by using material resources more efficiently

The aims of the strategy could be:

- Lowering the social costs and risks of EOCs
- Reducing the risk of harm to the environment by minimising the release of EOCs

- Increasing economic benefit and validating our "clean and green image" by more efficient use of potentially harmful EOCs
- Adopting a precautionary approach and preventing harm through anticipatory policies

The strategy would advise on the development of policies that would:

- Respond to the potential issues posed by EOCs
- Contribute to meeting the New Zealand sustainability goals
- Identify relevant environmental management principles (*e.g.* precautionary principle; Kaitiakitanga/stewardship; extended producer responsibility through life cycle management)

The strategy would require a lead agency such as the Ministry for the Environment (MfE) that would coordinate the partnership needed including research, policy, and key industrial participants. A multi-disciplinary research team would encompass expertise in analytical chemistry, environmental engineering, ecotoxicology, social and cultural aspects in order to increase collaboration, reduce duplication and negative competition. A priority of the strategy would be to ensure that the partnership is well linked with international initiatives to address the research questions defined in the previous section. The strategy would prioritise the limited resources to minimise the risk posed by EOCs. A case-by-case approach will ranked EOCs where easy short-term measures will bring immediate benefit while others may require medium- or long-term demand or ongoing commitment. For ranking EOCs, the strategy would need to set realistic and to measurable targets to generate good data and information to achieve the strategy's vision and goals.

A strategy must also include solution options and pathways for public and iwi engagement.

4. CONCLUDING REMARKS

There is an increasing global awareness of the real or potential adverse environmental effects arising from EOCs and the potentially damaging consequences to our "clean and green image" and the "Pure New Zealand" branding. We must establish whether these effects are occurring in the New Zealand environment now and in the future, in order to protect our native heritage, our health and our commercial interests. The HBRC shares these concerns about the risk of EOCs and the lack of information to address potentially significant issues that might arise. It is likely that other territorial authorities are facing similar situations and so there is a need to generate nationally relevant information on EOCs.

To achieve this national goal, a coordinated research effort involving research institutions, relevant government departments, regional and city councils will be required to establish the sources, levels, environmental effects and treatment strategies for EOCs.

This report has focused on organic contaminants but if knowledge of their environmental concentrations and risks to human and ecosystem health of EOCs is still largely unknown particularly in New Zealand, then effects arising from the new engineered nanoparticles are even less well known. Nanoparticles can arise from natural (volcanic eruptions, hydrothermal vents, weathering of rocks *etc*.), or anthropogenic (industrial and combustion) processes (Farré *et al.* 2011). Another potential "emerging" issue is the development of drug-resistant microbes which is closely related to the issue of usage of pharmaceuticals.

In addition to the international and national review of EOCs data, this report has suggested a blueprint for the establishment of a strategy to stimulate further New Zealand-wide research to identify gaps in our knowledge of EOCs. The strategy would underpin and coordinate research effort for generating more comprehensive data on the actual levels of EOCs in surface/ground waters, hot spots, links between land use/activities and relevant EOCs, and effects on our unique environment/fauna with regards to ecosystems (soil, freshwater, estuarine, and marine). This information would feed into the development of improved management practices for all parts of the New Zealand environment. The strategy also needs to engage the general public and iwi to explore behavioural patterns associated with EOCs and develop possible solutions.

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6. GLOSSARY

Anthropogenic	Effects, processes, or materials that are derived from human activities.
Antibiotic	Medicines that fight bacterial infections.
Antifouling	The process of removing or preventing the accumulation of fouling organisms.
Bioaccumulation	Accumulation of a chemical by an organism.
Biosolids	Nutrient-rich organic materials resulting from the treatment of sewage sludge.
Catchment	Area of land bounded by watersheds draining into a river, basin, or reservoir.
Contaminant	Any substance (including gases, odorous compounds, liquids, solids, and micro-organisms) or energy (excluding noise), or heat, that results in an undesirable change to the physical, chemical, or biological environment. Also called pollutant.
Detection limit	A value below which the laboratory analyst is not confident that any apparent concentration is real.
Ecotoxicology	Study of the effects of toxic chemicals on biological organisms, especially at the population, community, ecosystem level.
Endocrine system	System of glands, each of which secretes a type of hormone directly into the bloodstream to regulate the body.
Effluent	Liquid waste or sewage discharged into a river or the sea.
Estrogens	Group of compounds named for their importance in the estrous cycle of humans and other animals.
Flame retardants	Chemicals used in thermoplastics, thermosets, textiles and coatings that inhibit or resist the spread of fire.
Groundwater	Water located beneath the ground surface in soil pore spaces and in the fractures of rock formations.
Herbicide	Type of pesticide used to kill unwanted plants.
Hormone	Chemical released by a cell or a gland in one part of the body that sends out messages that affect cells in other parts of the organism.
Influent	The stream of water that enters any system or treatment unit (environmental).
Iwi	A Maori tribal group.
Leachate	A product or solution formed by leaching.
Microorganism	Unicellular organism including bacteria, fungi, archaea, and protists.
Parasiticide	An agent or preparation used to destroy parasites (can be both external (ecto) or internal (endo).
Pesticide	Substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest.
Sediment	Particles or clumps of particles of sand, clay, silt, or plant or animal matter carried in water.
Stormwater	Flow of water from urban surface areas after rainfall.

Surface water	Water collecting on the ground or in a stream, river, lake, wetland, or ocean.
Surfactant	Compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid.
Wastewater	Any water that has been adversely affected in quality by anthropogenic influence.

7. APPENDICES

Appendix 1. Drinking-water Standards for New Zealand (Ministry of Health 2005)
Maximum acceptable values (MAVs) in mg/L for organic determinands of health significance (including cyanotoxins and pesticides)

Name	MAV	Remarks
acrylamide	0.0005	For excess lifetime cancer risk of 10^{-5}
Alachlor	0.02	Pesticide. For excess lifetime cancer risk of 10^{-5}
Aldicarb	0.01	Pesticide
aldrin + dieldrin	0.00004	Pesticide. The sum of, not each
Anatoxin-a	0.006	Cyanotoxin. PMAV
Anatoxin-a(s)	0.001	Cyanotoxin. PMAV
Atrazine	0.002	Pesticide. Cumulative for atrazine and congeners DEA, DIA, and DACT
azinphos methyl	0.004	Pesticide. PMAV
bentazone	0.4	Pesticide. PMAV
benzene	0.01	For excess lifetime cancer risk of 10^{-5}
benzo(□□□pyrene	0.0007	For excess lifetime cancer risk of 10^{-5}
bromacil	0.4	Pesticide. PMAV.
bromodichloromethane	0.06	For excess lifetime cancer risk of 10^{-5}. THM
bromoform	0.1	THM
carbofuran	0.008	Pesticide
carbon tetrachloride	0.005	
chlordane	0.0002	Pesticide
chloroform	0.2	THM
chlorotoluron	0.04	Pesticide
chlorpyriphos	0.04	Pesticide
cyanazine	0.0007	Pesticide
cylindrospermopsin	0.001	Cyanotoxin. PMAV
2,4-D	0.04	Pesticide
2,4-DB	0.1	Pesticide
DDT + isomers	0.001	Pesticide. Sum of all isomers
di(2-ethylhexyl)adipate	0.1	PMAV
di(2-ethylhexyl)phthalate	0.009	
diazinon	0.01	Pesticide. PMAV
1,2-dibromo-3-chloropropane	0.001	Pesticide. For excess lifetime cancer risk of 10^{-5}
dibromoacetonitrile	0.08	DBP (chlorination)
dibromochloromethane	0.15	THM
1,2-dibromoethane	0.0004	PMAV. For excess lifetime cancer risk of 10^{-5}
dichloroacetic acid	0.05	PMAV. DBP (chlorination)
dichloroacetonitrile	0.02	PMAV. DBP (chlorination)
1,2-dichlorobenzene	1.5	ATO
1,4-dichlorobenzene	0.4	ATO
1,2-dichloroethane	0.03	For excess lifetime cancer risk of 10^{-5}
1,1-dichloroethene	0.03	
1,2-dichloroethene	0.06	Total of cis and trans isomers
dichloromethane	0.02	

Name	MAV	Remarks
1,2-dichloropropane	0.05	Pesticide. PMAV
1,3-dichloropropene	0.02	Pesticide. Total of cis and trans isomers. For excess lifetime cancer risk of 10^{-5}
dichlorprop	0.1	Pesticide
dimethoate	0.008	Pesticide
diquat	0.01	Pesticide. PMAV
diuron	0.02	Pesticide. PMAV
EDTA (editic acid)	0.7	
endosulfan	0.02	PMAV
endrin	0.001	Pesticide
epichlorohydrin	0.0005	PMAV
ethylbenzene	0.3	ATO
fenoprop	0.01	Pesticide
fluoranthene	0.004	PMAV
formaldehyde	1	DBP
heptachlor and its epoxide	0.00004	Pesticide. PMAV. Mainly occurs as the epoxide
hexachlorobenzene	0.0001	Pesticide. PMAV.
hexachlorobutadiene	0.0007	
hexazinone	0.4	Pesticide. PMAV
homoanatoxin-a	0.002	Cyanotoxin. PMAV
isoproturon	0.01	Pesticide
lindane	0.002	Pesticide
malathion	1	Pesticide. PMAV
MCPA	0.002	Pesticide
MCPB[1]	0.03	Pesticide. PMAV
mecoprop	0.01	Pesticide
metalaxyl	0.1	Pesticide. PMAV
methoxychlor	0.02	Pesticide
methyl parathion	0.01	Pesticide. PMAV
metolachlor	0.01	Pesticide
metribuzin	0.07	Pesticide. PMAV
microcystins	0.001	Cyanotoxin. PMAV Expressed as MC-LR toxicity equivalents)
molinate	0.007	Pesticide
monochloroacetic acid	0.02	DBP (chlorination)
monochlorobenzene	0.3	PMAV. ATO
nitrilotriacetic acid (NTA)	0.2	
nodularin	0.001	Cyanotoxin. PMAV
oryzalin	0.4	Pesticide. PMAV
oxadiazon	0.2	Pesticide. PMAV
pendimethalin	0.02	Pesticide
pentachlorophenol	0.009	Pesticide. PMAV
permethrin	0.02	Pesticide. PMAV
phenylphenol	1.4	Pesticide. PMAV
picloram	0.2	Pesticide. PMAV
pirimiphos methyl	0.1	Pesticide. PMAV
primisulfuron methyl	0.9	Pesticide. PMAV

Name	MAV	Remarks
procymidone	0.7	Pesticide. PMAV
propanil	0.02	Pesticide. PMAV. Some degradation products may be toxic
propazine	0.07	Pesticide. PMAV
pyridate	0.1	Pesticide. PMAV
pyriproxifen	0.4	Pesticide
saxitoxins	0.003	Cyanotoxin. Expressed as STX equivalent. PMAV
simazine	0.002	Pesticide
styrene	0.03	ATO
2,4,5-T	0.01	Pesticide
terbacil[1]	0.04	PMAV.
terbuthylazine	0.008	Pesticide
tetrachloroethene	0.05	
thiabendazole	0.4	Pesticide. PMAV
toluene	0.8	ATO
tributyltin oxide	0.002	PMAV
trichloroacetaldehyde	0.01	PMAV
trichloroacetic acid	0.2	DBP (chlorination)
trichlorobenzenes	0.03	PMAV. Total concentration of all isomers. ATO
1,1,1-trichloroethane	2	PMAV
trichloroethene	0.08	PMAV
2,4,6-trichlorophenol	0.2	For excess lifetime cancer risk of 10^{-5}. ATO
triclopyr	0.1	Pesticide. PMAV
trifluralin	0.03	Pesticide. Technical grade may contain carcinogens
trihalomethanes (THMs)		The sum of the ratio of the concentration of each THM to its respective MAV should not exceed one. The individual members of this group are indicated in the table as THM
vinyl chloride	0.0003	For excess lifetime cancer risk of 10^{-5}
xylenes (total)[1]	0.6	ATO
1080	0.0035	Pesticide. PMAV

Notes:

- ATOConcentrations of the substance at or below the health-based guideline value that may affect the water's appearance, taste or odour.
- DBPDisinfection by-product. Any difficulty meeting a DBP MAV must never be a reason to compromise adequate disinfection. Trihalomethanes and haloacids are DBPs. Some DBPs may also have other sources.
- PMAVProvisional MAV (because it is provisional in the WHO Guidelines (WHO 2004) or WHO has no guideline value but the DWSNZ has retained a MAV or developed its own).
- THMTrihalomethane, of which there are four: bromoform, bromodichloromethane, chloroform and dibromochloromethane.

Appendix 2. List of first 20 priority EOCs out of 100 considered in United States of America waters were prepared using their overall rank scores to aid water utilities in conducting category-specific monitoring and/or removing specific EOCs from water (Kumar & Xagoraraki 2010).

Ranking list was developed for pharmaceuticals, personal care products (PCPs), endocrine disrupting chemicals (EDCs), antibiotics, teratogenic compounds in surface water based on current available literature data. EOCs can belong to more than one category.

Priority	Pharmaceuticals	PCPs	EDCs	Antibiotics	Teratogenic compounds
1	**Mestranol[1]**	**AHTN[2]**	**Mestranol[1]**	*Erythromycin[1]*	**Mestranol[1]**
2	**Estrone[1]**	Celestolide [2]	**Bisphenol A**	***Triclosan[1]***	**Estrone[1]**
3	Bezafibrate	Ethylhexyl methoxycinnamate[2]	**AHTN[2]**	*Demeclocycline[1]*	Atorvastatin[1]
4	Atorvastatin[1]	Musk xylene[2]	**TDIP**	*Azithromycin[1]*	**Lindane**
5	**17β-Estradiol[1]**	Musk ambrette[2]	**Estrone[1]**	**Flumequine[1]**	**17β-Estradiol[1]**
6	Gemfibrozil[1]	Propylparaben[2]	**Linuron**	*Sulfadimethoxine[1]*	Gemfibrozil[1]
7	**Testosterone[1]**	**HHCB[2]**	**HHCB[2]**	*Sulfamethoxazole[1]*	Testosterone[1]
8	Erythromycin[1]	Benzophenone-3[2]	**Lindane**	*Tetracycline[1]*	*Erythromycin[1]*
9	**17α-estradiol[1]**	Musk Ketone[2]	**17β-Estradiol[1]**	Trimethoprim[1]	Risperidone[1]
10	Dehydronifedipine[1]	Musk moskene[2]	**Bis(2-ethylhexyl)phthalate**	*Lincomycin[1]*	Norfluoxetine[1]
11	***Triclosan[1]***	Octocrylene[2]	**Testosterone[1]**	*Sulfathiazole[1]*	Carbamazepine[1]
12	**Equilenin[1]**	N,N-diethyltoluamide[2]	**17α-estradiol[1]**	*Enrofloxacin[1]*	Atenolol[1]
13	**Equilin[1]**	Ethylparaben[2]	***Triclosan[1]***	*Ciprofloxacin[1]*	**19-norethisterone[1]**
14	Risperidone[1]	Methylparaben[2]	**Equilenin[1]**	*Tylosin[1]*	Diphenhydramine[1]
15	Norfluoxetine[1]	**Triethylcitrate[2]**	**Equilin[1]**	*Roxithromycin[1]*	**Estriol[1]**
16	Carbamazepine[1]	Methylbenzyldene camphor[1] [2]	**Benzo(a)pyrene**	*Norfloxacin[1]*	*Demeclocycline[1]*
17	**Cis-androsterone[1]**	Acetophenone [2]	**Cis-chlordane**	*Sulfamethizole[1]*	*Azithromycin[1]*
18	Atenolol[1]	3-Methyl-1H-indole (skatol)[2]	**Pentachlorophenol**	*Chlortetracycline[1]*	Diclofenac[1]
19	**19-norethisterone[1]**	NA	**Cis-androsterone[1]**	*Sarafloxacin[1]*	Fluoxetine[1]
20	Diphenhydramine[1]	NA	**19-norethisterone[1]**	*Oxytetracycline[1]*	**Diazinon**

Notes:
AHTN: 7-acetyl-1,13,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene; HHCB: 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran; NA—not applicable.
Notations for categories-of-concern: pharmaceuticals: chemicals with suffix [1]; Personal care products: chemicals with suffix [2]; EDCs: bold-face chemicals; Antibiotics: italicized chemicals; Teratogenic compounds: underlined chemicals.