An Update on Emerging Organic Contaminants of Concern for New Zealand with Guidance on Monitoring Approaches for Councils

March 2016 Technical Report 2016/006

Auckland Council
Technical Report 2016/006
ISSN 2230-4525 (Print)
ISSN 2230-4533 (Online)

ISBN 978-0-9941336-8-7 (Print)
ISBN 978-0-9941336-9-4 (PDF)

This report has been peer reviewed by the Peer Review Panel.

Submitted for review on 7 August 2015
Review completed on 9 March 2016
Reviewed by two reviewers

Approved for Auckland Council publication by:

Name: Dr Lucy Baragwanath

Position: Manager Research and Evaluation Unit (RIMU)

Date: 9 March 2016

Recommended citation

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

An Update on Emerging Organic Contaminants of Concern for New Zealand with Guidance on Monitoring Approaches for Councils

Michael Stewart
Streamlined Environmental Ltd

Grant Northcott
Northcott Research Consultants Ltd

Sally Gaw
University of Canterbury

Louis A Tremblay
Cawthron Institute/University of Auckland

Executive summary

There is global concern that the presence of emerging organic contaminants (EOCs) in the environment may lead to adverse effects on human and ecological health. This concern is primarily associated with the lack of knowledge of the fate and effects of EOCs. Many EOCs are linked explicitly to human activities and, with the world becoming increasingly urbanised, pressures from these contaminants will likely only increase if not addressed in the short term. The main sources of urban EOCs are wastewater effluent, stormwater, landfill leachate and some specific industrial and marine activities. Smaller loads of some EOCs may enter the environment through recreational activities, such as the application of sunscreen and insect repellent.

There are thousands of EOCs potentially present in the environment and their physico-chemical properties range from highly water-soluble (hydrophylic) to highly water-insoluble (hydrophobic). Hydrophilic EOCs are water soluble and generally more transient while hydrophobic EOCs are associated with the solid phase (sediment) and generally more persistent. The environmental fate of EOCs is dependent on these properties, and so state of the environment (SoE) monitoring programmes need to account for these different routes.

Regional councils undertake various monitoring programmes to assess the state of the environment (SoE), to understand environmental status and trends and to measure the effectiveness of policies and plans. Currently these monitoring programmes include legacy persistent organic pollutants (POPs) but do not include EOCs. However, mounting evidence suggests some EOCs may cause delterious environmental effects. With no current national strategy on EOCs, it is necessary for each regional council to provide their own impetus to ensure they are meeting their obligations for environmental protection. Consequently, New Zealand's three largest regional councils Auckland Council (AC), Environment Canterbury Regional Council (ECAN) and Greater Wellington Regional Council (GWRC) have initiated this review with two main goals:

a) A literature review to summarise recent national strategies to identify EOC research priorities, along with national and international legislation, guidelines and research on EOCs;
b) Provide recommendations for future monitoring of EOCs in the urban environment,[1] primarily (but not restricted to) sediments.

[1] The review has gone beyond this to include freshwater and rural issues, where applicable.

Literature review

The literature review covered information from 2011 and updated material from a previous review on EOCs for Hawke's Bay Regional Council (Tremblay et al., 2011).[2]

Despite holding a number of workshops since 2011 the principal goal of developing a New Zealand strategy on EOCs has not yet been achieved. Key government departments and industry bodies appear reluctant to acknowledge EOCs as an issue of significant importance in New Zealand and to progress the development of a national strategy.

Meanwhile, the number of international and national studies on EOCs has increased significantly since 2011. There are a variety of international research programmes and strategies addressing EOCs directly, further supporting the notion that a more focused and centralised approach is needed within New Zealand to address this issue. New Zealand studies demonstrate that EOC sources, concentrations in receiving environments, accumulation in sediment, and uptake and bioaccumulation in biota are similar to those observed in comparable studies overseas. However, there is still a paucity of information on EOCs in the New Zealand receiving environment.

Regulatory bodies around the world are starting to take a considerable amount of action regards restrictions or bans on selected EOCs, with many more placed on watch lists for future assessment. Some BDE[3] and PFOS[4]/PFOA[5] have been identified for elimination or reduction by their inclusion in the Stockholm Convention on Persistent Organic Pollutants. Reduction or elimination of other EOCs are being addressed on a case-by-case basis by international regulatory authorities. Within New Zealand, the Environmental Protection Authority (EPA) has the ability to re-assess approvals for EOCs, and recently revoked approvals for the antifouling co-biocides irgarol and chlorothalonil, and 18 veterinary medicine and insecticide products, including carbaryl, chlorpyrifos and diazinon.

Guidelines for EOCs - predominantly in water, but sediment guidelines are starting to be developed - are being set in the EU and North America for some of the more commonly known EOCs, including:

---

[2] It should be noted that the current review is specific to EOCs and does not include other areas for which there is "emerging" concern, such as nanomaterials, microbes/pathogens or cyanotoxins.

[3] Brominated diphenylethers

[4] Perfluorooctanesulfonic acid

[5] Perfluorooctanoic acid

- Flame retardants (BDEs[6], HBCD[7]);
- Phthalate plasticisers;
- Surfactants (alkylphenols, PFOS[8]);
- Antifouling agents (diuron, isoproturon, irgarol);
- Pesticides (chlorpyrifos, glyphosate, permethrins).

Within New Zealand, ANZECC have water "indicative" quality guidelines for some EOCs (nonylphenols, phthalates, chlorpyrifos, diuron, glyphosate, alkyl surfactants). ANZECC have acknowledged endocrine disrupting chemicals (but not other EOCs with different modes of action) in their revisions and biosolid guidelines are being developed for some EOCs.

Recommended monitoring

International research programmes provide guidance about approaches to assess the potential risk of EOCs and much general information and guidance can be obtained from these. In general, risk assessment approaches are being used to prioritise which EOCs to focus on for monitoring. There is no common approach but each strategy provides useful information to characterise the risk of certain classes of EOCs. However, the significant number of individual EOCs released into the environment, combined with the high cost of analysis, means it is impossible to identify and analyse all of the individual chemicals that will be present. Instead, researchers have either focused on analysing specific modes of action of EOCs (e.g. endocrine disruption, pharmacokinetics); individual compounds that are representative of specific classes of chemicals; or used strategies to look only at high production or commonly occurring EOCs, or those with highest ecological risk. The issue, from a SoE monitoring perspective, is that restricting monitoring of EOCs to specific classes or effects will likely result in the omission of other important chemical stressors and reduce the ability to examine synergistic or cumulative effects. Likewise, risk-based approaches to identify EOCs are based on assumptions, and no two approaches will provide the same answer.

Therefore, we consider the most appropriate and pragmatic monitoring strategy is to use a tiered approach. A first assessment (Tier 1) will aim to identify key EOC classes of concern through analysis of representative EOC "markers" at a larger number of sites (see below). Refinement of EOC classes and sites can then be made based on the first assessment

[6] Brominated diphenylethers

[7] Hexabromocyclododecane

[8] Perfluorooctanesulfonic acid

and future monitoring of only the most highly impacted sites (Tier 2) undertaken on this refined list. Further assessments of EOC bioavailability and non-lethality effects are recommended for the refined EOCs and sites (Tier 3).

Tier 1

Site selection

Site selection should include three types: “core”, “specific” and “reference”. “Core Sites” are those that have a large urban land use component and need to integrate the three major sources of EOCs (i.e sewage effluent, stormwater and landfill). “Specific Sites” are those that do not have a high urban land use component but integrate other sources of EOCs, such as rural marinas (antifouling agents) and high-density swimming beaches (UV-filters). “Reference Sites” are those that are predominantly rural and as far as practical free from urban influence and drainage from septic tanks.

EOC selection

The core EOC “markers” selected for analysis (Table 1-1) have been selected using a combination of criteria, including:

- They are the most representative of their chemical class and cover the main sources (sewage, stormwater, landfill, recreation, and agricultural practises)
- Wastewater “markers” which have been demonstrated to persist during sewage treatment;
- Pesticides which are released directly into aquatic environments without any treatment via urban or rural stormwater runoff;
- Many of the chemicals have been detected in sediment within freshwater systems receiving WWTP effluents or within the marine receiving environment which demonstrates they accumulate and persist in sediment;
- Many of these same chemicals have been detected in and observed to bioaccumulate within bivalves;
- Many of these chemicals are included within other international research and/or monitoring programmes which provides the opportunity for direct comparison between New Zealand derived and overseas data;
- Many of these chemicals are the subject of initiatives for removal or reduction;
- A number of these chemicals have guidelines against which levels can be compared.

The breadth of the classes, and individual chemicals, included in Table 1-1 is necessary to encompass the wide range of different chemicals that comprise EOCs and are released daily into estuarine environments. “Core Sites” and “Reference Sites” should be analysed for the full suite of EOCs in Table 1-1.

Specific marker EOCs (Table 1-2) are location and/or season specific. For example, antifouling agents are likely only present at levels of concern within ports and marinas, while UV-filters are only likely to be present at popular swimming beaches in summer. “Specific Sites” should be analysed for relevant EOCs only (Table 1-2) unless they are also subject to other discharges such as wastewater or stormwater.

New Zealand now has improved, and is improving, analytical laboratory capability to measure a wide range of EOCs in sediment, water, wastewater and biota. Although methods are generally not accredited, this allows flexibility and laboratories can “tailor” their suite of analytes to fit the application.

Assessment

Identify which sites and EOCs are of most concern, based on either likely effects (when risk information is available) or most elevated concentrations of “markers” (when no risk data is available). The results from the assessment should provide useful information to define links between EOCs and land use types to inform management processes.

Refine the sites necessary for future monitoring to include only the most highly impacted sites.

Refine the initial suite of EOC “markers” based on information from above to include extra representatives of those EOC classes of most concern and remove EOCs of low concern.

Table 1-1. “Core” list of “marker” EOCs recommended for initial phase (Tier 1) of sediment monitoring

Class	Representative EOC[a,b]	CAS	Major Sources[c]	Reason[d]
Flame retardants	BDE47	5436-43-1	SEW,SW,LF	1,2,3,5,6
	BDE99	60348-60-9	SEW,SW,LF	1,2,3,5,6
	BDE209	1163-19-5	SEW,SW,LF	1,2,3,5,6
	TDCP	13674-87-8	SEW,SW,LF	1,2,4,6
	TPP	115-86-6	SEW,SW,LF	1,2,4,6
	TCPP	13674-84-5	SEW,SW,LF	1,2,4,6
Plasticisers	DEHP	117-81-7	SEW,SW,LF	2,3,5
	BBP	85-68-7	SEW,SW,LF	2,3,5
	Bisphenol A	80-05-7	SEW,SW,LF	1,5
Surfactants	Nonylphenol	84852-15-3	SEW,SW,LF,AG	1,2,3,5,6
	LAS	25155-30-0	SEW,SW,LF,AG	2,4
Perfluorinated compounds	PFOS/PFOA	1763-23-1/335-67-1	SEW,SW,LF	1,2,4,6
Musk fragrances	Galaxolide	1222-05-5	SEW,SW,LF	2,3,4,6
	Tonalide	21145-77-7	SEW,SW,LF	2,3,4,6

Class	Representative EOC[a,b]	CAS	Major Sources[c]	Reason[d]
Pesticides	Glyphosate	1071-83-6	AG	1,2,3,5
Neonicotinoid insecticide	*Imidacloprid*	138261-41-3	AG	1,4
Pyrethroid insecticide	Bifenthrin	82657-04-3	SEW,SW,LF,AG	2,4
Pyrethroid insecticide	Permethrin	52645-53-1	SEW,SW,LF,AG	2,4
Pharmaceuticals	Acetaminophen	103-90-2	SEW,SW,LF,REC	2,3,5
	Diclofenac	15307-86-5	SEW,SW,LF,REC	2,3,5
	Ibuprofen	15687-27-1	SEW,SW,LF,REC	2,5
	Carbamazepine	298-46-4	SEW,SW,LF,REC	2,4
Steroid estrogen	Estrone	53-16-7	SEW,AG	4,5
Personal Care Products	Triclosan	3380-34-5	SEW,SW,LF	1,2,6
	Methyltriclosan	1/01/40	SEW,SW,LF	1,2,5,6
Preservative	Methylparaben	99-76-73	SEW,SW,LF	2,5
Corrosion inhibitor	*Benzotriazole*	95-14-7	SEW,SW	2,4

[a] BDE = brominated diphenyl ether; DEHP = Bis(2-ethylhexyl)phthalate; BBP = benzyl butyl phthalate; LAS = linear alkylbenzene sulfonate; PFOS = perfluorooctanesulfonic acid; PFOA = perfluorooctanoic acid; TCPP = Tris (1-chloro-2-propyl) phosphate; TDCP = Tris[2-chloro-1-(chloromethyl)ethyl]phosphate; TPP = Triphenylphosphate.

[b] Currently no laboratory capability for analysis of italicized EOCs in New Zealand.

[c] Major sources see Table 2-1. SEW = sewage; SW = stormwater; LF = landfill; AG = agriculture/horticulture; AQ = aquaculture; REC = recreation.

[d] 1 Initiative to remove. Stockholm Convention (POPs) or individual initiatives; 2 High production chemical; 3 Highest concentrations detected in urban marine receiving environment; 4 Knowledge gap (not previously monitored); 5 Previously detected in NZ marine sediments; 6 Persistent Bioaccumulative and Toxic (PBT).

Table 1-2. “Specific” list of “marker” EOCs recommended for initial phase (Tier 1) of sediment monitoring

Class	Representative EOC	CAS	Site	Reason[a]
Antifouling agents	Diuron	330-54-1	Port/Marina	1,5
	Isoproturon	34123-59-6	Port/Marina	1,4
UV-filter	Benzophenone-3	131-57-7	Beach	2,6

[a] 1 Initiative to remove. Stockholm Convention (POPs) or individual initiatives; 2 High production chemical; 3 Highest concentrations detected in urban marine receiving environment; 4 Knowledge gap (not previously monitored); 5 Previously detected in NZ marine sediments; 6 Persistent Bioaccumulative and Toxic (PBT).

Tier 2

Analyse sediment concentrations of the most highly impacted sites for the refined suite of relevant EOCs.

Tier 3

Carry out further risk characterisation of most highly impacted sites by assessment of bioavailability of EOCs, through either passive sampling or biota procedures, or a combination of the two.

Carry out non-lethal chronic effects-based measurements and assessments of the most highly impacted sites on key receptor species.

This approach can also be tailored for sites or catchments influenced by rural or aquaculture activities.

Table of contents

List of figures

List of tables

1.0 Background

1.1 Scope

Auckland Council (AC), Environment Canterbury Regional Council (ECAN) and Greater Wellington Regional Council (GWRC) require a review on updates in the emerging organic contaminant (EOC) space since 2011. Research prior to this time was summarised in a previous report for Hawke's Bay Regional Council (Tremblay et al., 2011).

This current review primarily has an urban focus, and recommends which EOCs Auckland, Wellington and Christchurch Regional Councils (RCs) should include in their marine sediment contaminant monitoring programmes. Where applicable, it also broadly covers freshwater and rural (agricultural and horticultural) issues. However, due to the wide variety of EOCs associated with agricultural and horticultural practises, a specific assessment would be required to address these.

This review is specific for EOCs and does not include other areas for which there is "emerging" concern such as nanomaterials, microbes or algal toxins.

Literature on EOCs has increased substantially in the last few years. A Google Scholar search for "emerging contaminants" reveals 11,900 articles, of which 95 percent (11,300) have been published in the last decade and 60 percent (7,240) since 2011. As such, a focused approach was used to filter out only relevant reference, report and website information.

The full scope is provided in Appendix A, while major questions to be addressed are summarised by chapter.

Chapter 2: Introduction to EOCs
An introduction to EOCs including major classes and sources.

Chapter 3: National Strategy
An update on progress since 2011 on a national strategy on EOCs including summaries of the August 2015 SETAC conference and Global Horizon Scanning Project; summary and history of previous workshops; including the most recent (May 2013) workshop in Wellington.

Chapter 4: Recent Research in New Zealand
An update on recent (since 2011) research on EOCs in NZ. A brief review of the 2011 report will provide some background while research since 2011 is grouped into studies on sources/source removal; receiving environment/fate, toxicity; biota and alternatives for monitoring (e.g. passive sampling).

Chapter 5: International Research Programmes
A review and assessment of what the drivers are of current international research programmes.

Chapter 6: Risk assessment
A review of effects and current knowledge of risks of EOCs.

Chapter 7: Legislation and guidelines
Current international and national legislation, guidelines (water, sediment and biota) and initiatives to reduce EOCs.

Chapter 8: Monitoring Strategies
Summary of monitoring strategies adopted for significant research programmes for sediment, water and 'bioavailable' EOCs via biota and passive sampling techniques. Approaches to the selection of indicator compounds for monitoring and fate assessment.

Chapter 9: Sampling and archiving
Recommended sampling, archiving and storage approach for EOCs in sediment, water, biota and passive sampling samples.

Chapter 10: Laboratory capabilities within New Zealand
A summary of current laboratory capability in New Zealand including trace chemical, bioassay and biological assessment.

Chapter 11: Recommendations for future monitoring programmes
Recommendations and guidance about what Auckland, Wellington and Christchurch RCs should be including in future monitoring programmes, including how and where monitoring should take place. This will be primarily marine sediment focused but also contain options for monitoring 'bioavailable' EOCs via biota and/or passive sampling.

2.0 Introduction to EOCs

2.1 What are emerging contaminants?

There are multiple definitions for emerging contaminants (ECs) in the literature, and other inter-changeable terms are used, for example, contaminants of emerging concern (CEC), or contaminants of emerging environmental concern (CEEC). Furthermore, definitions of ECs vary. However, a commonly accepted definition is provided by the US Geological Survey (USGS) who define an 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".*[9]

Despite the accepted definitions, there is still a great amount of confusion as to what constitutes an EC. This is partly due to the complexities involved when addressing a wide range of chemical classes and individual chemicals. One possible approach is to divide the term into subcategories. For instance, there are "new" ECs, which are recently manufactured chemicals. Then there are "old" ECs, which have been around for several decades, but had not previously been measured in the environment, or for which analytical methods did not exist until recently. Furthermore, there are "ECs within complex mixtures", such as industrial effluents, oil residues, hospital effluent, etc. of which either the mixture itself, or newly identified (subgroups) of components within, may be considered ECs. Perhaps most complex of all are "transformation derived" ECs, which are metabolisation or transformation products of other emerging contaminants, legacy contaminants, or benign chemicals (Arp, 2012). Therefore, the validity of any "contaminant" being assessed as an EC needs to be carefully considered against the above criteria.

As the scope for this review does not include microorganisms, and many chemical ECs are organic rather than inorganic - for example, industrial chemicals and pharmaceuticals and personal care products - we have generally used the term "emerging organic contaminant" (EOC) throughout this review. Where studies also include reference to issues outside EOCs, we have used the terminology "emerging contaminants" (ECs).

As the definition of EOCs covers a wide range of chemicals, they are often grouped into classes depending on their chemical group, their use, or their mode of action. With an

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

urban focus, the major groups of EOCs that are reviewed and discussed in this report include industrial chemicals (flame retardants, plasticisers), pesticides, antifouling agents, preservatives, and pharmaceuticals and personal care products (PPCPs).

With a wide range of EOCs, physico-chemical properties will be a continuum from hydrophilic ("water loving") to hydrophobic ("water fearing"). Transport and eventual fate of EOCs is dependent on their physico-chemical properties: hydrophillic EOCs will primarily be dissolved in the water phase and be of a more transient nature; while hydrophobic EOCs will primarily be particulate-associated and be more persistent. With persistent EOCs generally of more concern (for example see Stockholm Convention), the primary focus of a monitoring programme should be on sediment monitoring. However, many hydrophilic transient EOCs are considered "pseudo-persistent" due to their ongoing discharges (Daughton and Ternes, 1999) and so consideration should also be given to water monitoring.

2.2 Sources of EOCs in the marine environment

Major EOC sources are summarised below. There is considerable overlap of sources (see Table 2-1) and pathways into the environment (see Figure 2-1) of many EOCs, and so, from a monitoring perspective, programmes need to be designed that will initially focus less on specific sources and more on adequate representation of EOCs.

Sewage

Sewage contains a cocktail of EOCs, including excreted pharmaceuticals and metabolites, illicit drugs, personal care product compounds washed off during bathing, food additives, household chemicals and industrial chemicals. These EOCs are not fully removed by current wastewater treatment plant technologies (for recent reviews see: Luo et al., 2014; Margot et al., 2015). As a result, sewage disposal is the main pathway for EOCs to enter the marine environment either through direct discharge from wastewater treatment plants into coastal zones or indirectly via wastewater discharges into rivers and streams. Sewer overflows and leaking pipes can result in untreated sewage being discharged directly into the environment (Lara-Martín et al., 2014). In rural areas discharge from septic tanks can contaminate ground and surface waters with EOCs (Phillips et al., 2015). Sewage can be discharged directly from boats and large ships. Increases in the concentrations of sewage indicators and pharmaceuticals in coastal areas of Europe have been attributed to cruise ships which can have passenger numbers equivalent to small towns (Nödler et al., 2014).

The recycling of biosolids from wastewater treatment plants and irrigation of Wastewater Treatment Plant (WWTP) effluents to land can introduce a range of EOCs into soil (Weiss et al., 2008). The risk of EOCs migrating from sites of application and entering surrounding

environments depends on the application regime, soil characteristics, and climate. The risk of EOCs migrating from land irrigated with WWTP effluent or receiving applications of biosolids can be minimised by the implementation of appropriate site-specific management protocols.

Stormwater

Potential sources of EOCs in stormwater include EOCs released from building materials and vehicles, waste materials disposed of down stormwater drains, poorly managed industrial sites as well as sewer overflows and leaking sewers (Xu et al., 2011; Zgheib et al., 2011). While there are limited data, classes of EOCs that have been measured in stormwater include alkylphenols, phthalates, musk fragrances, flame retardants, plasticisers and resin monomers, and pharmaceuticals (Zgheib et al., 2011). There is considerable overlap of EOC classes between stormwater and wastewater.

Landfill leachate

A further pathway of EOCs entering marine environments is landfill leachates (Ramakrishnan et al., 2015). A wide range of classes of EOCs are likely to be present in landfill leachates, as they will be released as deposited waste materials degrade. Examples of EOCs measured in landfill leachates include pharmaceuticals, musk fragrances, insect repellent, flame retardants, UV-filters and perfluorinated compounds (Eggen et al., 2010).

Recreational activity

Topically applied personal care products such as sunscreens, insecticides and pharmaceuticals can be washed off people’s skin during recreational activities including diving and swimming. Higher concentrations of UV-filter compounds from sunscreens have been reported in summer at popular swimming beaches (Sankoda et al., 2015).

Antifouling paints

Antifouling paints are used on commercial shipping and leisure craft to prevent aquatic organisms from fouling and building up on hulls. Antifouling paints may also be used on submerged structures including aquaculture facilities. These protective paints/structures can contain antifouling co-biocides that are EOCs (see section 7.1.1).

Animal husbandry, horticulture and aquaculture

Internationally animal husbandry, including agriculture and aquaculture, is a significant source of pharmaceutically active compounds including veterinary medicines and steroid hormones entering the environment (Grigorakis and Rigos, 2011; Kools et al., 2008). As

there is currently limited use of prophylactic antibiotics, and less use of feeding lots, in New Zealand compared with other countries, agriculture is likely to be a less significant source of veterinary medicines entering waterways than in other countries. The recycling of biosolids from WWTPs and irrigation of WWTP effluents to land can introduce a range of EOCs into soil (Weiss et al., 2008).

In New Zealand the dairy farming industry is a significant source of steroid hormones released into the environment (Gadd et al., 2010a, 2010b). The concentration of estrogenic steroid hormones in dairy shed effluents released to waterways or irrigated onto pasture exceed those in WWTP effluent. The greater bulk of dairy cow waste is deposited directly to pasture by defecation and urination without treatment. Steroid hormones in animal waste, irrigated oxidation pond effluents and oxidation pond slurry spread to pasture can migrate through soil into groundwater or be transported from pasture into nearby waterways (Gadd, 2008). As a consequence estrogenic steroid hormones have been detected in ground water and stream waters of intensively farmed dairy catchments in New Zealand (Gadd, 2008).

Horticulture, along with pasture management, is a source of insecticides and herbicides entering waterways either by leaching to groundwater or being washed into streams by runoff (Gaw et al., 2008; Shahpoury et al., 2013). New Zealand still permits the use of selected antibiotics for some horticultural applications, for example to control the *Pseudomonas syringae* pv. *actinidiae* (Psa) outbreak in kiwifruit (Vanneste, 2013).

The lower density of aquacultural activities suggests that input of EOCs from aquaculture will currently be limited.

EOCs arise from multiple sources and their pathways to the marine receiving environment can be complex. A graphical overview of major sources and associated pathways of EOCs into marine ecosystems is provided in Figure 2-1 (modified from Gaw et al., 2016).

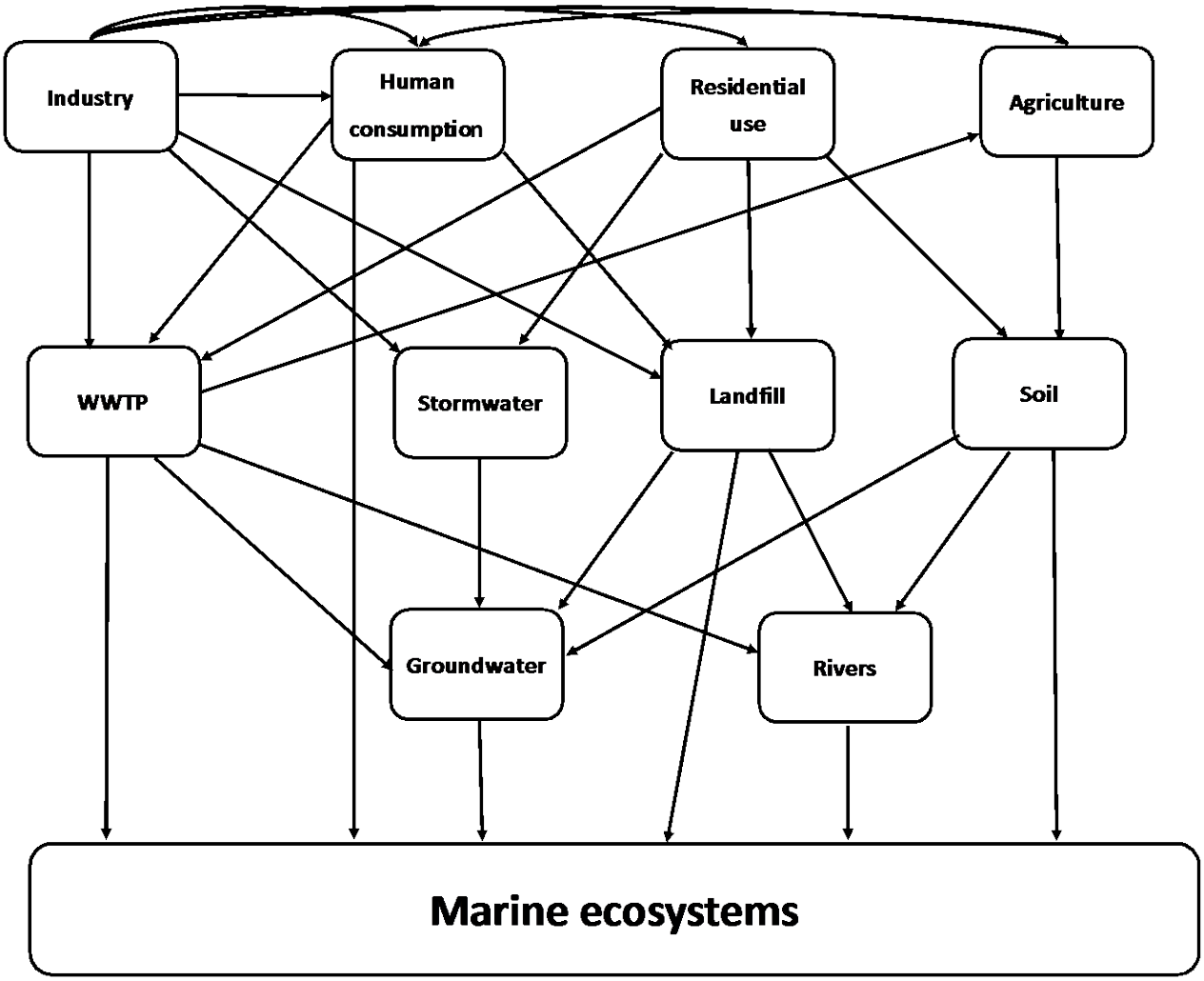

Figure 2-1. Sources and pathways of EOCs into the marine receiving environment.

2.3 EOC classes

Chemical classes of the most common EOCs by source are provided in Table 2-1. There is some overlap between sources (for example, pharmaceuticals can be present in wastewater or landfill leachate). However, overall loads from each source and individual EOCs within each class may vary significantly.

Table 2-1 Classes of EOCs by major sources

EOC Class	Sewage	Stormwater	Landfill leachate	Agriculture and Horticulture	Aquaculture /Marine industry	Recreation
Pharmaceuticals	☐	☐	☐			☐
Plasticisers	☐	☐	☐			
Antimicrobials	☐	☐	☐			
Corrosion inhibitors	☐	☐				
Flame retardants	☐	☐	☐			
Surfactants	☐	☐	☐	☐		
UV-filters	☐	☐	☐	☐		☐
Steroid hormones	☐			☐		
Musk fragrances	☐	☐	☐			
PFOAs etc	☐	☐	☐			
Veterinary medicines				☐	☐	
Pesticides				☐		
Antifouling cobiocides					☐	

2.4 Effects

There is global concern that the presence of EOCs in the environment may lead to adverse effects on human and ecological health. This is due to the significant absence of data on the fate of EOCs and the criteria used to assess the environmental risk of EOCs. Information on the fate of EOCs is slowly being addressed via a multitude of programmes to assess their distribution in water, sediment and biota. However, assessment of effects has been hampered by a lack of appropriate testing regimes, in particular sub-lethal chronic toxicity assessments.

There are limited marine ecotoxicological laboratory data for EOCs. For example, data have only be reported for seven of the twenty pharmaceuticals most frequently reported in seawater, and only one of these studies investigated toxicity to benthic organisms (Gaw et al., 2014).

Despite the paucity of ecotoxicological data a wide variety of adverse effects have been reported for marine organisms exposed to pharmaceuticals, for example the effects of analgesics include reduced feeding rates, survival, binding of mussels to rock surfaces, and changes in immune response and biochemical markers (Gaw et al., 2014). Serotonin uptake inhibitory anti-depressants have negatively impacted the neurobehaviour and spawning success of fish. There is increasing concern regarding the potential adverse effects on primary producers in aquatic ecosystems.

Field studies of EOCs have so far proven inconclusive in predicting their effects within receiving environments. Reliable predictive outcomes for EOCs have not been forthcoming as many of these studies have focused on a single chemical or class, a specific mechanism of action or test assay, a single organism, and/or exposure concentrations that are environmentally unrealistic (Novak et al., 2011).

3.0 National strategy update

3.1 Summary of previous workshops

Over a number of years, attempts have been made to coordinate and develop science and policy related to managing EOCs in New Zealand.

The inaugural workshop "*Developing a New Zealand strategy for emerging contaminant issues*" was jointly organised by the Institute of Environmental Science and Research (ESR), Landcare Research, Plant and Food Research and Scion, and hosted by ESR at the Kenepuru Science Centre in Porirua in October 2009. The goal of the workshop was to establish a platform from which to develop a cohesive research and policy strategy on EOCs in New Zealand. The workshop participants expressed the importance of identifying a champion(s) within appropriate Government Departments to raise awareness of EOCs with regulators, policy makers, and funding agencies.

The second emerging contaminant workshop, organised and hosted by Howard Ellis of Ministry for the Environment (MfE), was held at MfE Wellington Offices in June 2010. The objective of the meeting was to bring together scientists and policy makers in New Zealand and identify a pragmatic strategy for building a knowledge base, capability, policies, and management practices appropriate to evaluating, protecting and managing the risk to the New Zealand environment from EOCs. Discussion centred on developing a strategy that would fit with the development of future policy on environmental issues in New Zealand and Howard Ellis (MfE) was nominated to lead this initiative.

Two follow up workshops were held in 2012. The first was hosted by Graham Sevicke-Jones at the offices of Greater Wellington Regional Council in February 2012. The objective of this workshop was to introduce staff from Government Departments to the issue of EOCs, and identify a new champion(s) to advance a New Zealand Strategy on EOCs in response to the retirement of Howard Ellis from MfE.

A follow up workshop on the theme "*Emerging Contaminants - is it an issue in New Zealand?*" was hosted by the University of Auckland in December 2012. The workshop identified short term actions (website creation, conference presentations) to raise awareness of EOC research in New Zealand.

In 2013 another workshop, "*Emerging Contaminants- securing the future*", was held in May at the offices of Greater Wellington Regional Council. The objective of the workshop was to explore options to establish a Special Interest Group (SIG) with the overall aim to

provide a strategic framework and roadmap for managing ECs in NZ. It was agreed there was a need for a central government agency to take ownership of this issue, e.g. MfE, and an effective SIG needs to be proactive, not reactive on this environmental issue, and focus on an evidence base to influence the long term nature of policy development.

An Environmental Protection Authority (EPA) *Tikanga and Technology wananga on Emerging Chemical Contaminants* was held at Takapuwahia Marea in Porirua in November 2014. The wananga provided the opportunity for members of the EPA Te Herenga group to hear from researchers who are working in the area of EOCs and from EPA staff including the Chief Executive Rob Furlong. Mr Furlong acknowledged the EPA were aware of issues related to EOCs but this was not a priority topic for the EPA. The forum provided an improved understanding of Maori issues and concerns to incorporate into future initiatives regarding EOCs in New Zealand.

3.2 SETAC Global Scanning Project

The Society of Environmental Toxicology and Chemistry (SETAC) is currently running the Global Horizon Scanning Research Prioritization Project[10]. The aims of this project are to collect and prioritise the most important future research questions on a geographic basis as suggested by scientists from around the globe working in government, academia and industry. Each SETAC geographic unit is being asked to submit research questions which are then discussed at a workshop where the questions are prioritised. The approach followed by the SETAC steering committee is that SETAC members, within their own geographic unit, are first asked to submit research questions. The workshops are being held in 2015 and 2016. The SETAC Australasia workshop was held on the 25th of August 2015 in Nelson as part of the 2015 SETAC Australasia conference.

The information from this workshop is being assessed and will be incorporated into that obtained from other SETAC regional workshops. The outcome of the workshops will be revealed at a special session at the 7th SETAC 2016 World Congress in Florida. The outcomes will include a ranking of the top twenty research questions. The focus encompasses all stressors but it will identify research priorities for EOCs for future monitoring and risk assessment.

[10] https://www.setac.org/news/150260/Become-Part-of-a-Novel-Global-Horizon-Scanning-Research-Prioritization-Project.htm

3.3 Summary comments

Despite holding a number of workshops and the enthusiasm of key participants the principal goal of developing a New Zealand strategy on EOCs has not yet been achieved. Key Government Departments - Ministry for the Environment (MfE), Environmental Protection Authority (EPA), Ministry for Primary Industries (MPI) and Ministry for Business, Innovation and Employment (MBIE) - and industry bodies in New Zealand (Dairy, Agricultural, Horticultural, Wastewater Treatment) appear reluctant to acknowledge EOCs as an issue of significant importance in New Zealand. The relative lack of funding for EOC research within the science sector in New Zealand limit the time and resources key individuals can allocate to the Strategy Project. Efforts to identify an enduring champion within Government to lobby the issue of EOCs have been unsuccessful to date.

Despite lack of central guidance, regional councils are obligated to monitor the environment for contaminants that may cause adverse human and/or ecological effects. With increasing evidence that EOCs fit this criteria, new monitoring strategies are necessary to achieve this requirement. Hence, the three regional councils who commissioned this report have taken the proactive approach of trying to identify appropriate monitoring strategies for EOCs as an interim step.

4.0 Summary of EOC research in New Zealand

4.1 Research up to 2011

Hawke's Bay Regional Council (HBRC) commissioned a report in 2011 (Tremblay et al., 2011) in recognition that there was a knowledge gap around the risk and management of EOCs which present challenges to territorial authorities, exacerbated by growing negative public perceptions in the region. HBRC were concerned about a range of EOCs that are potentially released from sewage outfalls and runoff from urban, industrial, and agricultural activities.

That report reviewed the international and national literature on EOCs, along with international policy and regulations to manage the risks of EOCs. Internationally there has been an exponential increase in research on EOCs, around sources, fate and effects, with establishment of research networks to address the complex nature of the EOC space. Within New Zealand, research has been more sporadic and *ad-hoc* as outlined below.

A scoping report in 2005 on Endocrine Disrupting Chemicals (EDCs) (Sarmah et al., 2005), outlined a New Zealand perspective, ranking them on a priority scale. This was followed by analysis of EDCs in animal wastes and sewage treatment plant effluents in the Waikato region (Sarmah et al., 2006), and a much larger study of dairy farm effluents (Gadd et al., 2010b) and treatment strategies for dairy effluent (Gadd et al., 2010a). Biological methods were developed to determine estrogenic and androgenic activity from sewage treatment plant effluents (Leusch et al., 2006a, 2006b). Further studies showed soil type was important in determining the fate of steroid estrogens (Sarmah et al., 2008; Scherr et al., 2009). Transport of estrogens through New Zealand soils was also studied (Steiner et al., 2010).

Urban EOC research - specifically around Auckland, but of relevance to all urban centers - was addressed by a literature review (Ahrens, 2008) which expanded the focus beyond EDCs, provided hazard risk categories and recommended a list of urban sourced EOCs for monitoring. This was followed up by a field analysis of EOCs around the Auckland marine receiving environment (Stewart et al., 2009).

PPCP research in New Zealand was initiated via a PhD study which assessed 12 pharmaceuticals in sewage effluent, biosolids, and the soil and pore water within the Rotorua District Council wastewater irrigation site within Waipa Forest (Gielen, 2007). Archived sediments sourced from the Auckland urban study were analysed for a suite of 46 pharmaceuticals (Stewart et al.2013, 2014). Pharmaceutical disposal practices in New

Zealand (Braund et al., 2009; Peake and Braund, 2009) and around the world (Tong et al., 2011) were also reported.

Pesticides were surveyed in New Zealand groundwater in 2006 as part of the 5th national pesticide survey, and concentrations were found to be very low. It was acknowledged that there was a paucity of data on pesticide residues in sediments in New Zealand (Gaw et al., 2008).

The 2011 report (Tremblay et al. 2011) also stated that although there was legislation in some countries to manage risks of selected EOCs (e.g. nonylphenol and bisphenol A) and veterinary medicines, there was no regulatory control of EOCs in New Zealand.[11] Internationally there were no drinking water standards for EOCs, although it was proposed to include some EDCs in a pre-cursor list that may require future regulation in the US. No ecological guidelines existed in New Zealand for EOCs at the time of writing.

Possibilities for future legislation of EOCs in New Zealand were discussed, with the conclusion that regulatory authorities in New Zealand will likely wait until overseas guidelines are developed and/or legislation is passed, rather than develop their own. One avenue for monitoring of EOCs in the New Zealand environment was highlighted, via consenting processes required by the Resource Management Act (RMA).

The report concluded by proposing a national strategy on EOCs that would be multi-disciplinary and suggested this should be led by an appropriate government agency such as MfE.

4.2 Research since 2011

Research on EOCs within New Zealand is summarised below, and these have been grouped by source/treatment (e.g. WWTP, stormwater) and receiving environment studies. Where these studies have components of both they are included in the source/treatment section.

[11] All potentially hazardous chemicals need to be approved by NZ EPA, although many EOCs have current approvals (see Section 7.1.1).

4.2.1 Wastewater and wastewater removal studies

Evaluation of the efficacy of the Beachlands/Maraetai STP to remove estrogenic and androgenic activity

This study (Tremblay et al., 2010) completed for Manukau Water Limited applied estrogenic and androgenic bioassay methods to assess the efficacy of the newly commissioned Beachlands/Maraetai Sewage Treatment Plant (STP) incorporating activated sludge, BardenPho (biological nutrient removal) and UV treatment to remove estrogenic and androgenic activity within the WWTP effluent. The study demonstrated the estrogenic activity in raw influent entering the WWTP was similar to that reported in the international literature, but the androgenic activity was lower. The final treated effluent contained no detectable levels of androgenic activity and only trace levels of estrogenic activity. The study concluded the residual trace levels of estrogenic activity in treated effluent released from the STP were highly unlikely to cause harm to the receiving environment.

Efficacy of the Gisborne District Council Biological Trickling Filter WWTP to remove EOCs

This ongoing project, led by Northcott Research Consultants, is assessing the ability of the Gisborne District Council (GDC) Biological Trickling Filter (BTF) WWTP to remove a wide range of EOCs from Gisborne City wastewater. This study includes the widest range of EOCs to be assessed to date in New Zealand, ranging from semi-volatile nitro- and polycyclic musks to steroid hormones, phenolic antimicrobials, preservatives and pharmaceuticals. Complimentary assessments of total estrogenic, androgenic, anti-estrogenic, anti-androgenic and dioxin-like activity by bioassay are also being obtained.

The results obtained to date confirm the conclusions of earlier studies, that the concentration of EOCs in WWTP effluent in New Zealand is comparable to those reported overseas. A significant point of difference in this study is the assessment of EOC residues in both the dissolved and particulate phases of WWTP influent and effluent. This study demonstrates the commonly accepted practice of filtering and only analysing dissolved phase contaminants within WWTP effluents significantly underestimates the total load of EOCs being discharged into receiving environments via WWTP effluents (Northcott and Jackman, 2015).

EOCs in treated effluent of 13 WWTPs in New Zealand

An ongoing PhD research project (Jason Strong, Waikato University) is investigating the concentration of EOCs in WWTP effluents released into aquatic receiving environments, their partitioning into sediment, and potential to bioaccumulate in benthic biota in New

Zealand. The data obtained to date demonstrates a wide range of EOCs are present in New Zealand WWTP effluents at comparable concentrations to those in WWTP effluents in Europe and North America (Northcott et al., 2013).

Removal of EOCs from wastewater using constructed wetlands and denitrifying bioreactors

This ongoing PhD research project (Morkel Zaayman, University of Canterbury, supervised by Sally Gaw and supported by the National Institute of Water and Atmospheric Research (NIWA) and ESR) is investigating the ability of different constructed wetland (CWs) designs to remove EOCs from post primary settled WWTP effluent. The site for this research is the NIWA constructed wetland facility at the Hamilton City Council Pukete WWTP. The wetland designs being assessed include vertical flow, horizontal flow, floating and two variations of denitrifying bioreactor wetlands. A wide range of EOCs are being investigated, including musk fragrances, phthalate esters and plasticisers, alkylphosphate flame retardants, phenolic antimicrobials, paraben preservatives, UV-filters and estrogenic steroids. Mass loading and removal of EOCs is being determined by analysing EOCs in both the dissolved and particulate phases of influent and effluent of the CWs, and their accumulation in solid matrices contained within each CW. A variety of molecular methods will be applied to ascertain the composition of the microbial community in each CW module and identify microorganisms capable of degrading EOCs. The analysis of samples from this study is underway and results are unavailable at present.

Ongoing research assessing the fate and effects of EOCs in biowaste

The Centre for Integrated Biowaste Research (CIBR) is carrying out research (CIBR, 2014) to improve the understanding of the potential risk EOCs in biowaste represent to New Zealand's environment. The research CIBR is currently undertaking on EOCs includes:

- Developing new methods to analyse EOCs in biowaste and receiving environments- particularly pharmaceuticals and brominated flame retardants;
- Quantifying the concentrations of EOCs in New Zealand biosolids;
- Modifying existing and developing new biological methods of analysis that provide improved endpoints to assess chronic effects on organisms exposed to EOCs, for example genetic markers in earthworms and Zebra fish; immune stimulation or suppression and protein expression in earthworm coelomocyte cells; microbial community function and structure; and cell based thyroid activity bioassays;
- Assessing the biological effects of mixtures of EOCs upon microorganisms, earthworms, Zebra fish embryos, microorganisms, and soil microbial function.

Analysis of hormonal activity and selected EDCs is Rotorua District Council sewage treatment plant wastewater and stream water samples

This study (Tremblay et al., 2013b) was undertaken to assess the concentration and activity of EDCs in effluents released from the Rotorua District Council WWTP and in the receiving environment, using trace chemical analysis and bioassays. The concentration of two estrogenic steroids in the membrane bioreactor (MBR) and Bardenpho (biological nutrient removal) treated effluents (estrone and 17α-ethynylestradiol) exceeded the Predicted No Effect Concentrations (PNECs) for the protection of aquatic wildlife within the MBR and Bardenpho treated effluents.

The study concluded that the concentration of estrone and 17α-ethynylestradiol would be reduced by dilution upon discharge within the Puarenga Stream and would then be unlikely to cause harm to aquatic biota within the receiving waterways.

4.2.2 Stormwater and sewer overflow studies

Fate of EOCs from sewer overflows in urban streams of Christchurch

This current MSc research project (Gemma Wadworth, University of Canterbury, supervised by Sally Gaw) is assessing sewer overflows as sources of EOCs, determining their potential effect within urban waterways in the city of Christchurch. Samples of sewer overflow, stream water and sediment will be analysed for residues of selected phenolic antimicrobial chemicals (triclosan etc.), to determine if residues of antimicrobial chemicals are accumulating in sediments of urban streams and impacting resident microbial communities. Results from this study are unavailable at this time.

***Tiakina te whanga – ka ora* Urban stormwater and sediment contaminant project**

This ongoing project, led by Landcare Research, assessed a range of urban pollutants, including a suite of nine nitro- and polycyclic musks, within stormwater entering urban waterways and estuaries, and their receiving sediments. The only musk chemical detected in stormwater and sediments was the polycyclic musk galaxolide which was present in stormwater and sediments in parts per trillion and in low parts per billion concentration range, respectively. A manuscript is in preparation, however results from this study are unavailable at this time.

A corresponding assessment of the toxicity of sediments in the urban waterways undertaken in collaboration with the Aquatic Ecology and Toxicology Group at the

University of Heidelberg demonstrated the sediments exerted significant cytoxicity and EROD (dioxin-like) activity but a lesser genotoxic response.

EOCs in urban stormwater

A US National Science Foundation funded EAPSI project (Rachael Lane, University of Kansas) hosted by Sally Gaw at the University of Canterbury is determining the types and concentrations of UV-filters, phenolic antimicrobials, paraben preservatives and steroid hormones present in Christchurch urban waterways. Samples of stream water have been collected upstream and downstream of housing subdivisions to determine inputs of EOCs from residential areas. Data from this project is unavailable to report at this time.

4.2.3 Receiving environment studies/fate

Pharmaceuticals in the Auckland marine receiving environment

The Auckland estuarine receiving environment field study from 2009 was supplemented by a multi-residue pharmaceutical analysis of archived sediments from this study, in collaboration with the Spanish research group of Petrovic and Barcelo. Forty-six pharmaceuticals were analysed, of which 21 were detected at one or more sites. Nonsteroidal anti-inflammatory drugs (NSAIDs) were among the highest concentrations detected. Numbers quantified were higher at sites either downstream of WWTP discharges (Puketutu and Mahurangi) or areas where sewage infiltration of surface waters occurs (Coxs Bay and Meola). These results were reported separately for Auckland Council (Stewart, 2013). All reported EOC results around Auckland were subsequently published together (Stewart et al., 2014).

EOCs in sediment and waters of Whakaraupo (Lyttleton) Harbour

A PhD research project (Emnet, 2013) investigated the source and temporal variation of paraben preservatives, UV filters, alkylphenols, trilcosam and estrogenic steroid hormones in Whakaraupo Harbour originating from the treated effluent discharged from three WWTPs. This study demonstrated the effluents of the Lyttelton, Governors Bay, and Diamond Harbour WWTPs to be sources of octylphenol (OP); the UV-filters 4-methylbenzylidene camphor (4-MBC), benzophenone-1 (BP-1) and benzophenone-3 (BP-3); triclosan (TCS), methyl triclosan; bisphenol A (BPA), and estrone (E1) into Whakaraupo Harbour. The concentrations of EOCs in WWTP effluents were comparable to those observed from overseas studies.

Commonly detected micro-pollutants in seawater, sediment, and green-lipped mussels of Whakaraupo harbour included:

- mParaben, 4-MBC, BP-3, BPA, octyl methoxycinnamate (OMC), and E1 (seawater);
- mParaben, OP, 4-MBC, BP-3, BP-1, BPA, OMC, E1, and coprostanol (sediment);
- mParaben, OP, and BP-3 (mussels).

The presence of residues of some EOCs in samples from reference sites suggest much larger regions of the coastal environment are impacted by EOCs than previously thought. Significantly, the marine sediments of Whakaraupo Harbour were found to be a sink of EOCs, some of which were also observed to bioaccumulate in green-lipped mussels.

Analysis of Waikato River water samples for selected endocrine disrupting chemicals and hormonal activity

This study (Tremblay and Northcott, 2013) assessed the endocrine disruption potential of eight water samples collected from the Waikato River between Taupo and Tuakau. The concentration of selected EDCs and the total endocrine activity of the river water samples were assessed using trace chemical analysis and bioassay methods. The study confirmed the concentrations of EDCs measured in the Waikato River are one to three-orders of magnitude below their respective predicted-no-effect concentration (PNEC). The bioassay responses were similarly low, and the report concluded the current concentration of these chemicals in Waikato River water pose negligible risks to aquatic biota.

4.2.4 Toxicity studies

Toxicity of diclofenac to indigenous New Zealand fish

Two research projects at the University of Canterbury (supervised by Sally Gaw) are assessing the toxicity of diclofenac - a non-steroidal anti-inflammatory - to New Zealand indigenous fish species. Nicole McRae (PhD) is determining the toxicity of diclofenac singly and in mixtures with metals to inanga (*Galaxias maculatus)* and Kerri-Anne Regan (MSc) is assessing the toxicity of diclofenac to the common bully (*Gobiomorphus cotidianus*). These studies will demonstrate if fish indigenous to New Zealand are more or less sensitive to diclofenac than fish species in other countries.

Risk assessment of chemicals commonly found in household products

There is on-going research at CIBR to assess the potential environmental impacts of active ingredients found in common household cleaning and personal care products in order to offer less harmful alternatives. Characteristics of the chemicals (including toxicity and ability to bioconcentrate) were used to attribute a weighted score for risk assessment. The scores were then assigned to a traffic light system ranking according to: green (lowest 1/3 of the score range), yellow (medium 1/3 of the score range) and red (highest 1/3 of the

score range). An example of risk score for 9 EOCs is provided in Table 4-1 (Tremblay et al., 2013a). This type of information can be used to characterise the risk of chemicals and to prioritise EOCs for future investigation within the CIBR research programme and as a communication and education tool within community engagement exercises. The CIBR programme is currently funded to September 2017.

Table 4-1. Ranking (weighted scores) for 9 EOCs present in commonly used household products.

Chemical	Property	Category scoring				Ranking[a]
		log P	K*oc*	BCF	IC_{50}	
Benzophenone	Fixative/fragrance	3	4	6	8	21
Bisphenol A	Plasticiser	4	4	6	12	26
Chloroxylenol	Antibacterial	3	4	6	16	29
DEET	Insect repellent	3	3	8	4	18
Diclofenac	Pharmaceutical	5	3	4	8	20
Octyl-methoxycinnamate	Sunblock	6	5	10	12	33
2-Phenoxyethanol	Fixative/antibacterial	2	2	4[b]	4	12
2-Phenylphenol	Disinfectant	3	5	6	8	22
Triclosan	Antibacterial	5	5	6	12	28

[a] Colour coded score ranking: green (lowest 1/3), yellow (medium 1/3) and red (highest 1/3).

[b] No data available, intermediate value applied; log P = partition coefficient; K_{OC} = Soil Organic Carbon-Water Partitioning Coefficient; BCF = bioconcentration factor; IC_{50} = half maximal inhibitory concentration.

4.2.5 Biota

Auckland Council Shellfish Contaminant Monitoring Programme (SCMP) Review

Auckland Council (AC) commissioned a review of their SCMP with an objective to ensure it was still providing relevant information. One aspect of relevance to the current report is EOCs. The review (Stewart et al., 2013) recommended:

> *"Consideration should be given to the future inclusion of selected emerging chemicals of concern (ECCs) in the analytical suite to provide a more relevant suite of organic contaminants. It is recommended that a pilot study is initiated to analyse perfluorooctanesulfonic acid (PFOS) and brominated diphenyl ether congeners-47/99 in mussels and oysters from the Auckland region. Furthermore - although outside the objectives of the SCMP, but within the general State of the Environment monitoring requirements - measurement of ECCs should also occur in sediment and water."*

The report also recommended that if the SCMP was disestablished (as it subsequently has been), AC should explore two potential avenues to provide an assessment of bioavailable

contaminants in the environment: an expanded sediment contaminant monitoring programme *in conjunction* with benthic health monitoring; and passive sampling devices (PSDs).

Anticoagulants

Concerns about anticoagulant rodenticides were first identified in the late 1990s around the transfer of brodifacoum residues in New Zealand environments, and secondary poisoning of wildlife, resulting from field applications for pest control. More recent monitoring has identified anticoagulants to be ubiquitous in certain vertebrate wildlife, with trophic transfer the likely source. Furthermore, domestic rodenticides are likely reaching the wider environment (reviewed in Cavanagh and Ward, 2014).

4.2.6 Passive sampling

It is widely acknowledged that accurately determining the 'bioavailable' proportion of 'total' contaminant concentrations is important as this is the component that directly affects ecosystem health (see Section 8.2 for further discussion). A feasibility field study was carried out by NIWA and Auckland Council to assess whether passive sampling devices (PSDs) have the potential to replace the SCMP (see 4.2.5) in providing meaningful bioavailable concentrations of heavy metals plus selected EOCs (PBDEs, PPCP wastewater markers) and Polycyclic Aromatic Hydrocarbons (PAHs) (Stewart et al., 2015). The blueprint for this study was recent international developments in using PSDs in environmental monitoring (Allan et al., 2011; Alvarez et al., 2014; Perron et al., 2013).

PSDs offer significant advantages over biota sampling:

- They are significantly cheaper to deploy;
- They do not suffer from mortality or environmental variability, such as species, seasonal, and condition variability, and;
- they do not carry a potential existing body burden of contaminants.

However, an important difference between PSDs and biota monitoring is that PSDs do not include particulate-associated concentrations and so potentially do not represent the whole bioavailable component, where particulate matter is taken up by the biota.

Results of the study showed that PSDs were capable of providing time-average water concentrations as low as pg/L (parts-per-quadrillion). Although there were some differences between uptake of some classes of EOCs in PSDs and mussels, it was confirmed that PSDs are a useful tool for estimating the bioavailability of EOCs in the

aquatic environment and in some situations have the potential to replace biota in EOC bioavailability monitoring (Stewart et al., 2015).

4.3 Summary comments

Within New Zealand, there has been an increase in studies on EOCs since 2011, which mirrors the international situation. However, as was the case prior to 2011, research has proceeded on an ad-hoc basis and there is still no central coordination of effort or overarching research programme to underpin future research.

The studies demonstrate that EOC sources, concentrations in receiving environments, accumulation in sediment, and uptake and bioaccumulation in biota are similar to those observed in comparable studies overseas.

However, studies of EOCs in the New Zealand environment have focused on a relatively small number of chemical classes and individual chemicals, principally personal care products, and there is a paucity of data on residues of pharmaceuticals and industrial EOCs (for example, flame retardants and plasticisers) in the New Zealand receiving environment. In light of the similarity in sources and concentration of EOCs observed between New Zealand and overseas studies it is valid to assume the concentration of other EOCs that remain to be analysed, will also be similar to concentrations reported in overseas studies. Therefore, we can expect these same EOCs will elicit a similar range of effects in the New Zealand environment to those observed in overseas studies.

5.0 International research programmes

Currently there is no national level strategy or guidance on EOCs. In the absence of this, regional councils are having to create their own policies and monitoring strategies to fulfil their obligations for SoE monitoring. Internationally, research programmes have recently been created, including government department-led, researcher-led and community-led initiatives. This section summarises key findings or activities that have occurred in major international research programmes, mostly but not exclusively, since 2011. This section is not comprehensive, but highlights the significant amount of resource being assigned to EOCs internationally.

5.1 World Health Organisation and United Nations Environment Programme - Endocrine Disrupting Chemicals

In 2012 the World Health Organisation (WHO) and the United Nations Environment Program (UNEP) released a report *"State of the Science of Endocrine Disrupting Chemicals"* prepared by a panel of international experts (WHO/UNEP, 2012). Key findings from the expert panel include:

- Eight hundred chemicals are known or suspected to be endocrine disrupting chemicals (EDCs);
- Humans and wildlife populations are exposed to EDCs and laboratory evidence supports the hypothesis that chemical exposures contribute to endocrine disorders;
- Endocrine related diseases and disorders are increasing in humans and wildlife populations and the speed of increase of endocrine disorders excludes genetics as the sole explanation;
- The most sensitive exposure window is during critical periods of development;
- The disease risk for EDCs may be underestimated;
- Exposure to EDCs needs to be reduced.

5.2 World Health Organisation Working Group on Pharmaceuticals in Drinking Water

WHO convened a *Working Group on Pharmaceuticals in Drinking Water*[12], comprised of scientists from a diverse group of countries. The working group addressed:

- Environmental occurrence and sources of pharmaceuticals in finished drinking water and source water;

[12] http://water.epa.gov/scitech/swguidance/ppcp/who.cfm

- Approaches to assess health risks to vulnerable populations;
- Environmental chemistry of pharmaceuticals in natural waters;
- Advances in treatment methods and analytical methods, including treatment effectiveness;
- Availability of data and information to assess risks to human health, and;
- Existing pharmaceutical take-back and safe disposal programmes to reduce water pollution.

Based on available data, it was concluded that the margin of safety between the low concentrations of pharmaceuticals in drinking water and minimum therapeutic doses suggested a very low risk to human health. As a result, the working group did not consider the development of formal health-based guideline values for pharmaceuticals in drinking water to be necessary.

5.3 North America

5.3.1 USGS Emerging Contaminants in the Environment

The United States Geological Survey (USGS) *Emerging Contaminants in the Environment* research project[13] aims to provide information to evaluate the threat of emerging contaminants to environmental and human health. Research activities include:

- Development of analytical methods to measure chemicals and microorganisms or their genes in a variety of matrices (e.g. water, sediment, waste);
- Determining the environmental occurrence of these potential contaminants;
- Characterising the myriad of sources and source pathways that determine contaminant release to the environment;
- Defining and quantifying processes that determine their transport and fate through the environment, and;
- Identifying potential ecological effects from exposure to these chemicals or microorganisms.

The USGS programme has focused on freshwater, with target EOCs including pesticides, pharmaceuticals, cyanotoxins and alkylphosphate-based flame retardants. Highlights from the programme include the first major study demonstrating the widespread distribution of pharmaceutical residues, hormones and other organic wastewater contaminants within rivers and streams in the US. Follow up studies have demonstrated some classes of pharmaceuticals can accumulate in fish. This programme also documented EOCs from

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

streams can infiltrate shallow groundwater and that landfill leachate can contain elevated concentrations of EOCs. Glyphosate and neonicotinoid pesticides were found to be widespread in rural streams within agricultural catchments in the US and pyrethroid contamination of streams increased with increasing urbanisation. The research programme has also investigated the impacts of EOCs (EDCs in particular) on fish and bacteria.

5.3.2 USEPA Columbia River Basin Toxics Reduction Action Plan

The United States Environmental Protection Agency (USEPA) joined with federal, state, tribal, and local governments, industry, and nonprofit partners to form the Columbia River Toxics Reduction Working Group. The goal was to reduce toxics in the Columbia River basin, an important watershed contaminated with a variety of toxic contaminants as a result of human activities, including urban settlement and development, agriculture, transport and recreation. An action plan was developed in 2010 which identified knowledge gaps with respect to EOCs (USEPA, 2010), and was followed up by a strategy to address EOCs directly in 2014 (USEPA, 2014a). This strategy is covered in more detail in section 8.1.

5.3.3 USEPA Strategy for Addressing PPCPs in Water

The USEPA *Strategy for Addressing PPCPs in Water*[14] is a four-pronged approach to strengthen science, improve public understanding, build partnerships and promote stewardship opportunities and to take regulatory action when required. Activities underway to strengthen science include the development of analytical methods, conducting and funding studies on sources and the occurrence of pharmaceuticals in wastewater, biosolids, fish and tissue along with research on exposure pathways and effects on health and aquatic life.

Recent outputs from this strategy include the development of guidelines for consumers for the disposal of unused pharmaceuticals, and best management practices for unused pharmaceuticals at health care facilities The USEPA has developed analytical methods for approximately 100 pharmaceuticals, personal care products, steroids, and hormones in wastewater and biosolids (USEPA methods 1694 and 1698).

[14] *http://water.epa.gov/scitech/swguidance/ppcp/basic.cfm*

5.3.4 USEPA Contaminants of Emerging Concern in Fish

The USEPA conducted an extensive series of national and regional-scale studies to establish the median concentrations of polybrominated diphenyl ether (PBDE) (USEPA, 2013a) and perfluorinated compound (PFC) (USEPA, 2013b) residues in freshwater fish.[15]

5.3.5 NOAA Mussel Watch California Demonstration Project

The National Oceanic and Atmospheric Administration's (NOAA) Mussel Watch Program has been running since 1986. In 2009, NOAA partnered with local, regional and state agencies in California to develop a two-year pilot study investigating EOCs in mussels, fish, sediment and seawater. The classes of EOCs included PPCPs, contemporary use pesticides, flame retardants, alkylphenols/alkylphenol ethoxylates, and PFCs. This research programme is covered in more detail in section 8.2.1.

5.3.6 Water Environment Research Foundation (WERF)

The Water Environment Research Foundation[16] is an independent scientific research organisation dedicated to wastewater and stormwater research. It is funded by the US federal government and industry and regulatory agency subscribers. Current projects include:

- Developing diagnostic tools to evaluate impacts of trace organic compounds;
- Developing and evaluating analytical methods for EDCs and PPCPs via interlaboratory comparison;
- Evaluating advanced oxidation processes and other technologies to degrade and/or remove emerging contaminants from wastewater streams;
- Categorising wastewater treatment processes by their efficiency in reducing concentrations of a suite of indicator trace organic compounds, and;
- Assessing the ability of land application to remove EOCs from recycled wastewater.

[15] http://water.epa.gov/scitech/cec/

[16] http://www.werf.org

5.3.7 Canada

The Canadian Water Network[17] is a virtual network centre of excellence comprised of members from academia, industry, government and not for profit organisations. The network is completing a 22-month project (2013-2015) to identify significant effects of EOCs from wastewater on aquatic ecosystems.

5.4 Europe

5.4.1 NORMAN Network

The NORMAN network[18] is a network of reference laboratories, research centres and related organisations, and was formed with the purpose of monitoring emerging environmental substances (containing, but not restricted to, EOCs). The mission of the network is to:

- Enhance the exchange of information and collection of data on emerging environmental substances;
- Encourage the validation and harmonisation of common measurement methods and monitoring tools so that the demands of risk assessors can be better met, and;
- Ensure the knowledge of emerging pollutants is maintained and developed by stimulating coordinated, interdisciplinary projects on problem orientated research and knowledge transfer to address identified needs.

The network has six working groups:

- Prioritisation of emerging substances (WG1);
- Bioassays and biomarkers in water quality monitoring (WG2);
- Effects directed analysis for hazardous pollutant identification (WG3);
- Engineered nanoparticles (WG4);
- Wastewater reuse and contaminants of emerging concern (WG5), and;
- Emerging substances in the indoor environment (WG6).

The NORMAN network organises a range of activities, including expert group meetings, workshops, databases and method validation exercises.

[17] http://www.cwn-rce.ca/

[18] http://www.norman-network.net/

5.4.2 ECsafeSEAFOOD

ECsafeSEAFOOD[19] is a European Community funded project assessing food safety issues related to priority contaminants present in seafood as a result of environmental contamination (including those originating from harmful algal blooms and those associated with marine litter) and evaluating their impact on public health. The project is focused on unregulated contaminants including brominated flame retardants, EDCs, toxic element species (metals), PPCPs, PFCs, microplastics and marine biotoxins.

A key output from the project is the development of a database on contaminants of emerging concern in shellfish.[20] A focus of the project is the development of multi-residue analytical techniques for fish and shellfish covering several classes of EOCs.

5.4.3 PHARMAS

PHARMAS[21] is a consortium of scientists from academia and industry (Denmark, France, Germany, Sweden, The Netherlands and the United Kingdom) assembled to assess the risk of pharmaceuticals to wildlife and humans. The PHARMAS project is supported by the EU Seventh Framework Programme and is focussing on anti-cancer drugs and antibiotics.

Aims of the project include determining human and animal exposure to target molecules, investigating toxicity of realistic mixtures, identifying stable transformation products of drugs of interest and investigating environmental concentrations and ecotoxicity of target chemicals.

The PHARMAS project has demonstrated that sewage treatment provides limited degradation of pharmaceuticals and the primary mechanism of removal is sorption rather than biodegradation. A screening tool has been developed for the location-specific prioritization of human pharmaceuticals in Europe. The *Mixture Tools* software provides three sets of tools and analysis instruments for predicting and assessing toxicities of mixtures.

[19] http://www.ecsafeseafood.eu/ecsafeseafood-consortium

[20] http://www.ecsafeseafooddbase.eu/

[21] http://www.pharmas-eu.net/news

5.4.4 The SOLUTIONS project

The SOLUTIONS project consists of 39 partners from eighteen different countries supported by the European Union Seventh Framework Programme.[22] The consortium comprises scientific expertise in advanced effect-based tools for ecological and human risk detection, including state-of-the-art *in vitro* assays and multi-endpoint receptor gene assays and toxicogenomics, *in vivo* bioassays and biomarkers, and population and community level effect assessment tool. SOLUTIONS will develop the tools for the identification, prioritisation and assessment of those water contaminants that may pose a risk to ecosystems and human health. New generations of chemical and effect-based monitoring tools will be developed and integrated with a full set of exposure, effect and risk assessment models. The approach used is expected to provide transparent and evidence based candidates or River Basin Specific Pollutants in the case study basins and to assist future review of priority pollutants under the EU Water Framework Directive (WFD) as well as potential abatement options (Brack et al., 2015).

5.5 Australia

The Commonwealth Scientific and Industrial Research Organisation (CSIRO) undertakes research on EOCs within the *Mitigating Environmental Contaminants* stream of the CSIRO Land and Water Flagship Program.[23] This research focusses on characterising the fate, transport and bioavailability of EDCs and PPCPs in landscapes and water bodies. It measures and predicts their ecotoxicological effects on biota in aquatic and terrestrial ecosystems.

Water Research Australia has funded research assessing the fate of EOCs during wastewater treatment and their effect upon discharge to receiving environments.[24] These include:

- An investigation of endocrine disruption in Australian aquatic environments;
- Tools for analysing androgenic, thyroid, glucocorticoid and progestagenic activity in environmental waters;
- Treating wastewater for potable reuse by removal of chemicals of concern using advanced oxidation processes;
- EDC Toolbox II - Analysing a wider range of hormonal activities in environmental waters.

[22] http://www.solutions-project.eu/project/

[23] http://www.csiro.au/en/Research/LWF/Areas/Environmental-contaminants

[24] http://www.waterra.com.au/research/programs-overview/

5.6 Asia

Based on numbers of publications alone, research on EOCs is expanding in Asia, and in China in particular. Despite this, research on EOCs within Asia appears to be on an *ad-hoc* basis. For instance, in China, legislative and administrative regulation of ECs is currently lacking (Zhang, 2014), so there are likely no overarching research programmes.

5.6.1 Japan

The Japanese Science and Technology Agency is funding a Core Research for Evolutionary Science and Technology (CREST) programme focussing on sustainable water use. Sub-projects are assessing optimal advanced water treatment, re-use of sludges from wastewater and assessment of contaminant sources.[25]

5.6.2 Singapore

Singapore has introduced a four taps strategy for ensuring the long-term security of their water supply. One component of the strategy is water reclamation from wastewaters. All domestic and industrial wastewaters in Singapore are collected and used for water reclamation. Surface water is also collected from urbanised catchments and treated to potable water standards. The Public Utilities Board has funded a range of projects to ensure the safety of the reclaimed water supply. These projects have included assessment of suitable treatment options including membrane technology (e.g. Qin et al., 2004). Water quality within the Marina catchment, an urbanised catchment covering 17 percent of Singapore was assessed for 13 EOCs including alkylphenol ethoxylate metabolites (APEMs), hormones (estriol, estrone), pharmaceuticals (chloramphenicol, ibuprofen, naproxen), bisphenol A, and the pesticide fipronil (Xu et al., 2011). A parallel study investigated the presence of 19 perfluorochemicals in the Marina catchment that drained an urbanised section of Singapore, with perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) the dominant components (Nguyen et al., 2011).

[25] http://www.water.jst.go.jp/en/index.html

5.7 Summary comments

There are a variety of international research programmes addressing EOCs directly, further supporting the notion that a more focused and centralised approach is needed within New Zealand to address this issue.

6.0 Risk assessment of EOCs

A chemical hazard is defined as a chemical that is reasonably likely to cause harm or damage to humans or the environment with sufficient exposure or dose. The risk of a chemical is defined as the probability that exposure to the chemical will lead to a negative consequence. Simply put the risk of a chemical is a function of its inherent toxicity and dose received by an organism: Risk = Hazard x Dose (Exposure). Therefore, a highly hazardous (extremely toxic) chemical does not pose a risk until exposure occurs.

There is growing international concern that the presence of EOCs in the environment may lead to adverse affects to human and ecological health. While a growing body of research is demonstrating the potential for EOCs to elllicit detrimental effects this area of research has developed recently and there remains an absence of fate and effects data to assess the environmental risk of EOCs.

The noted effects that EOCs can exhibit within the environment and to exposed wildlife include endocrine disruption, unexpected bioaccumulation of residues, behavioural changes, physiological alteration, toxicity, and induced antimicrobial resistance.

6.1 Traditional Risk Assessment and Toxicity Testing

Of the 15,000 high-production-volume chemicals in commercial use in the US and the European Union only 25 percent have been subjected to basic toxicity testing (Drewes et al., 2009). Unlike agricultural and industrial chemicals most EOCs have not undergone screening to determine whether or not they will have an adverse environmental effect. Furthermore, even for those that have been tested, the standardised test methods used to assess the impact of chemicals in the environment assess acute effects, or the amount of chemical resulting in the death of test organisms. The amount of most EOCs needed to cause the death of an organism is very high, and for this reason they have previously been considered safe.

The majority of risk assessment frameworks for organic contaminants were developed in response to the need to regulate organic chemicals that are persistent, bioaccumulative and toxic. The primary endpoint of effect measure in first generation persistent, bioaccumulative and toxic-based risk frameworks is acute toxicity, as determined by the EC_{50} of a chemical or the concentration resulting in 50 percent mortality of a test organism. Various modifications of these risk frameworks incorporate higher levels of protection to exposed organisms by the adopting reduced degrees of mortality by introducing EC_{20} and EC_{10} values.

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

When these approaches are used to determine the toxicity of EOCs they are commonly deemed to be of little or no risk to exposed organisms in receiving environments. For example, due to their rate of consumption, persistence and toxicity, the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin have been identified as chemicals of particular concern in aquatic environments by scientists around the world (Johnson et al., 2015). Predicted concentrations of these antibiotics in European rivers were within the range of reported measurements (Johnson et al., 2015) and varied from between two to six orders of magnitude lower than concentrations known to be toxic to fish, *Daphnia magna*, duckweed and cyanobacteria or green algae. A risk assessment of the four antibiotics of concern concluded it unlikely they were causing acute toxicity to wildlife within European rivers on their own (Johnson et al., 2015). However, this study assessed acute toxicity and did not consider the ability of these four antibiotics to exert longer term chronic effects upon biota in the riverine systems, or whether or not exposure to the mixture of the four antibiotics resulted in additive or synergistic toxicity.

6.2 Exposure

Many EOCs degrade in the environment and this has contributed to the perception they do not persist and can be considered environmentally safe. While many EOCs degrade in the environment within a matter of days they are constantly replenished by fresh inputs, for example, from wastewater treatment plant effluents which continually release treated effluent and its load of residual EOCs into the aquatic environment. This replenishment means there is a continuous source of un-degraded EOCs being introduced into the environment that effectively replaces the fraction being degraded within the receiving environment, leading to what has been described as ‘pseudo persistence’ (Daughton and Ternes, 1999). Similarly the pseudo persistence of some EOCs can lead to their bioaccumulation in exposed organisms which would otherwise be unexpected due to their degradability.

6.3 Direct toxicity assessment

The direct toxicity assessment (DTA) approach is commonly used to assess the potential impacts of a chemical or complex mixtures (such as treated WWTP effluent). The tests are conducted with species from various phylogenetic levels likely to be present in the receiving environment. In New Zealand, those species often include algae, an invertebrate like an amphipod and the larvae of the blue mussel that show a range of sensitivities to complex mixtures. These tests assess the baseline acute or chronic toxicity of chemicals but rarely provide information at the mechanistic level. DTA of chemicals is the accepted means of assessment by which regulatory bodies determine the risk of chemicals to humans and the environment.

6.4 Endocrine disruption

Of all the EOCs, EDCs have been the subject of extensive research over past decades due to their potential to disrupt endocrine functions in wildlife, invertebrates, fish, and human populations.

Despite the vast amount of research literature on EDCs, it remains challenging to assess their risk within receiving environments due to the extremely low concentrations at which they remain biologically active (Hotchkiss et al., 2008). There is extensive information on the risk of EOCs with estrogenic activity. Predicted-No-Effect Concentrations (PNECs) have been derived for 17β-estradiol and 17α-ethinylestradiol at 2 ng/L and 0.1 ng/L (parts per trillion), respectively (Caldwell et al., 2012). The European Union has derived PNECs of 0.33, 0.10 and 1.50 µg/L respectively for the three EDCs 4-n-nonylphenol, triclosan (WFD-UKTAG, 2009), and bisphenol-A (EU, 2008). The low PNEC values for these EDCs (parts-per-billion: ppb) reflect the high potency of these biologically active chemicals. In comparison to estrogenic chemicals there is a paucity of information regarding the fate and effects of EDCs with androgenic or progestogenic properties in the environment.

6.5 Multiple modes of action and New Pathways for effects

Assessing the risk of EOCs in the environment is further complicated by many EOCs displaying multiple modes of action. For example, many pharmaceuticals display endocrine activity, in addition to their recognised primary mode of action as antibiotics, β-blockers, and/or antiepileptics.

Other EOCs have similarly been demonstrated to produce previously unknown chronic effects in aquatic organisms. Some of the most commonly used organophosphate flame

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

Most EOCs have been produced for human use and those that have been subjected to toxicological assessment have been assessed for their potential effects on humans and other mammals. Pharmaceuticals provide a useful example. Some common antibiotics used to treat humans are also used as veterinary medicines for the treatment of sick animals. But, scientists have little knowledge of the type or magnitude of effect these chemicals may impart on non-mammalian species such as insects, fish, and birds.

Cutting-edge research is beginning to show us the effects of EOCs upon exposed organisms (for example the zebra fish) are insidious and may be profound. A suitable example is provided by selective serotonin reuptake inhibitors (SSRI) such as the anti-depressant, Prozac (i.e. fluoxetine). These have proven to accumulate in fatty tissue in freshwater fish, specifically in the brain, where they have an effect on their behaviour. Fish exposed to fluoxetine exhibit anxiety and anti-social and aggressive behaviours that are detrimental for the breeding success of fish. Therefore while SSRIs do not have a direct toxic effect that will kill a population of exposed fish they elicit a behavioural change that may ultimately produce the same outcome of a reduced or disappearing fish population. This provides a salient example of the unintended consequences and impacts of a chemical displaying multiple modes of action (Maximino et al., 2013).

New test methods currently under development will provide new ways to measure the chronic long-term effects of EOCs on exposed organisms, for example genomic approaches are being applied to assess the trans-generational effects of chemical exposure (Vandegehuchte and Janssen, 2014).

6.6 The effects of mixtures of contaminants

Another important aspect about the risk assessment of EOCs is that once released in the environment, they combine with other pollutants and environmental stressors and their potential combined or synergistic effects remain unknown. This is particularly the case in estuarine environments receiving EOCs from WWTP discharges that combine with other contaminant sources from the greater catchment. As a consequence, in the environment, organisms (including humans) are exposed to complex chemical mixtures of contaminants where the individual chemicals may be present at concentrations too low to raise concern. The limited information available suggests complex mixtures of chemicals may increase the potency of contaminants in an additive or synergistic manner (Schwarzenbach et al., 2006) .

6.7 Multi-generational effects

New test methods are currently being developed to measure the long-term effects of EOCs on exposed organisms. For instance, the multi-generational effects of chemical exposure can be assessed through epigenetic mechanisms modulating gene expression (Vandegehuchte and Janssen, 2014).

6.8 Current state of knowledge about the risks of EOCs

The assessment of human and ecotoxicological risks caused by the release of EOCs into the environment is difficult to quantify. At present our knowledge of the range and relative importance of sources of EOCs into aquatic environments is incomplete. Our understanding of the fate and degree of natural attenuation of EOCs in receiving environments is poor. It is therefore difficult to predict the fate of EOCs in receiving environments and therefore the concentrations at which organisms are exposed to them (Pal et al., 2010).

The research completed to date demonstrates the impacts of EOCs are more subtle and potentially result in chronic or long-term effects that are more difficult to assess, but are no less significant than short term acute effects. On top of this is the issue of mode of action of the many individual chemicals within the complex mixtures present in WWTP effluents and receiving environments

In conclusion, there is mounting evidence that EOCs exert multiple effects upon exposed organisms within receiving environments. These effects are much more subtle than the traditionally accepted acute ecotoxicity endpoints and instead impart chronic and/or multi-

generational effects. Current accepted standard ecotoxicity methods are not optimised to discern chronic or multi-generational effects imparted by many EOCs and new test paradigms are required before the true impact of EOCs released into the environment can be fully understood. This research will lead to a greater understanding and appreciation of the impact of EOCs in the environment and ultimately the development of robust risk assessments and exposure limits. The group of EOCs for which realistic effect level limits have been derived are those with demonstrated endocrine disrupting activity (EDCs).

7.0 Legislation and guidelines

7.1 New Zealand legislation

7.1.1 HSNO

The role of New Zealand's Environmental Protection Agency (EPA) under the Hazardous Substances and New Organisms (HSNO) Act[26] is the regulation of pesticides, dangerous goods, household chemicals, pharmaceutical active ingredients (through a group standard[27]) and other dangerous substances. EPA have put controls in place to manage the risks of hazardous substances to safeguard people and the environment.

Hazardous substances, including petrol, solvents, industrial chemicals, agrichemicals, household cleaners and cosmetics, need to be approved before they can be used in New Zealand. Therefore, there is a process in place to prevent "new" EOCs from entering New Zealand, provided they are an "active ingredient" (e.g. a new pesticide or pharmaceutical) and not arriving through incorporation into other materials (e.g. flame retardants). Of particular relevance to EOCs, HSNO new chemical approvals are based on human or ecological toxicity and not non-lethal endpoints such as endocrine disruption or multi-generational effects.

Currently registered chemicals for which concerns have arisen since regulation approval can be re-assessed, however there is no legislative requirement to do this unless a formal re-assessment request is lodged. This is usually at the cost to the applicant but can be initiated by the EPA Chief Executive.

In 2013 the EPA reassessed antifouling paints for use on vessels and marine structures. Approvals for irgarol and chlorothalonil were declined. Antifouling paints containing diuron, octhilinone or ziram were given approval for four years and thiram for 10 years. All other antifouling paints assessed remain approved but are subject to additional controls around use and labelling. Active ingredients that remain approved for antifouling paints in New Zealand include copper, 4,5-dichloro-2-octyl-1,2-thiazol-3(2H)-one (DCOIT), dichlofluanid, zinc, zineb, tolyfluanid and mancozeb (EPA, 2013).

[26] http://www.epa.govt.nz/hazardous-substances/about/Pages/default.aspx

[27] Group standards are general and industrial use products with similar uses and hazards

EPA is continuing a process of re-evaluation of pesticides of concern and has recently banned the manufacture and importation or placed strict controls on use, of various organophosphate and carbamate insecticides in New Zealand.[28]

7.1.2 PHARMAC

The Pharmaceutical Management Agency (PHARMAC) is the New Zealand Crown agency that decides, on behalf of District Health Boards, which medicines and related products are subsidised for use in the community and public hospitals.[29] PHARMAC do not play a role in determining legislative procedures for the control of pharmaceuticals but (via funding decisions) indirectly controls the type and quantities of pharmaceuticals available for prescription, which ultimately enter domestic wastewater streams and the environment.

7.2 European legistation

7.2.1 EU REACH

REACH[30] is the Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals in the EU and came into force on 1st June 2007. This legislation requires companies manufacturing or importing chemical substances into the European Union to register these substances with the European Chemicals Agency (ECHA).

Companies are required to provide a chemical safety assessment that includes the physicochemical, toxicological and ecotoxicological properties of the substance, hazard assessment and exposure assessment. Chemicals are also assessed to determine if they are persistent and bioaccumulative. Substances can be classified as substances of very high concern if they are carcinogenic, mutagenic, toxic for reproduction or meet the criteria for persistent, bioaccumulative and toxic. Many EOCs do not fulfil these criteria (see section 6.0). and so will likely be approved.

7.2.2 European Medicines Agency

An environmental risk assessment is required for all new marketing authorisation applications for a medicinal product in the EU. If the predicted environmental concentration of a drug is equal to or greater than 0.01 µg/L, a Phase II environmental fate and analysis is required. Drug substances with a log K_{OW} >4.5 (i.e. lipophilic and likely to

[28] http://www.epa.govt.nz/news/news/Pages/Hazardous-Substances-Update-June-2015.aspx

[29] http://www.pharmac.health.nz

[30] http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm

bioaccumulate) are required to be screened for persistence, bioaccumulation and toxicity (European Medicines Agency, 2006).

In addition, Regulation (EU) No 1235/2010 directs member states to monitor and evaluate the risk of environmental effects of human medicines (European Commission, 2010).

7.3 Guidelines

7.3.1 Sediment guidelines

New Zealand

The Australian and New Zealand Environment and Conservation Council (ANZECC) set Interim Sediment Quality Guidelines (ISQG) for ecological protection in 2000 for a range of heavy metals and persistent organic pollutants (e.g. PAHs, PCBs, OCPs). ISQG were not set for any EOCs and current revisions do not include any EOCs (Simpson et al., 2013).

Canada

Canadian Council for Ministers for the Environment (CCME)
CCME have developed ISQG for nonylphenol and its ethoxylates: 1400 µg/kg (freshwater) and 1000 µg/kg (marine).[31]

Environment Canada
Environment Canada has developed Federal Environmental Quality Guidelines for PBDEs (Environment Canada, 2013). Federal Environmental Quality Guidelines are benchmarks for quality of the ambient environment and are voluntary unless prescribed in regulatory tools. The guidelines (Table 7-1) are derived using toxicological effects or hazards of specific substances or groups of substances.

Table 7-1. Federal Environmental Quality Guidelines (FEQG) for Polybrominated Diphenyl Ethers (PBDEs)

Homologue*	Congener	Water (ng/L)	Fish Tissue (ng/g ww)	Sediment** (ng/g dw)	Wildlife Diet[1] (ng/g ww food source)	Bird Eggs (ng/g ww)
triBDE	total	46	120	44	–	–
tetraBDE	total	24	88	39	44	–
pentaBDE	total	0.2	1	0.4	3 (mammal) 13 (birds)	29[2]
pentaBDE	BDE-99	4	1	0.4	3	–
pentaBDE	BDE-100	0.2	1	0.4	–	–

[31] http://st-ts.ccme.ca/

Homologue*	Congener	Water (ng/L)	Fish Tissue (ng/g ww)	Sediment** (ng/g dw)	Wildlife Diet[1] (ng/g ww food source)	Bird Eggs (ng/g ww)
hexaBDE	total	120	420	440	4	–
heptaBDE	total	17[3]	–	–	64	–
octaBDE	total	17[3,4]	–	5600[4]	63[4]	–
nonaBDE	total	–	–	–	78	–
decaBDE	total	–	–	19[4,5]	9	–

*FEQG for triBDE (tribromodiphenyl ether), tetraBDE (tetrabromodiphenyl ether), hexaBDE (hexabromodiphenyl ether), heptaBDE (heptabromodiphenyl ether), nonaBDE (nonabromodiphenyl ether) and decaBDE (decabromodiphenyl ether) are based on data for the congeners: BDE-28, BDE-47, BDE-153, BDE-183, BDE-206, and BDE-209, respectively unless otherwise noted.
** Values normalized to 1% organic carbon.
[1] Applies to mammalian wildlife unless otherwise noted.
[2] Value based on the commercial PentaBDE formulation, DE-71, which contains mostly pentaBDE and some tetraBDE.
[3] Values based on commercial OctaBDE mixture DE-79, which is composed mainly of heptaBDE and octaBDE (octabromodiphenyl ether).
[4] Values adopted from Ecological Screening Assessment Report (Environment Canada 2006). Sediment guidelines for octaBDE and decaBDE were adapted from the SAR by being corrected for the sediment organic carbon in the actual tests, then normalised to 1% organic carbon instead of the 4% in the SAR.
[5] Values based on commercial decaBDE mixture which is composed mainly of nonaBDE and decaBDE.

Norway

The Norwegian Pollution Control Authority revised the Norwegian classification system for contaminants in sediment. The classifications (Table 7-2) are defined as I background levels; II no toxic effects on aquatic organisms; III toxic effects following chronic exposure; IV toxic effects following short term exposure; and V severe acute toxic effects.

Table 7-2. Norwegian classification of EOCs in sediment

EOC	I Background	II Good	III Moderate	IV Bad	V Very bad
SCCP		<1000	1000-2800	2800-5600	>5600
MCCP		<4600	4600-27000	27000-54000	>54000
Octylphenol		<3.3	3.3-7.3	7.3-36	>36
Nonylphenol		<18	18-110	110-220	>220
Bisphenol A		<11	11-79	79-790	>790
TBBPA		<63	63-1100	1100-11000	>11000
PBDE		<62	62-7800	7800-16000	>16000
HBCD	<0.3	0.3-86	86-310	310-610	>610
PFOS	<0.17	0.17-220	220-630	63-3100	>3100
Diuron		<0.71	0.71-6.4	6.4-13	>13
Irgarol		<0.08	0.08-0.50	0.5-2.5	>2.5

Units are µg/kg
SPCC short-chained (C10-13) polychlorinated paraffins, MPCC middle-chained (C14-17) polychlorinated paraffins, TBBPA tetrabromobisphenol A, PBDE pentabromodiphenylether, HBCD hexabromocyclododecane, PFOS perfluorated octylsulphonate

7.3.2 NZ Biosolids Guidelines

Water New Zealand is undertaking a review of the Guidelines for the safe application of biosolids to land in New Zealand (New Zealand Water Wastes Association, 2003), including a major revision of organic contaminants in organic wastes including biosolids (Water New Zealand, 2015). A review of the organic contaminants included within the NZ Biosolids Guidelines has recommended the current organic contaminants (chlorinated persistent organic pollutants, or Cl-POPs) listed in Table 4.2 of the Guideline (New Zealand Water Wastes Association, 2003) can be considered obsolete and should be replaced with selected EOCs (CIBR, 2014). The EOCs recommended for inclusion in the revised guideline include EDCs (e.g. steroids, nonylphenols), flame retardants (e.g. HBCD and selected PDBEs), antimicrobial agents (e.g. triclosan and ciprofloxacin); pharmaceuticals (e.g. carbamazepine, diclofenac); persistent herbicides (clopyralid); and surfactants (e.g. Linear Alkylbenzene Surfactants (LAS)).

The incorporation of EOCs into the modified Guidelines represents a significant departure from the emphasis government departments, regulatory organisations and industry representing bodies in New Zealand place on managing POPs. Adoption of the proposed revisions into a modified Guideline will provide the first example of the acceptance of EOCs as organic contaminants of concern in New Zealand by a significant industry body (Water New Zealand, 2015).

7.3.3 Water Quality Guidelines

ANZECC

Recommended guideline values for a number of EOCs are contained within the National Water Quality Management Strategy ANZECC guidelines for freshwater and marine waters (ANZECC, 2000) (Table 7-3). Wherever possible the chemical-specific guideline values for toxicants have been derived according to risk assessment principles. The values are not intended for use as simple pass/fail criteria. Instead, they are considered to be trigger values which, if exceed, may initiate a decision-tree process that allows a guideline value to be assessed and tailored for the environmental conditions of a specific locality or region.

Table 7-3. Fresh and marine water quality guidelines (95% level of species protection) for EOCs recommended in the ANZECC water quality guidelines (ANZECC, 2000)

Chemical	Trigger value (µg/L) Freshwater	Trigger value (µg/L) Marine
nonylphenols	0.1 [A]	1.0 [B]
dimethylphthalate	3700 [C]	3700 [B]
diethylphthlate	1000 [A]	900 [D]
di-n-butyl phthalate	35 [A]	25 [B]
di-2-(ethylhexyl)phthalate	1 [A]	1 [B]
chlorpyrifos	0.01 [E]	0.009 [F]
diuron	0.20 [A]	1.8 [B]
glyphosate	1200 [C]	370 [B]
Linear alkylbenzene sulfonates (LAS)	280 [E]	0.1 [B]
Alcohol ethoxylated sulphates (AES)	650 [E]	650 [B]
Alcohol ethoxylate surfactants (AE)	140 [E]	140 [B]

[A] Low reliability trigger value for freshwater (µg/L), indicative interim working level only
[B] Low reliability trigger value for marine water (µg/L), indicative interim working level only
[C] Moderate reliability trigger value for freshwater (µg/L)
[D] Moderate reliability trigger value for marine water (µg/L), indicative interim working level only
[E] High reliability trigger value for freshwater (µg/L)
[F] High reliability trigger value for marine water (µg/L)

ANZECC guidelines released in 2000 are currently being reviewed and updated (Warne et al., 2014). A technical review (Batley et al., 2014) stated:

> *"Canadian WQGs (CCME, 2007) admit traditional endpoints (i.e. growth, reproduction, and survival), as well as non-traditional endpoints (e.g. behaviour, predator avoidance, swimming ability, swimming speed, etc.) and physiological/biochemical changes, including endocrine-disrupting ability, if their ecological relevance can be demonstrated, i.e. whether the non-traditional endpoints influence a species' ecological competitiveness and lead to an ecologically relevant negative impact (i.e. they affect traditional endpoints).*
>
> *In the revised method, non-traditional endpoints such as biochemical and physiological responses are admissible for use in GV derivation, but only*

those based on in vivo testing, i.e. data from in vitro tests cannot be used, and where their ecological relevance can be demonstrated. Non-traditional endpoints, including those for mutagenicity and genotoxicity, that have not had their ecological relevance unambiguously demonstrated, should only be used as an additional line of evidence in weight-of-evidence (WOE) based risk assessments. An argument for the inclusion of non-traditional endpoints can be made by the developer of a proposed GV, but the decision on whether it unambiguously demonstrates ecological relevance will need to be verified by through an independent review process."

This suggests the next series of guidelines by ANZECC will not include non-traditional effects and that these are still some way off.

EU Marine Framework Directive

The EU Marine Directive was adopted in 2008 by the European Union to protect the marine environment across Europe (European Commission, 2008a). The aim of the Marine Directive is to achieve *Good Environmental Status* of marine waters in the EU by 2020. While EOCs are not directly mentioned in the Marine Framework strategy, two of the descriptors of good environmental status are relevant for EOCs:

- Descriptor 8. Concentrations of contaminants are at levels not giving rise to pollution effects;
- Descriptor 9. Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards.

EU Water Framework Directive

The EU Water Framework Directive was established in 2000 and a first list of priority substances was established that presented a significant risk to or via the aquatic environment.

The list has undergone iterations and the current directive (Directive 2013/39/EU) (European Commission, 2013a) has identified a number of EOCs (Table 7-4) as priority substances (of which some have been afforded a priority hazardous status[32]), and derived environmental quality standards (EQS) for some EOCs in surface waters (Table 7-5).

[32] Among those priority substances, certain substances have been identified as priority hazardous substances for which Member States should implement necessary measures with the aim of ceasing or phasing out emissions, discharges and losses (European Commission, 2008b).

Table 7-4. EU WFD priority substances (European Commission, 2013a)

EOC	Acronym	Identified as priority hazardous substance[1]
Brominated diphenylethers	BDEs	Yes
Chlorpyrifos		No
Di(2-ethylhexyl)phthalate	DEHP	Yes
Diuron		No
Isoproturon		No
Nonylphenols	NPs	Yes
Tributyltin compounds	TBTs	Yes
Cypermethrin		No
Perfluorooctane sulfonic acid and its derivatives	PFOS	Yes
Hexabromocyclododecanes	HBCD	Yes

[1] EU Member States should implement necessary measures with the aim of ceasing or phasing out emissions, discharges and losses.

Table 7-5. EU Environmental Quality Standards (European Commission, 2013a)

	Inland surface waters		Other surface waters		
EOC	AA-EQS (µg/L)	MAC-EQS (µg/L)	AA-EQS (µg/L)	MAC-EQS (µg/L)	Biota (µg/kg, ww)
BDEs		0.14		0.014	0.0085
Chloropyrifos	0.03	0.1	0.03	0.1	
DEHP	1.3	NA	1.3	NA	
Diuron	0.2	1.8	0.2	1.8	
Isoproturon	0.3	1	0.3	1	
Nonylphenols	0.3	2	0.3	2	
Octylphenol	0.1	NA	0.01	NA	
Tributyltin compounds	0.0002	0.0015	0.0002	0.0015	
PFOS	6.5×10^{-4}	36	1.3×10^{-4}	7.2	9.1
Cypermethrin	8.0×10^{-5}	6.0×10^{-4}	8.0×10^{-6}	6.0×10^{-5}	
HBCD	0.0016	0.5	0.0008	0.05	167

AA = Annual Average; MAC = Maximum Allowable Concentration
Water concentrations µg/L; biota concentrations µg/kg

The EU has also established a watch list of 3 EOCs - diclofenac, 17α-ethinylestradiol, and 17β-estradiol - for which monitoring data are to be gathered for the purpose of supporting future prioritisation exercises.

North America

Within North America, water quality criteria for protection of aquatic life have been established for a limited number of EOCs on the basis of acute and/or chronic effect endpoints (Table 7-6).

Table 7-6. North American Water Quality guidelines for protection of aquatic life

	Freshwater		Saltwater	
	CMC[1] (acute) (µg/L)	**CCC[2] (chronic) (µg/L)**	**CMC[1] (acute) (µg/L)**	**CCC[2] (chronic) (µg/L)**
USA (USEPA, 2014b)				
Chloropyrifos	0.083	0.041	0.011	0.0056
Nonylphenol	28	6.6	7	1.7
Parathion	0.065	0.013		
Canada (CCME, 2011)				
Chloropyrifos	0.02	0.002		0.002
DEHP	No data	16	No data	Insufficient data
DBP	No data	19	No data	Insufficient data
DOP	No data	Insufficient data	No data	Insufficient data
Glyphosate	27,000	800	NRG[2]	NRG[2]
Nonylphenol and its ethoxylates	No data	1	No data	0.7
Permethrin	No data	0.004	No data	0.001
Tributyltin	No data	0.008	No data	0.001
Triphenyltin	No data	0.022	No data	No data

[1] The Criteria Maximum Concentration (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. (i.e., an acute guideline).

[2] No recommended guideline.

[2] The Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. (i.e., a chronic guideline).

Norway

The Norwegian Pollution Control Authority revised their guideline for classification of contaminants in seawater in 2007 and extended the guidelines to cover 50 compounds including 11 EOCs (Bakke et al., 2010) (Table 7-7). These classifications are based on their toxicity to aquatic organisms and their potential impacts on human health.

Table 7-7. Norwegian classification of EOCs in seawater (Bakke et al., 2010)

EOC	I Background	II Good	III Moderate	IV Bad	V Very bad
SCCP		<0.5	0.5-1.4	1.4-2.8	>2.8
MCCP		<0.1	0.10-0.59	0.59-1.2	>1.2
Octylphenol		<0.12	0.12-0.27	0.27-1.3	>1.3
Nonylphenol		<0.33	0.33-2.1	2.1-4.1	>4.1
Bisphenol A		<1.6	1.6-11	11-110	>110
TBBPA		<0.052	0.052-0.9	0.9-9	>9
PBDE		<0.53	0.53-1.4	1.4-2.8	>2.8
HBCD		<0.31	0.31-1.1	1.1-2.2	>2.2
PFOS		<25	25-72	72-360	>360
Diuron		<0.2	0.2-1.8	1.8-3.6	>3.6
Irgarol		<0.008	0.008-0.05	0.05-0.25	>0.25

Units are µg/L

SCCP short-chained (C10-13) polychlorinated paraffins, MCCP middle-chained (C14-17) polychlorinated paraffins, TBBPA tetrabromobisphenol A, PBDE pentabromodiphenylether, HBCD hexabromocyclododecane, PFOS perfluorooctane sulfonate

7.3.4 Drinking water limits

United States

Drinking water limits have been developed for PFOS and PFOA for various states in the US. In Minnesota the drinking water limit for PFOA and PFOS is 0.3 µg/L while in North Carolina and New Jersey the limit for PFOA is 0.63 µg/L and 0.04 µg/L respectively (Minnesota Department of Health, 2008).

Netherlands

The Dutch National Institute for Public Health and the Environment (RIVM) has derived environmental risk limits for PFOS in fresh and marine water (Table 7-8) (Moermond et al., 2010).

Table 7-8. Dutch environmental risk limits for PFOS (Moermond et al., 2010)

Environmental Risk Limit	MPC	MAC_{eco}	NC	SRC_{eco}
Freshwater	6.5×10^{-4}	36	6.5×10^{-6}	930
Surface water intended for drinking water abstraction	0.53			
Marine water	5.3×10^{-4}	7.2	5.3×10^{-6}	930

Units are μg/L; MPC maximum permissible concentration; MAC_{eco} maximum acceptable concentration for ecosystems; NC negligible concentration; SRC_{eco} serious risk concentration for water ecosystems.

7.4 Initiatives to remove or reduce EOCs of concern

7.4.1 General POPs

The Stockholm Convention is an international environmental treaty which was signed in 2001 to protect human health and the environment from persistent organic pollutants (POPs). Parties to the convention (New Zealand ratified the convention in 2004) must take measures to:

- *Eliminate* the production and use of the chemicals listed under Annex A;
- *Restrict* the production and use of the chemicals listed under Annex B;
- Take measures to reduce or eliminate releases from *unintentional* production (Annex C).

Many legacy POPs (e.g. dieldrin, PCBs, chlordane) are listed under Annex A, while DDT is listed under Annex B. Annex C includes polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) and PCBs.

The list has been amended since 2001 to include some EOCs. In 2009, four brominated diphenyl ethers (BDEs) [hexabromodiphenyl ether and pentabromodiphenyl ether, the main components of commercial octabromodiphenyl ether; tetrabromodiphenyl ether and pentabromodiphenyl ether, the main components of commercial pentabromodiphenyl ether] were listed as POPs in Annex A. Hexabromobiphenyl was also included in Annex A in 2009 (UNEP, 2009). In 2013, Annex A was amended to include the flame retardant hexabromocyclododecane (HBCD) (UNEP, 2013).

Perfluorooctanesulfonic acid (PFOS), its salts and perfluorooctanesulfonyl fluoride (PFOSF) are man-made fluorosurfactants and global pollutants. They were added to Annex B in 2009 (UNEP, 2009).

7.4.2 Specific EOCs

Triclosan

A risk assessment of triclosan (TCS) by the Norwegian Scientific Committee for Food Safety, concluded: *"Widespread use of triclosan, including use in cosmetic products, selects for development of triclosan resistance"* (Norwegian Scientific Committee for Food Safety, 2005). In 2005, an expert panel convened by the United States Federal Drug Agency (FDA) concluded the use of antiseptics does not provide a measurable health benefit to consumers.[33] This assessment has not changed in the intervening years and late 2013 the FDA issued notice to industrial producers of its intent to restrict the use of TCS in consumer products.

These ongoing concerns have led to restrictions on the use and sale of products containing TCS and voluntary removal of TCS from consumer products by some manufacturing companies, including:

- A ban of the sale of liquid soaps containing TCS in state of Minnesota by 2017;
- Pending legislation to control the use of TCS in the State of New York;
- A ban on the use of TCS in textiles, leather and rubber, paints or plastic films by the European Commission;
- The Canadian government classifying TCS as toxic to the environment in 2014. Designating a chemical as toxic under the Canadian Environmental Protection Act triggers a process to find ways to curtail a chemical's use and for TCS this could extend to a ban in personal-care products;
- The decision by Proctor and Gamble, Johnson and Johnson, and Avon to remove or phase out triclosan in products they manufacture.

In New Zealand TCS currently has EPA approval status in the cosmetic products group standard, with a maximum authorised concentration of 0.3 percent.[34]

Bisphenol A

Regulations on the use of bisphenol A (BPA) have been aimed at reducing human and in particular babies' exposure to BPA. Canada, in 2010, was the first country to prohibit the

[33] http://www.fda.gov/ohrms/dockets/ac/05/minutes/2005-4184M1.pdf

[34] http://www.epa.govt.nz/publications/gs-cosmetic.pdf

use of polycarbonate in baby bottles.[35] The European Union banned the use of BPA in baby bottles in 2011,[36] and the US FDA prohibited the use of BPA in baby bottles and sippy cups in 2012[37] and infant formula packaging in 2013.[38]

In France, BPA was banned in food products aimed at children less than three years old (2013) and in all food containers (2014). From 2015, the manufacture, import, export and marketing of all food containers including BPA is banned by the French Senate.

The use of BPA in cans containing food for children under the age of three has been banned in Sweden since 2012.

In New Zealand BPA currently has EPA approval status.[39]

Glyphosate

The International Agency for Research on Cancer has recently classified glyphosate as *probably carcinogenic to humans* (Group 2A).[40] Several countries including the Netherlands, Bermuda, France and Sri Lanka have prohibited over the counter sales of glyphosate. Weed species have developed resistance to glyphosate and as a result the EPA will require a weed resistance management plan for glyphosate.

In New Zealand, glyphosate is on the EPA's Chief Executive Initiated Reassessment Programme list. EPA are actively monitoring its status and international developments and a future reassessment may be initiated if considered relevant to New Zealand.[41]

Neonicotinoid pesticides

Concerns have been raised over the effects of neonicotinoid pesticides on bees and aquatic insects. The EU is restricting the use of three neonicotinoid pesticides; clothianidin,

[35] http://www.chemicalsubstanceschimiques.gc.ca/challenge-defi/batch-lot-2/bisphenol-a/bpa-risk_hazard-eng.php

[36] http://europa.eu/rapid/press-release_IP-11-664_en.htm

[37] https://www.federalregister.gov/articles/2012/07/17/2012-17366/indirect-food-additives-polymers

[38] https://www.federalregister.gov/articles/2013/07/12/2013-16684/indirect-food-additives-adhesives-and-components-of-coatings

[39] http://www.epa.govt.nz/search-databases/Pages/ccid-details.aspx?SubstanceID=4763

[40] http://www.iarc.fr/en/media-centre/iarcnews/pdf/MonographVolume112.pdf

[41] http://www.epa.govt.nz/hazardous-substances/pop_hs_topics/glyphosate_learn/Pages/Glyphosate_regulation.aspx

imidacloprid and thiametoxam for two years from 2013 to 2015 (European Commission, 2013b). Ontario, in Canada, introduced new regulations from July 2015 to reduce the use of neonicotinoid pesticides.[42]

In New Zealand, the use of neonicotinoid insecticides has been strictly controlled for many years, including special measures to protect bees. EPA are keeping a watching brief on neonicotinoid insecticides and may initiate a re-assessment if there was evidence that they were causing harm in New Zealand.[43]

Nonylphenols

In 2014, the USEPA proposed a significant new use rule (SNUR)[44] under the Toxic Substances Control Act for four nonylphenols (NPs) and eleven nonylphenol ethoxylates (NPEOs). The SNUR would require the EPA to be notified 90 days prior to manufacture (including import) or processing of these 15 chemicals for a significant new use.
In 2003 the EU restricted the concentration of NPs and NPEOs to less than 0.1 percent in products used for cleaning, processing of textiles and leather, metal working, pulp and paper manufacture, cosmetics, personal care products and pesticides (European Commission, 2003).

In June 2015, the European Chemicals Agency (ECHA) recommended branched and linear 4-nonylphenol ethoxylates should be included on the list of substances in Annex XIV to REACH.[45] As such 4-nonylphenol ethoxylate has been classified as a toxic chemical and added to the 'authorisation list' of substances that should be banned for use in the EU, except in specially licensed cases.

In New Zealand, nonylphenol ethoxylates have current EPA approval (with controls).[46]

Flame retardants

Certain BDEs and (hexabromocyclododecane) HBCD have been added to Annex A (elimination) of the Stockholm Convention (section 7.4.1), however other flame retardants are raising concerns.

---

[42] http://news.ontario.ca/ene/en/2015/06/regulating-neonicotinoids.html

[43] http://www.epa.govt.nz/Publications/EPA_neonicotinoid_insecticides_information_sheet_2015.pdf

[44] http://www.epa.gov/oppt/newchems/pubs/cnosnurs.htm

[45] http://echa.europa.eu/view-article/-/journal_content/title/echa-proposes-15-substances-for-authorisation

[46] http://www.epa.govt.nz/search-databases/Pages/controls-details.aspx?SubstanceID=14780&AppID=3287

In the European Union, the alkylphosphate flame retardant - tris(2-chloroethyl)phosphate - is included on the European Chemicals Agency List of substances of very high concern for authorisation of inclusion on the list of substances in Annex XIV to REACH.

In the US, concern regarding the toxicity of flame retardants has resulted in proposals to ban certain flame retardants from upholstered furniture and children's products, and review the safety of all flame retardants. A legislative bill before the US Senate would restrict the content of ten specified flame retardants in children's products and upholstered furniture to 1000 ppm. The Council of the District of Columbia has extended this to prohibit the use of any of nine specified flame retardants in children's products and upholstered furniture beginning 1st July 2016. The flame retardants in question that are classified as EOCs include:

- 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB)
- Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (TBPH)
- Chlorinated paraffins
- Decabromodipheyl ether (DecaBDE)
- Hexabromocyclododecane (HBCD)
- Tetrabromobisphenol-A (TBBPA)
- Tris(1-choro-2-propyl)phosphate and Tris(2-choro-2-methylethyl)phosphate (TCPP)
- Tris (1,3,dichloro-2-propyl)phosphate (TDCPP)
- Tris(2-chloroethyl)phosphate (TCEP).

The Washington State Department of Ecology has also called for bans on the use of this range of flame retardants in children's products and upholstered furniture in the US.

Continued concern amongst consumers regarding the safety of flame retardants in upholstered furniture led to Ashley Furniture - the largest manufacturer of and retailer of furniture in the US - banning the use of toxic flame retardants in all of their furniture from 1st January 2015.

We are unaware of any initiatives to remove or reduce flame retardants in New Zealand.

Phthalates

In 2005, the EU restricted the use of six phthalates (DEHP, DBP, BBP, DINP, DIDP and DNOP) to concentrations not exceeding 0.1 percent in toys and childcare articles.[47] The Canada Consumer Protection Act Pthalate regulations also restrict the concentration of phthalates in children's toys.[48]

In addition, bis(2-ethylhexyl)phthalate (DEHP), dihexyl phthalate (DHP), diisobutyl phthalate (DIBP), and benzylbutyl phthalate (BBP) are included on the European Chemicals Agency List of substances of very high concern for authorisation of inclusion on the list of substances in Annex XIV to REACH. This is a first step in the process of banning or significantly reducing the use of these chemicals.

In June 2015, the European Chemicals Agency (ECHA) also recommended that seven additional plasticisers (six of which are phthalates) should be included on the list of substances in Annex XIV to REACH.[45] The plasticisers were:

- Diisopentylphthalate;
- 1,2-benzenedicarboxylic acid di-C6-8-branched alkyl esters;
- 1,2-benzenedicarboxylic acid di-C7-11--branched and linear alkyl esters;
- 1,2-benzenedicarboxylic acid dipentyl branched and linear alkyl esters;
- Bis(2-methoxyethyl) phthalate;
- Dipentyl phthalate;
- n-pentyl-isopentyl phthalate.

We are unaware of any initiatives to remove or reduce phthalates in New Zealand.

Chlorpyrifos

From a re-assessment of 28 organophosphate and carbamate-based insecticides in 2013 by EPA, new measures were put in place to manage risks of these pesticides. From 1 July 2015, only specially-qualified people will be able to buy and use chlorpyrifos.

[47] http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32005L0084&from=en

[48] http://www.hc-sc.gc.ca/cps-spc/pubs/indust/toys-jouets/index-eng.php#a345

In January 2016, EPA revoked approval for 18 veterinary medicine and insecticide products containing carbaryl, chlorpyrifos and diazinon.[49] One liquid product containing 1.3 percent carbaryl was approved with controls. A three year phase out period (until 28 February 2019) has been put in place.

With these controls in place, (i.e. proper use and disposal) it is likely that chlorpyrifos concentrations will reduce significantly in the future.

7.5 Summary of current and/or proposed regulatory limits for EOCs

Regulatory bodies around the world are starting to take a considerable amount of action regards restrictions or bans on selected EOCs, with many more placed on watch lists for future assessment.

Guidelines for EOCs - predominantly in water, but sediment guidelines are starting to be developed - are being set in the EU and North America for some of the more commonly known EOCs, including:

- Flame retardants (BDEs, HBCD);
- Phthalate plasticisers;
- Surfactants (alkylphenols, PFOS);
- Antifouling agents (diuron, isoproturon, irgarol);
- Pesticides (chlorpyrifos, glyphosate, permethrins).

Within New Zealand, ANZECC have water quality guidelines for some EOCs (nonylphenols, phthalates, chlorpyrifos, diuron, glyphosate, alkyl surfactants). However many guidelines have low to medium reliability, so are considered indicative only. ANZECC have acknowledged EDCs (but not other EOCs with different modes of action) in their revisions and biosolid guidelines are being developed for some EOCs.

There are two points of discussion on the above lists. Firstly, the antifouling agents diuron and isoproturon are not new generation pesticides but are considered EOCs as, with the ban on tributyltin (TBT) compounds, they have found a new use, with potential for unknown effects. In 2013 the EPA reassessed antifouling paints and declined approval for irgarol and allowed the use of diuron with controls until 2017. Secondly, chlorpyrifos has been restricted within New Zealand for use by registered pest controllers only, so its use will decrease as these controls are implemented. As such, a strong case can be made to

[49] http://www.epa.govt.nz/search-databases/Pages/applications-details.aspx?appID=APP202098

include some antifouling agents in new monitoring programmes (with the exception of irgarol), but chlorpyrifos may be considered a reduced future risk.

Other EOCs which have not had regulatory limits set but are being subjected to removal or reduction of their use are triclosan, bisphenol A and neonicotinoid pesticides. Although there have been no specific measures to regulate these in NZ, as producers of products containing these compounds have voluntarily withdrawn them, their use is likely to decrease in New Zealand over time.

8.0 Monitoring strategies

When undertaking a new endeavour (such as a new monitoring programme), it is useful to obtain information from appropriate sources so as not to “re-invent the wheel”. The field of EOCs is rapidly advancing however comprehensive monitoring strategies are not widely available in the literature. Although we were not able to obtain strategies for sediment monitoring programmes for EOCs directly, overarching monitoring strategies are available that include sediment monitoring (Section 8.1). More specific strategies to monitor bioavailable EOCs (Section 8.2) and rank EOCs for fate assessment (Section 8.3) are covered.

8.1 USEPA Columbia River Basin Strategy

In 2005, USEPA joined with federal, state, tribal, and local governments, industry, and nonprofit partners to form the Columbia River Toxics Reduction Working Group. The goal was to reduce toxics in the Columbia River basin, an important watershed contaminated with a variety of toxic contaminants as a result of human activities, including urban settlement and development, agriculture, transport and recreation.

One initiative from the Working Group was to develop and implement a working plan for chemicals of emerging concern (CECs, but for purposes of this report they are effectively EOCs), in collaboration with USGS and other organisations and interest groups.

Recent sampling efforts had been undertaken to better characterize the occurrence and impacts of EOCs on the aquatic and terrestrial ecosystems in the basin however it was acknowledged that they did not know the impacts and a research and monitoring plan was required. A research and monitoring strategy focusing on EOCs was produced (USEPA, 2014a), providing a blueprint for how a monitoring programme should be developed.

The strategy contained the following elements:

1. Conceptual models of potential exposure and effects in the Basin to more accurately understand;
    a. Sources;
    b. Fate and transport;
    c. Foodweb interactions.
2. A list of EOCs known to occur in the Basin and an example of an EOC prioritization plan;
    a. PBDEs (water, sediment and tissues);
    b. Estrogens (through vitellogenin induction in fish and EDCs in WWTP

effluent);

   c. PPCPs (WWTP effluent, river water and sediments);
   d. Perfluorinated compounds (in bird eggs).

3. A description of known biological effects of EOCs;
   a. Reduced reproductive success;
   b. Increased stress, potentially due to bioaccumulation;
   c. Reproductive and genetic impacts;
   d. Long-term exposure and mixtures.
4. A description of known biological indicators of exposure to EOCs at various points in aquatic and terrestrial food webs;
   a. Enzymes involved in the metabolism of toxic contaminants, and serve as indicators of exposure,
   b. Biochemical or physiological responses such as changes in plasma chemistry or hormone levels,
   c. True injury that could have implications on the population level, such as impairment of growth or reproduction.
5. A summary including how research could be used to direct specific actions or policies.

Although certain general advice can be obtained from monitoring strategies such as that above, the situation for each environment is different, so considerations need to be made based on this. These include where to sample (taking into account various sources) and what to sample. This is covered in more detail in recommendations (section 11.0).

Although the focus of this review is on sediment monitoring, strategies for monitoring the bioavailable fraction of EOCs are covered below.

8.2 Bioavailable EOCs

It is widely acknowledged that accurately determining the ‘bioavailable’ proportion of ‘total’ contaminant concentrations is important as this is the component that directly affects ecosystem health. As estimations based on ‘total’ concentrations and geochemical properties, such as total organic carbon (TOC), are more complex than originally thought and difficult to quantify (Ghosh et al., 2014), it is preferable to measure ‘bioavailable’ concentrations directly. Previously this has been achieved by use of biota monitoring, however due to challenges (i.e. cost, mortality, species and seasonal variability), there has been a recent shift towards developing passive sampling devices (PSDs) to replace biota. Development of both biota and PSD methods for analysis of EOCs is summarised below.

8.2.1 Biota

In 2009, the National Oceanic and Atmospheric Administration (NOAA) reviewed the goals of the Mussel Watch Programme (run since 1986) and pressed for a strategy to monitor unregulated chemicals to develop an early warning network of EOCs. California was selected as a demonstration area and a list of EOCs was developed based on published research and pilot studies. It was also decided to continue with metal and legacy contaminants to ensure maintenance of historical records (Bricker et al., 2014). Native mussels (*Mytilus* spp.) from 68 stations, stratified by land use and discharge scenario, were collected in 2009-10 and analysed for 167 individual pharmaceuticals, industrial and commercial chemicals and current use pesticides. Passive sampling devices (PSDs) and caged mussels were co-deployed to expand the list of EOCs, and to assess the ability of PSDs to mimic bioaccumulation by *Mytilus* (Maruya et al., 2014).

The seven classes of ECs measured were alkylphenols, PPCPs, PBDEs, other flame retardants, current use pesticides, PFCs, and single walled carbon nanotubes. Of the 167 individual EOCs analysed, 98 percent were infrequently detected in mussels. Alkylphenol, PBDE, and PFC concentrations in mussels increased with urbanization and proximity to stormwater discharge and pesticides exhibited higher concentrations at agricultural stations. These results suggested that certain compounds; for example, alkylphenols, the antibiotic lomefloxacin, and PBDEs, were appropriate for inclusion in future coastal bivalve monitoring efforts. This was based on maximum measured concentrations >50ng/g dry weight and detection frequencies >50 percent. Other compounds, for example PFCs and HBCD, were also suggested for inclusion due to >25 percent detection frequency and potential for biomagnification (Dodder et al., 2014).

8.2.2 Passive sampling devices

Passive sampling devices (PSDs) have gained recent popularity for measurement of bioavailable contaminant concentrations due to perceived superiority to biota. PSDs offer significant advantages over biota sampling. They are significantly cheaper to deploy; do not suffer from mortality or environmental variability, such as species, seasonal, and condition variability; and they do not carry a potential existing body burden of contaminants. Despite these perceived advantages, there are still hurdles in implementing PSDs for monitoring purposes. This is due predominantly to a lack of information on the effects of environmental variables (for example flow, temperature, biofouling) on contaminant uptake kinetics, and difficulties in correcting for non-equilibrium conditions, when samplers are used in the equilibrium mode. There are many types of PSDs available (Greenwood et al., 2007; Vrana et al., 2005) and the type chosen depends on the physico-chemical properties of the EOC of interest.

Two separate studies, completed by the USGS (Alvarez et al., 2014) and the USEPA (Perron et al., 2013) provide insight into recent strategies in assessing PSDs for environmental monitoring of EOCs.

In the USGS study, three PSDs: Polar Organic Chemical Integrative Samplers (POCIS); Polyethylene Devices (PEDs); and Solid-Phase Microextraction (SPME) samplers were deployed at the same sites in Californian coastal waters as described above for the mussel study. POCIS samplers are hydrophilic so target more water-soluble EOCs, whereas the PEDs and SPMEs are hydrophobic and so target POPs, such as more traditional contaminants such as PAHs and PCBs, but also PBDEs. Seventy one chemicals (including fragrances, phosphate flame retardants, pharmaceuticals, PAHs, PCBs, PBDEs, and pesticides) were measured in at least 50 percent of the PSDs deployed. Comparison of results obtained by the PSDs and mussel tissues (Dodder et al., 2014), demonstrated a positive correlation for 25 and 26 chemicals in common for the PEDs and SPME, respectively. Diphenhydramine was the only common chemical out of 40 analysed in both POCIS and tissues detected at a common site (Alvarez et al., 2014).

In the USEPA study, the performance of PE, SPME and polyoxymethylene (POM) devices were evaluated for sampling dissolved concentrations of PBDEs and triclosan. PE and POM were found to effectively accumulate BDEs and triclosan from the water column while SPME was not effective (Perron et al., 2013).

Following these examples and in a NZ first study, PSDs were recently used to measure dissolved concentrations of representative EOCs (BDEs, wastewater markers), plus PAHs and heavy metals around Auckland and to assess whether they could replace shellfish for measurement of bioavailable concentrations. Results suggest PSDs would be excellent complementary techniques to biota and sediment monitoring, however more research is necessary before they can be implemented for regulatory purposes (Stewart et al, 2015).

8.3 Approaches for ranking EOCs to select representative marker/indicator compounds for monitoring and fate assessment

8.3.1 Wastewater markers

The significant number of individual EOCs released into the environment, combined with the high cost of analysis, means it is impossible to identify and analyse all of the individual chemicals that will be present. Instead researchers have focused on analysing specific EOCs.

Various criteria have been applied to identify and select indicator compounds for use in studies assessing the removal of EOCs during wastewater treatment and their fate in receiving environments. These include prioritising:

- Those commonly detected in wastewater effluent;
- High production/volume chemicals;
- Those with highest ecological/human health risk.

Examples of studies using each approach are described below.

Commonly detected EOCs

A refined approach to selecting indicator compounds was adopted in a WERF sponsored research project. Potential indicator chemicals were first identified by comprehensively reviewing over 100 peer-reviewed journal articles and identifying those chemicals present in secondary and tertiary treated wastewater effluents, and for which viable methods of analysis were available (Drewes et al., 2008).

The resulting comprehensive list of potential indicator chemicals was reduced by determining the detection ratio of the chemicals, defined as the ratio of the median reported concentration and limit of quantitation of the chemical. Compounds demonstrating a detection ratio greater than five were accepted. While this approach has certain limitations it effectively eliminated compounds that were not ubiquitously present in WWTP effluents, and/or those for which adequately sensitive measurement techniques were not available.

Using this assessment criteria a total of 33 chemicals with detection ratios greater than five were identified from those reported to occur in both European and North American studies (Table 8-1).

Table 8-1. Commonly detected EOCs with potential as WWTP effluent indicators

Indicator compound	Uses
Acetyl cedrene	Fragrance
AHTN	Polycyclic fragrance
Benzyl acetate	Fragrance/aroma
Benzyl salicylate	Fragrance/ UV filter
Carbamazepine	Anticonvulsant/mood stabiliser
Clarithromycin	Antibiotic
Clofibric acid	Metabolite of clofibrate
Diclofenac	Non-steroidal anti-inflammatory drug
EDTA	Preservative/chelation medicine
Erythromycin	Antibiotic
Estradiol	Steroid hormone
Estrone	Steroid hormone
g-Methyl ionine	Fragrance/aroma
Galaxolide	Polycyclic fragrance
Gemfibrozil	Lipid lowering medicine
Hexyl salicylate	Fragrance/aroma
Hexylcinnamaldehyde	Fragrance/aroma
Ibuprofen	Non-steroidal anti-inflammatory drug
Isobornyl acetate	Fragrance/aroma
Ketoprofen	Non-steroidal anti-inflammatory drug
Methyl dihydrojasmonate	Fragrance/aroma
Methyl salicylate	Fragrance/aroma /analgesic
Musk ketone	Nitromusk fragrance
Musk xylene	Nitromusk fragrance
Naproxen	Non-steroidal anti-inflammatory drug
Nonylphenol	Detergent/emulsifier/solubilizer
NTA (nitrilotriacetic acid)	Chelating agent/water softener
OTNE (iso-E-super)	Fragrance/aroma
p-t-Bucinal	Fragrance/aroma
Salicylic acid	Anti-inflammatory/food preservative
Sulfamethoxazole	Antibiotic
Terpineol	Fragrance/aroma
Triclosan	Anti-microbial

High production EOCs

An alternative approach to identifying indicator compounds bases the primary selection criteria upon the mass/volumes in which they are produced. It is logical that chemicals produced in more substantive mass or volume are more widely used, and are more likely to be released into the environment. Many consumer product chemicals are classified as

high production volume (HPV) chemicals by the USEPA and the EU. The USEPA classifies HPV chemicals as those manufactured in, or imported into, the United States in amounts equal to (or greater than) 0.5 million kg per year.

This approach was adopted in another WERF study that selected household chemicals from a total list of 720 HPV compounds within eight main domestic activities: auto products, inside the home, pesticides, home maintenance, personal care/use, pet care, arts and crafts, and landscape/yard (Drewes et al., 2009). This generated an extensive list of high-production-volume chemicals which were subjected to a subsequent ranking based on the environmental relevance and feasibility for analytical quantification of the primary selected chemicals. This exercise produced two-tiers of priority chemicals. The shortlist of 11 Tier 1 chemicals was classified as high-production-volume consumer products, which are likely to be present in domestic wastewater due to their physico-chemical properties and reported environmental fate. The 13 Tier 2 chemicals included chemicals below the high-production-volume threshold but frequently used in household products, and likely to be present in domestic wastewater due to their physico-chemical properties and reported environmental fate (Drewes et al., 2009).

In addition to the identified Tier 1 and 2 chemicals, triclocarban was subsequently added to the compound list as a model compound representing EOCs for which limited information is available, and linear alkylbenzene sulphonates were added as a model for complex multicomponent mixtures. The final selection of indicator compounds is summarised in Table 8-2

In addition to the selected household product indicator chemicals a set of specific indicator pharmaceutical chemicals was also selected on the basis they had been previously identified in WWTP effluents and subject to research studies (Table 8-3).

Table 8-2. Major EOCs associated with household waste: Tier 1 and Tier 2 and model compounds.

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

Propylparaben	Preservative, cosmetics, pharmaceuticals and food
Simazine	Herbicide and biocide
Trifluralin	Herbicide
Selected model compounds	
Linear alkylbenzene sulphonates	Surfactant, detergents, laundry powders
Triclocarban	Anti-bacterial in soaps, lotions, deodorants

Table 8-3. Selected indicator pharmaceutical compounds

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

Risk based strategies

A review of international literature undertaken by CSIRO Land and the Smart Water Fund in Australia identified a number of priority EOCs within domestic wastewater streams (Shareef et al., 2008). Steroid hormones, surfactants, alkylphenols, plasticisers, fragrances, antimicrobial agents, UV filters and pharmaceuticals were identified as priority contaminants of emerging concern for inclusion in future research projects and monitoring programmes (Table 8-4).

Table 8-4. Priority contaminants of emerging concern identified for inclusion in future monitoring programmes in Australia

Chemical Class	Compound
Plasticisers	Bisphenol-A
	Di(ethylhexyl)phthalate
Musk Fragrances	Galaxolide
	Tonalide
Antimicrobial Agents	Triclosan
	Triclocarban
Insect Repellents	DEET
UV Filters	4-MethylBenzylidene Camphor (MBC)
	Ethylhexyl Methoxy Cinnamate (EMC)
Pharmaceuticals	Carbamazepine
	Ibuprofen
	Naproxen
Antidepressants	Fluoxetine
	Fluoxamine
	Sertraline
Fluoroquinolone Antibiotics	Ciprofloxacin
	Norfloxacin
	Ofloxacin
Brominated Flame Retardants	Tetra BDE 47
	Penta BDE 99

Two recent US studies provided conservative risk-based methods for prioritizing EOCs for wastewater and environmental monitoring (Anderson et al., 2012; Diamond et al., 2010). Both studies used a panel of experts who reviewed published and unpublished information and expert opinion to assess the environmental risks of more than 500 EOCs. In both cases, risk was derived from consideration of the maximum concentration of an EOC reported in the environment and the greatest ecological effect (worse-case scenario). Ecological effect was defined either based on short-term or, where available, long-term toxicity test results or by predicting toxicity based on chemical structure (QSAR).

These studies identified high priority EOCs for inclusion in WWTP monitoring programmes in the US.

The study of Diamond et al. (2010) used three different priority approaches to arrive at a list of high priority trace organic chemicals (Table 8-5).

Except for the synthetic hormones and steroids, results of all three prioritization approaches yielded only a few pharmaceuticals of high priority. Using a risk-based prioritization approach, predicted chronic toxicity endpoints were more sensitive than

endpoints based on estrogenic activity for most EOCs. The authors acknowledged that the prioritization list was not necessarily intended to be viewed as a list of compounds to be monitored or for which water quality criteria should be developed. They stated the process of developing the list(s) was as important as the list(s) itself and the appropriate use of any resulting list(s) will depend largely on the goals of the user.

Table 8-5. Listed as High Priority Using the Three Prioritization Approaches Indicating for Each if it is an Endocrine Disrupting Compound (EDC), the Most Sensitive Organism Type, the Most Sensitive Endpoint Type

Compound	Class	EDC[1]	Most Toxic[2]	Most Sensitive Endpoint[3]
4-n-nonylphenol	Surfactant	N	Fish	Toxicity
4-Nonylphenol	Surfactant	N	Fish	Toxicity
Bis(2-ethylhexyl)adipate	Plasticizer	N	Fish	Toxicity
17α-ethynylestradiol	Pharmaceutical	Y	Daphnid	Endocrine Activity
Bis(2-ethylhexyl)phthalate	Plasticizer	N	Fish	Toxicity
Campesterol	Natural hormone/steroid		Fish	Toxicity[4]
Cholesterol	Natural hormone/steroid	N	Fish	Toxicity
Coprostanol	Natural hormone/steroid	N	Fish	Toxicity
Desmosterol	Natural hormone/steroid	NA[4]	Fish	Toxicity[4]
Di-*N*-octyl phthalate	Plasticizer	N	Fish	Toxicity
Epicoprostanol	Natural hormone/steroid	N	Fish	Toxicity
Galaxolide	Deoderizer/Fragrance	NA[4]	Fish	Toxicity[4]
HBCD	Flame retardant	NA[4]	Daphnid	Toxicity[4]
Mestranol	Pharmaceutical	Y	Fish	Endocrine Activity
Musk ketone	Deoderizer/Fragrance	NA[4]	Fish	Toxicity[4]
para-nonylphenol	Surfactant	NA[4]	Fish	Toxicity[4]
PBDE-209	Flame retardant	NA[4]	Fish	Toxicity[4]
Pentachlorophenol	Industrial Chemical	N	Fish	Toxicity[4]
β-sitosterol	Natural hormone/steroid	NA[4]	Fish	Toxicity[4]
Stigmastanol	Natural hormone/steroid	NA[4]	Fish	Toxicity[4]
Stigmasterol	Natural hormone/steroid	NA[4]	Fish	Toxicity[4]
Tamoxifen	Pharmaceutical	Y	Fish	Endocrine Activity
Tonalide	Deoderizer/Fragrance	NA[4]	Fish	Toxicity[4]

[1] Yes if EAV normalized to EE2 was greater than 0.001

[2] Based on ECOSAR ChV values

[3] Lesser of Minimum Toxicity Value and Probable Effect Concentration based on estrogenic activity

[4] No estrogenic activity data available

NA = Not Available

The study by Anderson et al. (2012) identified sixteen EOCs recommended for screening from WWTP effluent, while to assess environmental impacts, three receiving water scenarios were considered (Table 8-6):

- Scenario 1: a WWTP effluent-dominated inland (freshwater) waterway;
- Scenario 2: a coastal embayment that receives both WWTP effluent and stormwater discharge, and;
- Scenario 3: offshore ocean discharge of WWTP effluent.

For each EOC the measured or predicted environmental concentration was compared to the monitoring trigger level to derive a monitoring trigger quotient (MTQ). When the MTQ was less than 1.0, the potential risk associated with a EOC based on currently available information was assumed to not be great enough to require monitoring. When the MTQ was greater than 1.0, an EOC was assumed to have the potential to pose a risk and monitoring was recommended (Table 8-6).

8.3.2 Summary

There is no specific recommended procedure to identify candidate compounds or a defined list of EOC indicator compounds to use in such assessments and the final selection is often based on the availability of appropriate analytical instrumentation and methods of analysis.

Regardless of the different criteria applied to select indicator compounds a number of chemicals are commonly identified despite the specific selection criteria that have been applied. These include triclosan and other anti-microbial chemicals, flame retardants, surfactants, parabens, fragrances, steroid hormones, anti-inflammatory drugs, lipid regulating drugs and antibiotics.

Table 8-6. EOCs recommended for initial monitoring by scenario and environmental matrix (i.e., aqueous, sediment, tissue).[a,b]

Compound	Class	WWTP Effluent	Scenario 1 - Inland Waters (Aq)	FW Stream - Stormwater (Aq and Sed)[c]	Scenario 2 - Embayment (Aq)	Scenario 2 - Embayment (Sed)	Scenario 3 - Marine (Sed)	Tissue
Bis(2-ethylhexyl) phthalate	Plasticiser	M-O	NA	NA	NA	NA	M (3.8)	NA
Bisphenol A	Plasticiser	M–E/F	M (8.7)	M	M (2400)	NA	NA	NA
Bifenthrin	Pyrethroid insecticide	M-E/F	M (210)	M	M (750)	M (1500)	NA	NA
Butylbenzyl phthalate	Plasticiser	M-O	NA	NA	NA	NA	M (16)	NA
Permethrin	Pyrethroid insecticide	M-E/F	M (46)	M	M (46)	M (260)	NA	NA
Chlorpyrifos	Organophosphate insecticide	M-E/F	M (220)	M	M (220)	NA	NA	NA
Estrone	Steroid horomone	M-E/F	M (12)	M	M (12)	NA	NA	NA
Ibuprofen	NSAID	M-F	M (10)	M	NA	NA	NA	NA
17-β estradiol	Steroid hormone	M-E/F	M (4.2)	M	M (4.2)	NA	NA	NA
Galaxolide (HHCB)	Polycyclic musk	M-E/F	M (4.0)	M	M (4.0)	NA	NA	NA
Diclofenac	NSAID	M-F	M (2.3)	M	NA	NA	NA	NA
p-Nonylphenol	Industrial surfactant	M-O	NA	NA	NA	NA	M (30)	NA
BDE-47 and 99	Industrial flame retardant	M-E/F/O	NA	M	NA	M (5700)	M (15)	M (850)
PFOS	Fluorosurfactant	M-E/F/O	NA	M	NA	M[d]	M[d]	M (1.8)
Triclosan	Antimicrobial	M-F	M (2.0)	M	NA	NA	NA	NA

[a] Modified from Anderson, et al. 2012.

[b] Monitoring Trigger Quotient values appear in parentheses.

[c] Addresses data gap on relative contributions of stormwater discharge and WWTP effluent.

[d] Addresses route of exposure and data gap for estimation of Biota-Sediment Accumulation Factors for tissue.

M = include in monitoring programme (discharges to: E = embayments, F = freshwater, O = ocean waters); NA = not applicable.

9.0 Sampling and archiving of EOCs

9.1 Sampling

All sampling should follow best practise. The greatest chance of error is from cross contamination or introduction of EOCs from unintended sources, for example use of soft plastic utensils and/or bags that have the potential to leak plasticisers. There is also the potential for cross contamination from personal care products and clothing worn by sampling personnel.

All equipment should be cleaned with ultratrace level solvents and high purity water prior to sampling and between sampling events. All bottles should be glass (preferably amber) and thoroughly pre-cleaned before use.

Sediment sampling should be in accordance with the 2009 procedure used to sample for EOCs from Auckland sediments (Stewart et al., 2009). The full procedure is replicated in Appendix B, however advice should be obtained before embarking on significant sampling. Shellfish sampling should be performed by standard council shellfish collection procedures. Procedures for passive sampling devices (PSDs) are constantly developing. Unlike sediment and water sampling, but akin to deployed mussels, PSDs are placed *in-situ* for a defined period of time and then retrieved. Advice should be obtained before considering using PSDs. Detailed sampling procedures for PSDs currently being assessed in Auckland are available from Stewart et al. (2015), or alternatively from similar studies in the United States (for example: Alvarez et al., 2014; Perron et al., 2013).

All sampling should incorporate an appropriate schedule of quality control including sample blanks (for example, acid washed sand, blank PSDs) and equipment blanks, replicate samples and chain of custody.

9.2 Archiving

There do not appear to be any established guidelines for archiving of samples for future EOC analysis, however a precautionary (best practise) approach is recommended. Some information on stability of archived biosolids provides information to corroborate current best practise approach to archiving of sediments.

110 biosolid samples collected in 2001 by USEPA were archived frozen at -20 °C. Mega composite samples (5) were prepared on thawed biosolid material for analysis of PPCPs in two separate studies (Chari and Halden, 2012; McClellan and Halden, 2010). The time

in storage was 7 and 9 years, for the 2010 and 2012 studies, respectively. McClellan and Halden (2010) acknowledged that prolonged storage of samples between sampling event and analysis may have allowed for the chemical degradation of labile analytes to occur and that due to pooling of a large number of samples, analytes occurring infrequently and at low concentrations may have been diluted out to below the detection limit. They concluded that the mean concentrations of all analytes show no statistically significant difference to original USEPA data and therefore, the prolonged storage did not impair the detection of multiple analytes at elevated concentrations in archived samples.

The Chari and Halden study 2 years later (2012), extended the PPCP analyte list further and also stated that the datasets for 30 PPCPs in common between the two studies were statistically indistinguishable, suggesting little degradation of PPCPs had occurred during storage of biosolid samples over 9 years at -20°C.

These two studies of PPCPs in archived biosolids suggest a best practise procedure of archiving and storing sediments samples at -20°C would be sufficient for long term stability of EOCs, bearing in mind biosolids have markedly higher biological activity than marine sediments and PPCPs are generally the class of EOCs most susceptible to degradation.

In the absence of definitive information, archiving of samples for future analysis of EOCs should follow current good practise to reduce the chance to degradation over time. The likely routes to degradation are microbial and enzymatic activity, light, oxidation and potentially acidic or alkaline samples. Freeze drying sediment destroys microbial action and removes water that facilitates enzyme and pH activity. Storing sediment samples dry at room temperature, in airtight containers and in the absence of light is current practise and will reduce degradation. However, the effects of freeze drying on the subsequent extraction of EOCs would need to be thoroughly assessed beforehand to ensure the extractability of certain classes of EOCs (acidic compounds and antibiotic pharmaceuticals) are not irreversibly bound to sediment by the drying process. If space allows, storing at -20 °C would further reduce potential for degradation. Biota samples contain higher enzyme content and so should be freeze-dried and stored at -80 °C, as is currently good practise for analysis of POPs such as PAHs, OCPs, and PCBs.

10.0 New Zealand analytical laboratory capability

Analytical laboratories in New Zealand are continually evolving their suites of contaminants and capability currently exists for many EOCs. Although it is not logistically feasible for any laboratory to provide a service for all EOCs, methods for their analysis are considered non-routine and a fair amount of flexibility exists to "tailor" the suite to suite the application. While currently there no clear consensus on what EOCs to monitor, this is an advantageous position, as expertise and equipment is available so that currently unavailable EOCs can be rapidly developed, where there is a need. Validation of the methods would be a desirable future development, however this brings reduced flexibility to add new analytes. If a particular analyte or group of analytes are beyond the analytical capabilities of New Zealand labs then the option of overseas laboratories could also be explored.

10.1 Current analytical laboratory capabilities in New Zealand

Analyis of EOCs within New Zealand can be undertaken by a few analytical laboratories, with varying instrumentation, analytical suites and detection limits. The three main laboratories are:

- AsureQuality[50], who have capability to analyse a large number of EOCs in water, wastewater, sediment, biosolids and biota;
- Northcott Research Consultants, work with Plant and Food Research (NRC/Pand F) to provide a large suite of EOCs for analysis in water, wastewater, sediments and biosolids;
- Hill laboratories[51] have well established methods for analysis of a range of EOCs in sediments and water;
- Watercare Laboratory Services[52] offer analysis of plasticisers in soil and water.

Full analytical suites are provided in Appendix C. Expert advice should be obtained prior to proceeding with any significant analysis of EOCs. For example advice should be sought on how reliable the particular technique is and whether it can deliver ecologically relevant detection limits for the environmental matrix in question.

Analytica[53] are have advanced mass spectroscopy systems including high-resolution accurate mass, LC-MS/MS, GC-MS/MS, and ICP-MS instruments. Analytica provide

[50] http://www.asurequality.com

[51] http://www.hill-laboratories.com

[52] http://www.watercarelabs.co.nz

custom analyses to fit the market. At present they do not have methods established for analysis of EOCs in environmental matrices.

10.2 Current bioassay capability in New Zealand

Bioassays provide an important means to estimate the biological effects of mixtures of EOCs in environmental samples. The results of bioassay analyses of environmental samples provide a complimentary set of data to that obtained by trace chemical analysis methods, and can be very useful for interpreting the potential effects of trace chemical analysis data.

A limited number of laboratories provide bioassay analysis capability in New Zealand and have previous experience in their application for assessing the effects of EOCs. These laboratories are contained within Research Institutes and as such they are developing new bioassay testing formats with endpoints that are more appropriate for assessing the effects of EOCs. In comparison to current accepted bioassays these new generation bioassays focus on measuring chronic exposure endpoints (endocrine disruption, enzyme activity, metabolic profiling) and multi-generation effects. The laboratories within New Zealand that are able to provide appropriate test methods for assessing the potential effects of EOCs include Landcare and Cawthron.

Landcare Research Toxicology Laboratory in Lincoln provides a range of bioassay tests including in-vitro assays for assessing estrogenicity (MELN assay), androgenicity (PALM assay) and anti-estrogenicity and adrogenicity; cytochrome P450, thyroid disruption, and oxidative stress. Landcare Research also provide standardised *in-vivo* bioassays using earthworms to assess the toxicity (acute endpoint) of chemicals and their effect upon reproduction (chronic endpoint). The laboratory is also collaborating with Chinese research groups to develop molecular approaches to assessing toxicant impacts on earthworms.

NIWA offers a range of standard and custom designed toxicity tests for both freshwater and marine environments. These include acute and chronic tests on algae, bacteria, invertebrate and fish species.

The Cawthron Institute Toxicology Laboratory provides a range of acute and chronic tests for direct toxicity assessment of individual contaminants, or more complex mixtures and sample types. The standardised tests use a wide range of methods to cover all integration

[53] http://analytica.co.nz

levels (i.e. cellular (*in-vitro*), physiological (*in-vivo*), and whole organism responses) and at least three taxa and trophic levels (e.g. algae, mussel, copepod, fish). These include *in-vitro* bioassays to assess estrogenicity (MELN assay) and androgenicity (PALM assay), and anti-estrogenicity and adrogenicity; and cytochrome P450. In-vivo bioassays include the Zebra fish embryo toxicity test, *Paracorophium excavatum* amphipod acute toxicity test, copeopod acute toxicity test and chronic reproduction test, and freshwater and marine chronic algae toxicity tests.

10.3 Future capability efforts

AsureQuality and NRC/Pand F both have established methodologies for analysis of a wide range of EOCs in a range of environmental matrices, such as water, wastewater, biosolids and sediment. Furthermore, AsureQuality have developed methods for analysis of EOCs from POCIS and polyethylene passive sampling devices.

Both labs have indicated that if there was a future need to include any EOC not currently in their analytical suite, this is relatively fast and inexpensive to implement.

11.0 Summary and recommendations for future monitoring programmes

Despite continual impetus from researchers and interested parties, there is still no national strategy for EOCs within New Zealand. This is despite an ever increasing body of literature showing that EOCs are of great environmental and human health concern. Therefore we recommend the continual promotion of a national strategy, including identifying a champion from a government department or regional council to lead this.

This review has shown that research on EOCs is rapidly increasing internationally and within New Zealand and new information is becoming more available, especially with regards to fate and toxicity. As such, current information may quickly become obsolete, so it is recommended that a follow-up review is undertaken within 5 years.

A key data gap is the contribution of stormwater to marine sediment concentrations of EOCs. Internationally stormwater has been less well characterised than other potential sources of EOCs. When stormwater systems have been assessed with respect to EOCs, the focus has been on waterbodies receiving wastewater discharges or combined sewer overflows. The types and concentrations of EOCs within urban stormwater in New Zealand and overseas remain to be assessed.

11.1 Future monitoring programme

The significant number of individual EOCs released into the environment, combined with the high cost of analysis, means it is impossible to identify and analyse all of the individual chemicals that will be present. Instead researchers have either focused on analysing specific modes of action of EOCs (e.g. endocrine disruption, pharmaceuticals); individual compounds that are representative of specific classes of chemicals; or used strategies to look only at high production or commonly occurring EOCs, or those with highest ecological risk. The issue, from a SoE monitoring perspective, is that restricting monitoring of EOCs to specific classes or effects will likely result in the omission of other important chemical stressors and reduce the ability to examine synergistic or cumulative effects. Likewise, risk-based approaches to identify EOCs are based on assumptions, and no two approaches will provide the same answer.

Therefore, we consider the most appropriate and pragmatic monitoring strategy is to use a tiered approach. A first assessment (Tier 1) will aim to identify key EOC classes of concern through analysis of representative EOC “markers” at a larger number of sites (see below).

Refinement of EOC classes and sites can then be made based on the first assessment and future monitoring of only the most highly impacted sites (Tier 2) undertaken on this refined list. Further assessments of EOC bioavailability and non-lethal chronic (long-term) effects are recommended for the refined EOCs and sites (Tier 3).

Tier 1

Site selection

A re-assessment of the validity of current SoE monitoring sites (sediment, biota) with regards suitability for EOC monitoring should be undertaken prior to any sampling event. Site selection should include three types: “core”, “specific” and “reference”. “Core Sites” are those that have a large urban land use component and need to integrate the three major sources of EOCs (i.e sewage effluent, stormwater and landfill). This is necessary as many EOCs arise from multiple sources and their pathways to the marine receiving environment can be complex. “Specific Sites” are those that do not have a high urban land use component but integrate other sources of EOCs, such as rural marinas (antifouling agents) and high density swimming beaches (UV-filters). “Reference Sites” are those that are predominantly rural and as far as practical free from urban influence and drainage from septic tanks.

The number of sites selected should be sufficient to give satisfactory spatial coverage from which to assess the impact of urbanisation on EOC fate.

For QA/QC purposes, replicate collection and analysis should be undertaken at a minimum of 2 sites.

EOC selection

The core EOC “markers” selected for analysis (
Table 11-1) have been selected using a combination of criteria. These are also summarised as footnotes in
Table 11-1.

The core EOCs listed in
Table 11-1 are the most representative of their chemical class and cover the main sources (sewage, stormwater, landfill, recreation, and agricultural practises: see Section 2.2). Wastewater “markers” have been demonstrated to persist during sewage treatment (see Section 8.3.1), and so be subsequently released into receiving environments. Pesticides are released directly into aquatic environments without any treatment via urban or rural stormwater runoff.

Many of the chemicals have been detected in sediment within freshwater systems receiving WWTP effluents (Tremblay et al., 2013b) or within the marine receiving environment (Emnet, 2013; Stewart et al., 2014), which demonstrates they accumulate and persist in sediment. Many of these same chemicals have been detected in and observed to bioaccumulate within bivalves (Dodder et al., 2014). Many of these chemicals are included within other international research and/or monitoring programmes (see Chapter 8) which provides the opportunity for direct comparison between New Zealand derived and overseas data. Many of these EOCs are the subject of initiatives for removal or reduction (see Section 7.4). A number of these chemicals have guidelines against which levels can be compared (see Section 7.3).

The breadth of the classes, and individual chemicals, included in Table 11-1 is necessary to encompass the wide range of different chemicals that comprise EOCs and are released daily into estuarine environments.

Specific marker EOCs**Error! No bookmark name given.**are location and/or season specific. For example antifouling agents are likely only present at levels of concern within ports and marinas (Gadd and Cameron, 2012), while UV-filters are only likely to be present at popular swimming beaches in summer.

"Core Sites" and "Reference Sites" should be analysed for the full suite of EOCs in **Error! Reference source not found.**. "Specific Sites" should be analysed for relevant EOCs only (

Table 11-2. "Specific" list of "marker" EOCs recommended for initial phase (Tier 1) of sediment monitoring

Class	Representative EOC	CAS	Site	Reason[a]
Antifouling agents	Diuron	330-54-1	Port/Marina	1,5
	Isoproturon	34123-59-6	Port/Marina	1,4
UV-filter	Benzophenone-3	131-57-7	Beach	2,6

[a] 1 Initiative to remove. Stockholm Convention (POPs) or individual initiatives; 2 High production chemical; 3 Highest concentrations detected in urban marine receiving environment; 4 Knowledge gap (not previously monitored); 5 Previously detected in NZ marine sediments; 6 Persistent Bioaccumulative and Toxic (PBT).

Tier 2

Analyse sediment concentrations of the most highly impacted sites for the refined suite of relevant EOCs. Note, this list cannot be compiled until information from Tier 1 is incorporated.

Tier 3

Carry out further risk characterisation of most highly impacted sites by assessment of bioavailability of EOCs, through either passive sampling or biota procedures, or a combination of the two.

Carry out non-lethal chronic effects-based measurements and assessments of the most highly impacted sites on key receptor species.

This approach can also be tailored for sites or catchments influenced by rural or aquaculture activities.

i.e. marina sites for antifouling co-biocides (diuron and isoproturon) and beaches for the UV-filter, Benzophenone-3, unless they are also subject to other discharges such as wastewater or stormwater

Assessment

Identify which sites and EOCs are of most concern, based on either likely effects (when risk information is available) or most elevated concentrations of “markers” (when no risk data is available). The results from the assessment should provide useful information to define links between EOCs and land use types to inform management processes.

Refine the sites necessary for future monitoring to include only the most highly impacted sites.

Refine the initial suite of EOC “markers” based on information from above to include extra representatives of those EOC classes of most concern and remove EOCs of low concern.

Table 11-1. “Core” list of “marker” EOCs recommended for initial phase (Tier 1) of sediment monitoring

Class	Representative EOC[a,b]	CAS	Major Sources[c]	Reason[d]
Flame retardants	BDE47	5436-43-1	SEW,SW,LF	1,2,3,5,6
	BDE99	60348-60-9	SEW,SW,LF	1,2,3,5,6
	BDE209	1163-19-5	SEW,SW,LF	1,2,3,5,6
	TDCP	13674-87-8	SEW,SW,LF	1,2,4,6
	TPP	115-86-6	SEW,SW,LF	1,2,4,6
	TCPP	13674-84-5	SEW,SW,LF	1,2,4,6
Plasticisers	DEHP	117-81-7	SEW,SW,LF	2,3,5
	BBP	85-68-7	SEW,SW,LF	2,3,5
	Bisphenol A	80-05-7	SEW,SW,LF	1,5
Surfactants	Nonylphenol	84852-15-3	SEW,SW,LF,AG	1,2,3,5,6
	LAS	25155-30-0	SEW,SW,LF,AG	2,4
Perfluorinated compounds	PFOS/PFOA	1763-23-1/335-67-1	SEW,SW,LF	1,2,4,6
Musk fragrances	Galaxolide	1222-05-5	SEW,SW,LF	2,3,4,6
	Tonalide	21145-77-7	SEW,SW,LF	2,3,4,6
Pesticides	Glyphosate	1071-83-6	AG	1,2,3,5
Neonicotinoid insecticide	*Imidacloprid*	138261-41-3	AG	1,4
Pyrethroid insecticide	Bifenthrin	82657-04-3	SEW,SW,LF,AG	2,4
Pyrethroid insecticide	Permethrin	52645-53-1	SEW,SW,LF,AG	2,4
Pharmaceuticals	Acetaminophen	103-90-2	SEW,SW,LF,REC	2,3,5
	Diclofenac	15307-86-5	SEW,SW,LF,REC	2,3,5
	Ibuprofen	15687-27-1	SEW,SW,LF,REC	2,5
	Carbamazepine	298-46-4	SEW,SW,LF,REC	2,4
Steroid estrogen	Estrone	53-16-7	SEW,AG	4,5
Personal Care Products	Triclosan	3380-34-5	SEW,SW,LF	1,2,6
	Methyltriclosan	1/01/40	SEW,SW,LF	1,2,5,6
Preservative	Methylparaben	99-76-73	SEW,SW,LF	2,5
Corrosion inhibitor	*Benzotriazole*	95-14-7	SEW,SW	2,4

[a] BDE = brominated diphenyl ether; DEHP = Bis(2-ethylhexyl)phthalate; BBP = benzyl butyl phthalate; LAS = linear alkylbenzene sulfonate; PFOS = perfluorooctanesulfonic acid; PFOA = perfluorooctanoic acid; TCPP = Tris (1-chloro-2-propyl) phosphate; TDCP = Tris[2-chloro-1-(chloromethyl)ethyl]phosphate; TPP = Triphenylphosphate.

[b] Currently no laboratory capability for analysis of italicized EOCs in New Zealand.

[c] Major sources see Table 2-1. SEW = sewage; SW = stormwater; LF = landfill; AG = agriculture/horticulture; AQ = aquaculture; REC = recreation.

[d] 1 Initiative to remove. Stockholm Convention (POPs) or individual initiatives; 2 High production chemical; 3 Highest concentrations detected in urban marine receiving environment; 4 Knowledge gap (not previously monitored); 5 Previously detected in NZ marine sediments; 6 Persistent Bioaccumulative and Toxic (PBT).

Table 11-2. “Specific” list of “marker” EOCs recommended for initial phase (Tier 1) of sediment monitoring

Class	Representative EOC	CAS	Site	Reason[a]
Antifouling agents	Diuron	330-54-1	Port/Marina	1,5
	Isoproturon	34123-59-6	Port/Marina	1,4
UV-filter	Benzophenone-3	131-57-7	Beach	2,6

[a] 1 Initiative to remove. Stockholm Convention (POPs) or individual initiatives; 2 High production chemical; 3 Highest concentrations detected in urban marine receiving environment; 4 Knowledge gap (not previously monitored); 5 Previously detected in NZ marine sediments; 6 Persistent Bioaccumulative and Toxic (PBT).

Tier 2

Analyse sediment concentrations of the most highly impacted sites for the refined suite of relevant EOCs. Note, this list cannot be compiled until information from Tier 1 is incorporated.

Tier 3

Carry out further risk characterisation of most highly impacted sites by assessment of bioavailability of EOCs, through either passive sampling or biota procedures, or a combination of the two.

Carry out non-lethal chronic effects-based measurements and assessments of the most highly impacted sites on key receptor species.

This approach can also be tailored for sites or catchments influenced by rural or aquaculture activities.

12.0 Commonly used acronyms

AC	Auckland Council
BBP	Benzylbutyl phthalate (plasticiser)
BPA	Bisphenol A (plasticiser)
CEC	Contaminants of Emerging Concern
CEEC	Contaminants of Emerging Environmental Concern
CIBR	Centre for Integrated Biowaste Research
DEHP	Bis(2-ethylhexyl)phthalate (plasticiser)
DHP	Dihexyl phthalate (plasticiser)
DIBP	Diisobutyl phthalate (plasticiser)
EC	Emerging Contaminant
ECAN	Environment Canterbury Regional Council
EDC	Endocrine Disrupting Chemical
EOC	Emerging Organic Contaminant
EPA	Environmental Protection Authority
GWRC	Greater Wellington Regional Council
HBRC	Hawke's Bay Regional Council
HPV	High Production Volume
ISQG	Interim Sediment Quality Guideline
LOEL	Lowest Observable Effects Level
MBIE	Ministry for Business, Innovation and Employment
MfE	Ministry for the Environment
MPI	Ministry for Primary Industries
NIWA	National Institute of Water and Atmospheric Research
NOAA	National Oceanic and Atmospheric Administration
NOEL	No Observable Effects Level
NP	Nonylphenol (surfactant)
NSAID	Nonsteroidal anti-inflammatory drug (e.g. acetaminophen, diclofenac).
OCP	Organochlorine Pesticide
PAH	Polycyclic Aromatic Hydrocarbons
PBT	Persistent Bioaccumulative and Toxic

PBDE	Polybrominated Diphenyl Ether (Flame retardant; there are 209 individual BDE congeners)
PCB	Polychlorinated Biphenyl (there are 209 individual PCB congeners)
PED	Polyethylene Device
PFC	Perfluorinated Compound (e.g. PFOS, PFOA)
PNEC	Predicted-No-Effect Concentration
POCIS	Polar Organic Chemical Integrative Sampler
POP	Persistent Organic Pollutant
PPCP	Pharmaceutical and Personal Care Product
PSD	Passive Sampling Device
SCMP	Shellfish Contaminant Monitoring Programme
SETAC	Society of Environmental Toxicology and Chemistry
SIG	Special Interest Group
SoE	State of the Environment
SPME	Solid-Phase Microextraction
TOC	Total Organic Carbon
TCS	Triclosan (antimicrobial)
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WERF	Water Environment Research Foundation
WWTP	Wastewater Treatment Plant

13.0 References

Ahrens, M., 2008. Review of Organic Chemicals of Potential Environmental Concern in Use in Auckland. Prepared by NIWA for Auckland Regional Council. Auckland Regional Council Technical Report 2008/028.

Allan, S.E., Sower, G.J., Anderson, K.A., 2011. Estimating risk at a Superfund site using passive sampling devices as biological surrogates in human health risk models. Chemosphere 85, 920–927.

Alvarez, D.A., Maruya, K.A., Dodder, N.G., Lao, W., Furlong, E.T., Smalling, K.L., 2014. Occurrence of contaminants of emerging concern along the California coast (2009–10) using passive sampling devices. Mar. Pollut. Bull. 81, 347–354.

Anderson, P.D., Denslow, N.D., Drewes, J.E., Olivieri, A.W., Schlenk, D., Scott, G.I., Snyder, S.A., 2012. Monitoring Strategies for Chemicals of Emerging Concern (CECs) in California's Aquatic Ecosystems. Recommendations of a Science Advisory Panel.

ANZECC, 2000. National Water Quality Management Strategy. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 2. Aquatic Ecosystems — Rationale and Background Information (Chapter 8).

Arp, H.P.H., 2012. Emerging Decontaminants. Environ. Sci. Technol. 46, 4259–4260.

Bakke, T., Källqvist, T., Ruus, A., Breedveld, G., Hylland, K., 2010. Development of sediment quality criteria in Norway. J. Soils Sediments 10, 172–178.

Batley, G.E.., van Dam, R.., Warne, M.S.., Chapman, J.C.., Fox, D.R.., Hickey, C.W.., Stauber, J.L., 2014. Technical Rationale for Changes to the Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants.

Brack, W., Altenburger, R., Schüürmann, G., Krauss, M., López Herráez, D., van Gils, J., Slobodnik, J., Munthe, J., Gawlik, B.M., van Wezel, A., Schriks, M., Hollender, J., Tollefsen, K.E., Mekenyan, O., Dimitrov, S., Bunke, D., Cousins, I., Posthuma, L., van den Brink, P.J., López de Alda, M., Barceló, D., Faust, M., Kortenkamp, A., Scrimshaw, M., Ignatova, S., Engelen, G., Massmann, G., Lemkine, G., Teodorovic, I., Walz, K.-H., Dulio, V., Jonker, M.T.O., Jäger, F., Chipman, K., Falciani, F., Liska, I., Rooke, D., Zhang, X., Hollert, H., Vrana, B., Hilscherova, K., Kramer, K., Neumann, S., Hammerbacher, R., Backhaus, T., Mack, J., Segner, H., Escher, B., de Aragão Umbuzeiro, G., 2015. The SOLUTIONS project: Challenges and responses for present and future emerging pollutants in land and water resources management. Sci. Total Environ. 503-504, 22–31.

Braund, R., Peake, B.M., Shieffelbien, L., 2009. Disposal practices for unused medications in New Zealand. Environ. Int. 35, 952–955.

Bricker, S., Lauenstein, G., Maruya, K., 2014. NOAA's Mussel Watch Program: Incorporating contaminants of emerging concern (CECs) into a long-term monitoring program. Mar. Pollut. Bull. 81, 289–290.

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

Cavanagh, J., Ward, N., 2014. Contaminants in estuarine and riverine sediments and biota in Southland. Prepared for: Environment Southland.

CCME, 2011. Canadian Environmental Quality Guidelines Summary Table [WWW Document]. URL http://st-ts.ccme.ca/

Chari, B.P., Halden, R.U., 2012. Validation of mega composite sampling and nationwide mass inventories for 26 previously unmonitored contaminants in archived biosolids from the US National Biosolids Repository. Water Res. 46, 4814–4824.

CIBR, 2014. Organic Materials Guidelines – Organic Contaminants Review. Report prepared for Water NZ. CIBR Report No. 012.

Coimbra, A.M., Peixoto, M.J., Coelho, I., Lacerda, R., Carvalho, A.P., Gesto, M., Lyssimachou, A., Lima, D., Soares, J., André, A., Capitão, A., Castro, L.F.C., Santos, M.M., 2015. Chronic effects of clofibric acid in zebrafish (Danio rerio): a multigenerational study. Aquat. Toxicol. 160, 76–86.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107, 907.

Diamond, J., Latimer, H., Munkittrick, K., Kidd, K., Thornton, K., Bartell, S., 2010. Diagnostic tools to evaluate impacts of trace organic compounds. Prioritisation framework for trace organic compounds. Report prepared for Water Environment Research Foundation (WERF).

Dodder, N.G., Maruya, K.A., Lee Ferguson, P., Grace, R., Klosterhaus, S., La Guardia, M.J., Lauenstein, G.G., Ramirez, J., 2014. Occurrence of contaminants of emerging concern in mussels (Mytilus spp.) along the California coast and the influence of land use, storm water discharge, and treated wastewater effluent. Mar. Pollut. Bull. 81, 340–346.

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

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

Eggen, T., Moeder, M., Arukwe, A., 2010. Municipal landfill leachates: a significant source for new and emerging pollutants. Sci. Total Environ. 408, 5147–5157.

Emnet, P.J., 2013. Presence, Fate, and Behaviour of Emerging Micropollutants in the New Zealand and Antarctic Coastal Environment. University of Canterbury. Chemistry.

Environment Canada, 2013. Canadian Environmental Protection Act, 1999 Federal Environmental Quality Guidelines Polybrominated Diphenyl Ethers (PBDEs).

EPA, 2013. Decision on the Application for reassessment of Antifouling Paints (APP201051).

EU, 2008. European Union Updated Risk Assessment Report. Bisphenol A, CAS No: 80-05-7. Institute for Health and Consumer Protection, European Chemicals Bureau, European Commission Joint Research Centre, 3rd Priority List, Luxembourg: Office for Official Publication.

European Commission, 2003. Directive 2003/53/EC of The European Parliament and of The Council of 18 June 2003.

European Commission, 2008a. Directive 2008/56/EC of The European Parliament and of The Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive).

European Commission, 2008b. Directive 2008/105/EC of The European Parliament and of The Council on environmental quality standards in the field of water policy.

European Commission, 2010. Regulation (EU) No 1235/2010 of The European Parliament and of The Council of 15 December 2010.

European Commission, 2013a. Directive 2013/39/EU of The European Parliament and of The Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.

European Commission, 2013b. Commission Implementing Regulation (EU) No 485/2013 of 24 May 2013.

European Medicines Agency, 2006. Pre-Authorisation Evaluation of Medicines for Human Use.

Gadd, J., Cameron, M., 2012. Antifouling biocides in marinas: Measurement of copper concentrations and comparison to model predictions for eight Auckland sites. Prepared by NIWA for Auckland Council. Auckland Council technical report TR2012/033.

Gadd, J.B., 2008. Steroid estrogens and estrogenic activity in farm dairy shed effluents. PhD thesis. University of Canterbury.

Gadd, J.B., Northcott, G.L., Tremblay, L.A., 2010a. Passive Secondary Biological Treatment Systems Reduce Estrogens in Dairy Shed Effluent. Environ. Sci. Technol. 44, 7601–7606.

Gadd, J.B., Tremblay, L.A., Northcott, G.L., 2010b. Steroid estrogens, conjugated estrogens and estrogenic activity in farm dairy shed effluents. Environ. Pollut. 158, 730–736.

Gaw, S., Close, M.E., Flintoft, M.J., 2008. Fifth national survey of pesticides in groundwater in New Zealand . New Zeal. J. Mar. Freshw. Res. 42, 397–407.

Gaw, S., Thomas, K., Hutchinson, T.H., 2016. Pharmaceuticals in the marine environment. In: Hester, R., Harrison, R. (Eds.), Issues in Environmental Science and Technology No 41 Pharmaceuticals in the Environment. The Royal Society of Chemistry.

Gaw, S., Thomas, K. V, Hutchinson, T.H., 2014. Sources, impacts and trends of pharmaceuticals in the marine and coastal environment. Philos. Trans. R. Soc. London B Biol. Sci. 369.

Ghosh, U., Kane Driscoll, S., Burgess, R.M., Jonker, M.T.O., Reible, D., Gobas, F., Choi, Y., Apitz, S.E., Maruya, K.A., Gala, W.R., Mortimer, M., Beegan, C., 2014. Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. Integr. Environ. Assess. Manag. 10, 210–223.

Gielen, G.J.H.P., 2007. The fate and effects of sewage-derived pharmaceuticals in soil. University of Canterbury.

Greenwood, R., Mills, G., Vrana, B., 2007. Passive sampling techniques in environmental monitoring. Elsevier.

Grigorakis, K., Rigos, G., 2011. Aquaculture effects on environmental and public welfare–the case of Mediterranean mariculture. Chemosphere 85, 899–919.

Hotchkiss, A.K., Rider, C. V, Blystone, C.R., Wilson, V.S., Hartig, P.C., Ankley, G.T., Foster, P.M., Gray, C.L., Gray, L.E., 2008. Fifteen Years after 'Wingspread'—Environmental Endocrine Disrupters and Human and Wildlife Health: Where We are Today and Where We Need to Go. Toxicol. Sci. 105, 235–259.

Johnson, A.C., Keller, V., Dumont, E., Sumpter, J.P., 2015. Assessing the concentrations and risks of toxicity from the antibiotics ciprofloxacin, sulfamethoxazole, trimethoprim and erythromycin in European rivers. Sci. Total Environ. 511, 747–55.

Kim, S., Jung, J., Lee, I., Jung, D., Youn, H., Choi, K., 2015. Thyroid disruption by triphenyl phosphate, an organophosphate flame retardant, in zebrafish (Danio rerio) embryos/larvae, and in GH3 and FRTL-5 cell lines. Aquat. Toxicol. 160, 188–96.

Kools, S.A.E., Boxall, A., Moltmann, J.F., Bryning, G., Koschorreck, J., Knacker, T., 2008. A ranking of European veterinary medicines based on environmental risks. Integr. Environ. Assess. Manag. 4, 399–408.

Lara-Martín, P.A., González-Mazo, E., Petrovic, M., Barceló, D., Brownawell, B.J., 2014. Occurrence, distribution and partitioning of nonionic surfactants and pharmaceuticals in the urbanized Long Island Sound Estuary (NY). Mar. Pollut. Bull. 85, 710–719.

Leusch, F.D.L., Chapman, H.F., van den Heuvel, M.R., Tan, B.L.L., Gooneratne, S.R., Tremblay, L.A., 2006a. Bioassay-derived androgenic and estrogenic activity in municipal sewage in Australia and New Zealand. Ecotoxicol. Environ. Saf. 65, 403–411.

Leusch, F.D.L., Van den Heuvel, M.R., Chapman, H.F., Gooneratne, S.R., Eriksson, A.M.E., Tremblay, L.A., 2006b. Development of methods for extraction and in vitro quantification of estrogenic and androgenic activity of wastewater samples. Comp. Biochem. Physiol. Part C Toxicol. Pharmacol. 143, 117–126.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C., 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci. Total Environ. 473-474, 619–41.

Margot, J., Rossi, L., Barry, D.A., Holliger, C., 2015. A review of the fate of micropollutants in wastewater treatment plants. Wiley Interdiscip. Rev. Water 2, 457–487.

Maruya, K.A., Dodder, N.G., Schaffner, R.A., Weisberg, S.B., Gregorio, D., Klosterhaus, S., Alvarez, D.A., Furlong, E.T., Kimbrough, K.L., Lauenstein, G.G., Christensen, J.D., 2014. Refocusing Mussel Watch on contaminants of emerging concern (CECs): The California pilot study (2009–10). Mar. Pollut. Bull. 81, 334–339.

Maximino, C., Puty, B., Benzecry, R., Araujo, J., Lima, M.G., Oliveira Batista, E. de J., de Matos Oliveira, K.R., Crespo-Lopez, M.E., Herculano, A.M., 2013. Role of serotonin in zebrafish (Danio rerio) anxiety: Relationship with serotonin levels and effect of buspirone, WAY 100635, SB 224289, fluoxetine and para-chlorophenylalanine (pCPA) in two behavioral models. Neuropharmacology 71, 83–97.

McClellan, K., Halden, R.U., 2010. Pharmaceuticals and Personal Care Products in Archived U.S. Biosolids from the 2001 EPA National Sewage Sludge Survey. Water Res. 44, 658–668.

Minnesota Department of Health, 2008. Health Risk Limits for Perfluorochemicals Report to the Minnesota Legislature 2008.

Moermond, C., Verbruggen, E., Smit, C., 2010. Environmental risk limits for PFOS: A proposal for water quality standards in accordance with the Water Framework Directive (Report 601714013/2010), National Institute of Public Health and the Environment, Netherlands.

New Zealand Water Wastes Association, 2003. Guidelines for the safe application of biosolids to land in New Zealand. New Zealand Water and Wastes Association.

Nguyen, V.T., Reinhard, M., Karina, G.Y.-H., 2011. Occurrence and source characterization of perfluorochemicals in an urban watershed. Chemosphere 82, 1277–85.

Nödler, K., Voutsa, D., Licha, T., 2014. Polar organic micropollutants in the coastal environment of different marine systems. Mar. Pollut. Bull. 85, 50–59.

Northcott, G.L., Jackman, G., 2015. Wastewater treatment and the fate of emerging organic contaminants – a story from the city of Gisborne. New Zealand Land Treatment Collective 2015 Conference. 25th to 27th March. Wanaka, New Zealand.

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

Norwegian Scientific Committee for Food Safety, 2005. Risk assessment on the use of Triclosan in cosmetics. Prepared by the Scientific Committee in cooperation with the Panel on Biological Hazards and the Panel on Food Additives, Flavourings, Processing Aids, Materials in contact with Food and Cosmetics.

Novak, P.J., Arnold, W. a, Blazer, V.S., Halden, R.U., Klaper, R.D., Kolpin, D.W., Kriebel, D., Love, N.G., Martinovi, D., Patisaul, H.B., Snyder, S. a, Saal, F.S., Weisbrod, a V, 2011. On the Need for a National (U . S .) Research Program to Elucidate the Potential Risks to Human Health and the Environment Posed by Contaminants of Emerging Concern. Environ. Sci. Technol. 3829–3830.

Pal, A., Gin, K.Y.-H., Lin, A.Y.-C., Reinhard, M., 2010. Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects. Sci. Total Environ. 408, 6062–6069.

Peake, B.M., Braund, R., 2009. Environmental Aspects of the Disposal of Pharmaceuticals in New Zealand. Chem. New Zeal. 73, 58–63.

Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., Pennell, K.G., 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 2. Emerging contaminants. Environ. Toxicol. Chem. 32, 2190–2196.

Phillips, P.J., Schubert, C., Argue, D., Fisher, I., Furlong, E.T., Foreman, W., Gray, J., Chalmers, A., 2015. Concentrations of hormones, pharmaceuticals and other micropollutants in groundwater affected by septic systems in New England and New York. Sci. Total Environ. 512, 43–54.

Qin, J.-J., Oo, M.H., Lee, H., Kolkman, R., 2004. Dead-end ultrafiltration for pretreatment of RO in reclamation of municipal wastewater effluent. J. Memb. Sci. 243, 107–113.

Ramakrishnan, A., Blaney, L., Kao, J., Tyagi, R.D., Zhang, T.C., Surampalli, R.Y., 2015. Emerging contaminants in landfill leachate and their sustainable management. Environ. Earth Sci. 73, 1357–1368.

Sankoda, K., Murata, K., Tanihata, M., Suzuki, K., Nomiyama, K., Shinohara, R., 2015. Seasonal and Diurnal Variation of Organic Ultraviolet Filters from Personal Care Products Used Along the Japanese Coast. Arch. Environ. Contam. Toxicol. 68, 217–224.

Sarmah, A.K., Northcott, G.L., Leusch, F.D.L., Tremblay, L.A., 2006. A survey of endocrine disrupting chemicals (EDCs) in municipal sewage and animal waste effluents in the Waikato region of New Zealand. Sci. Total Environ. 355, 135–144.

Sarmah, A.K., Northcott, G.L., Scherr, F.F., 2008. Retention of estrogenic steroid hormones by selected New Zealand soils. Environ. Int. 34, 749–755.

Sarmah, A.K., Northcott, G.L., Tremblay, L.A., 2005. A Scoping Report on Endocrine Disrupting Chemicals (EDCs) and their Relevance to New Zealand. Landcare Research Contract Report: .

Scherr, F.F., Sarmah, A.K., Di, H.J., Cameron, K.C., 2009. Degradation and metabolite formation of 17??-estradiol-3-sulphate in New Zealand pasture soils. Environ. Int. 35, 291–297.

Schwarzenbach, R.P., Escher, B.I., Fenner, K., Hofstetter, T.B., Johnson, C.A., von Gunten, U., Wehrli, B., 2006. The Challenge of Micropollutants in Aquatic Systems. Science (80-.). 313, 1072–1077.

Shahpoury, P., Hageman, K.J., Matthaei, C.D., Magbanua, F.S., 2013. Chlorinated pesticides in stream sediments from organic, integrated and conventional farms. Environ. Pollut. 181, 219–225.

Shareef, A., Kookana, R., Kumar, A., Tjandraatmadja, G., 2008. Sources of Emerging Organic Contaminants in Domestic Wastewater. An Assessment Based on Literature Review. Water for a Healthy Country Flagship Report series ISSN: 1835-095X.

Simpson, S., Batley, G., Chariton, A., 2013. Revision of the ANZECC/ARMCANZ Sediment Quality Guidelines. CSIRO Land and Water Science Report 08/07. CSIRO Land and Water.

Steiner, L.D., Bidwell, V.J., Hong, J.D.I., Cameron, K.C., Northcott, G.L., 2010. Transport and modeling of estrogenic hormones in a dairy farm effluent through undisturbed soil lysimeters. Environ. Sci. Technol. 44, 2341–2347.

Stewart, M., 2013. Pharmaceutical residues in the Auckland estuarine environment. Prepared by NIWA for Auckland Council. Auckland Council Technical Report, TR2013/002. NIWA, Hamilton.

Stewart, M., Ahrens, M., Olsen, G., 2009. Field analysis of chemicals of emerging environmental concern in Auckland's aquatic sediments. Prepared by NIWA for Auckland Regional Council. Auckland Regional Council Technical Report 2009/021.

Stewart, M., Cameron, M., McMurtry, M., Sander, S., Benedict, B., Graham, L., Hosie, M., Green, T., 2015. Development of passive sampling devices for bioavailable contaminants of current

and emerging concern: Waitemata Harbour case study. New Zeal. J. Mar. Freshw. Res. Submitted.

Stewart, M., Olsen, G., Gadd, J., 2013. Shellfish contaminant monitoring programme review. Prepared by NIWA for Auckland Council. Auckland Council technical report, TR2013/055.

Stewart, M., Olsen, G., Hickey, C.W., Ferreira, B., Jelić, A., Petrović, M., Barcelo, D., 2014. A survey of emerging contaminants in the estuarine receiving environment around Auckland, New Zealand. Sci. Total Environ. 468–469, 202–210.

Tong, A.Y.C., Peake, B.M., Braund, R., 2011. Disposal practices for unused medications around the world. Environ. Int. 37, 292–298.

Tremblay, L., Champeau, O., Biessy, L., Bowater, J., Northcott, G., 2013a. Risk assessment of chemicals in household products. Prepared for the Ministry for the Environment. CIBR Report No 4. 42 p.

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

Tremblay, L., Trought, K., Northcott, G., 2010. Evaluation of the efficacy of the Beachlands/Maraetai Sewage Treatment Plant to remove oestrogenic and androgenic activity. Landcare Research report prepared for Manukau Water Limited.

Tremblay, L.A., Northcott, G.L., 2013. Analysis of Waikato river water samples for selected endocrine disrupting chemicals and hormonal activity. Waikato Regional Council Technical Report 2013/55.

Tremblay, L.A., Stewart, M., Peake, B.M., Gadd, J.B., Northcott, G.L., 2011. Review of the Risks of Emerging Organic Contaminants and Potential Impacts to Hawke's Bay. Prepared for Hawke's Bay Regional Council. Cawthron Report No. 1973.

UNEP, 2009. Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and Annexes.

UNEP, 2013. An amendment to Annex A adopted by the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants at its sixth meeting (Decision SC-6/13).

USEPA, 2010. Columbia River Basin Toxics Reduction Action Plan. Prepared by: U.S. Environmental Protection Agency, Region 10 and The Columbia River Toxics Reduction Working Group.

USEPA, 2013a. Contaminants of Emerging Concern in Fish: Polybrominated Diphenyl Ethers (PBDEs). EPA-820-F-13-003.

USEPA, 2013b. Contaminants of Emerging Concern in Fish: Perfluorinated Compounds (PFCs). EPA-820-F-13-005.

USEPA, 2014a. Columbia River Toxics Reduction Working Group: Strategy For Measuring, Documenting And Reducing Chemicals Of Emerging Concern.

USEPA, 2014b. National recommended water quality criteria. Aquatic life criteria table.

Vandegehuchte, M.B., Janssen, C.R., 2014. Epigenetics in an ecotoxicological context. Mutat. Res. Genet. Toxicol. Environ. Mutagen. 764-765, 36–45.

Vanneste, J.L., 2013. Recent progress on detecting, understanding and controlling Pseudomonas syringae pv. actinidiae: a short review. New Zeal. Plant Prot. 66, 170–177.

Vrana, B., Allan, I.J., Greenwood, R., Mills, G.A., Dominiak, E., Svensson, K., Knutsson, J., Morrison, G., 2005. Passive sampling techniques for monitoring pollutants in water. Trends Anal. Chem. 24, 845–868.

Wang, Q., Lam, J.C.W., Han, J., Wang, X., Guo, Y., Lam, P.K.S., Zhou, B., 2015. Developmental exposure to the organophosphorus flame retardant tris(1,3-dichloro-2-propyl) phosphate: estrogenic activity, endocrine disruption and reproductive effects on zebrafish. Aquat. Toxicol. 160, 163–71.

Warne, M.S.J., Batley, G.E., Braga, O., Chapman, J.C., Fox, D.R., Hickey, C.W., Stauber, J.L., Van Dam, R., 2014. Revisions to the derivation of the Australian and New Zealand guidelines for toxicants in fresh and marine waters. Environ. Sci. Pollut. Res. 21, 51–60.

Water New Zealand, 2015. Progress towards New Guidelines for the Beneficial Use of Biowastes in New Zealand. [WWW Document]. URL https://www.waternz.org.nz/Category?Action=View&Category_id=816

Weiss, K., Schüssler, W., Porzelt, M., 2008. Sulfamethazine and flubendazole in seepage water after the sprinkling of manured areas. Chemosphere 72, 1292–1297.

WFD-UKTAG, 2009. Proposed EQS for Water Framework Directive Annex VIII substances: triclosan (for consultation). Report commissioned for the Environment Agenecy and the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER).

WHO/UNEP, 2012. State of the science of endocrine disrupting chemicals 2012 / edited by Åke Bergman, Jerrold J. Heindel, Susan Jobling, Karen A. Kidd and R. Thomas Zoeller.

Xu, Y., Luo, F., Pal, A., Gin, K.Y.-H., Reinhard, M., 2011. Occurrence of emerging organic contaminants in a tropical urban catchment in Singapore. Chemosphere 83, 963–969.

Zgheib, S., Moilleron, R., Saad, M., Chebbo, G., 2011. Partition of pollution between dissolved and particulate phases: What about emerging substances in urban stormwater catchments? Water Res. 45, 913–925.

Zhang, G.Y. and M.F. and G., 2014. Emerging contaminants in surface waters in China—a short review. Environ. Res. Lett. 9, 74018.

Appendix A Review scope

The original full scope for this review is as follows:
A review on updates in the emerging contaminant (EC) space since 2011 (covered in the Envirolink report carried out for Hawke's Bay on Emerging contaminants). The review will primarily have an urban focus and recommend what ECs Auckland, Wellington and Christchurch RCs should include in their marine sediment contaminant monitoring programmes. The review will also cover freshwater and rural (agricultural and horticultural) issues, where applicable. The review will include the following tasks:

1. Update on progress on a national strategy, comprising of:

- Summary of The SETAC Global Horizon Scanning Project and the SETAC Australasia contribution being undertaken at the SETAC Australasia 2015 meeting in Nelson. Graham Sevicke-Jones is a key figure in this and we will gain updates from him;
- Summary and history of previous workshops etc;
- Brief summary of recommendations from the most recent (May 2013) workshop in Wellington;
- Summary of Alistair Boxal's 20 questions project.

2. An update on recent (since 2011) research on ECs in NZ. This will include a brief review of 2011 report to provide some background and include following studies:

- EDCs in the Waikato River (Cawthron Institute/NRC Ltd);
- EDCs in RDC WWTP effluents and Waipa Forest catchment streams (Cawthron Institute/NRC Ltd);
- Fate of ECs during treatment in the GDC WWTP BTF (NRC Ltd);
- ECs in sediment and waters of Lyttleton Harbour (Phil Emnett Phd, UoC);
- Fate of ECs from sewer overflows in urban streams of Christchurch (MSc, UoC) plus other relevant research projects at UoC (Gaw et al);
- ECs in treated effluent of 13 WWTPs in NZ (Jason Strong PhD);
- Auckland sediment data (Stewart et al 2013, 2014) and SCMP review (Stewart et al 2013) which has EC components and leads onto passive samplers;
- ECs and passive samplers study (Stewart, Cameron et al);
- CIBR on EOCs including zebrafish work at Cawthron;
- Anti-coagulants in Southland (Cavanagh et al 2014);
- Invercargill project on stormwater and sediments for Galaxolide and other musk fragrances;
- Envirolink project on pesticides for Nelson City Council.

3. An update on the international, national and NZ situation with a focus on Auckland, Wellington and Christchurch. This will include effects and ecotox, major sources, and reported concentrations (including Jason Strong's PhD work).

- Summary of significant research programmes in North America, EU, and Australia etc;
- Focus on sources released into Auckland, Wellington and Christchurch environments with particular emphasis on the estuarine receiving environments but also to include freshwater where relevant, for example due to effects of sewage overflow as a result of CHCH earthquakes;
- Including WWTP effluents, stormwater, sewage overflows, landfill leachate, industrial site run-off. Primary focus will be urban however recognition will be given towards rural sources (agricultural, horticultural);
- Pesticides as a special case: Clarification on which pesticides would be considered to be ECs? For example, Neonicotinoids? Glyphosate/AMPA? What control measures are already in place (eg. HSNO act).

4. Legislation. What is happening in NZ and other areas of interest (EU, US especially), including recommendations on which initiatives to keep a watching brief on for future developments. Legislative initiatives to cover are specifically:

- Future changes to ANZEEC guidelines with respect to endocrine disruption. Input from Rick van Dam, Rai Kookana (Australia), Chris Hickey (NIWA);
- Initiatives to remove/eliminate ECs of concern, i.e. triclosan;
- The EU REACH program and chemical registration in the EU;
- Summary of current and/or proposed regulatory limits for ECs;
- EU Water Framework Directive;
- Stockholm Convention, i.e. PBDEs and PFOAs.

5. Monitoring approaches and indicator development and use, including:

- Summary of monitoring strategies adopted for significant research programs, i.e. USGS Toxic Hydrology program, USEPA Emerging Contaminant program, EU Poseidon, WERF etc, NOAA, EU/Kevin Thomas etc;
- Use of marine biota in estuarine environments - more literature recently published on uptake of ECs into shellfish;
- Passive sampling methodology to assess bioavailable ECs (USGS, USEPA)
- Summary of approaches ranking ECs to select representative marker/indicator compounds for monitoring and fate assessment.

6. Recommended sampling, archiving and storage approach for ECs in sediment samples. The procedures for long-term sample archiving are expected to be very different to those for POPs due to the widely different chemical properties of many ECs, i.e. acids, bases, phenols etc. This will involve:

- Review of literature to identify current practise for
    - time/flow average sampling (water),
    - passive sampling (water and sediment),
    - sediment,
    - biota.
- Collaborators will also be contacted to gain insight into their methodology with (e.g. USGS and Kevin Thomas).

7. Laboratory capability available in NZ. This will not predicate recommendation of which ECs should be monitored but will:

- Summarise current commercial and research laboratory capabilities in NZ.
- Highlight future capability efforts (if required) of commercial and research laboratories based on recommendations from this review (for example PFOAs);
- Trace chemical, bioassay and biological assessment.

8. Recommendations and guidance about what Auckland, Wellington and Christchurch RCs should be including in future monitoring programmes, including how and where monitoring should take place. This will be primarily marine sediment focus but also contain brief options for biota monitoring and 'bioavailable' fraction e.g. via passive samplers. Other recommendations may be to:

- Fund and support a research project(s) to investigate some of the identified areas of uncertainty, for example:
    - the effect of sample treatment/storage on stability of ECs;
    - assessing bioavailability via, for example passive samplers versus biota;
    - assess which ECs are persisting and accumulating in sediments in NZ? Outcome would be used to confirm recommended indicator compounds.

Appendix B Procedure for sampling, processing and archiving of sediments for EOCs

Taken from Sections 3.1 and 3.2 of Stewart et al. (2009)

To avoid potential contamination with plasticisers, only plastics that do not leach phthalates were used for collection[54]. All plastics were washed with detergent, rinsed with deionised (DI) water and acetone prior to use. To keep costs to a minimum and remove site spatial variability from the final results, sediments were collected as follows: With the exception of the marinas, each site was marked with a quadrat of 50 x 50 cm and two replicate samples taken randomly within that quadrat. Only the top 3 cm of the sediment (surface sediment) was collected and transferred immediately into clean solvent rinsed glass jars and chilled, on ice. The total wet weight of sediment sampled for each replicate was ca. 2 kg. Three different protocols of sampling were used:

- where sediment could hold its form without collapsing, cleaned and rinsed polypropylene housings were used to take sediment samples (Protocol A; Figure 1). The top 3 cm was extruded through the corer;
- for sites that had either sediment that was sloppy and would not hold its form, or a high-density of mangroves, a corer was not feasible. In this situation a plastic scoop was used to scrape off the top 3 cm (Protocol B; Figure 2); and
- for sampling subtidal sediments inside marinas a Jenkins corer was used to collect sediment. By using this method (Protocol C; Figure 3) it was possible to sample the top 3 cm of sediment without disturbing the sediment.

[54] For clarity, use rigid high density polyethylene (HDPE) plastic for sampling. Alternatively, if not measuring heavy metals, stainless steel can be used.

Figure 1:

Technique for collection of firm sediments: Protocol A.

Figure 2:

Technique for collection of sloppy sediments: Protocol B.

Figure 3:
Jenkins corer for sampling at marinas. Protocol C.


A


B


C

A: Jenkins corer being lowered into the water. **B:** Jenkins corer after it has been retrieved. **C:** The core after cleaning and removal from trigger device. The top 3 cm of each core was carefully extruded out of the top of the housing using a plunger.

3.2 Sediment Processing and Archiving

Sediments were stored at 4ºC until processing. For processing, each replicate sample was transferred to a large foil tray and stirred with a stainless steel spoon to form a homogenised mixture. Large debris (stones, shellfish, plant material) were removed at this

time by hand. Once a homogenised sample was obtained, sub-sampling was carried out into relevant pre-cleaned labelled vessels.

Samples were apportioned as follows:

AsureQuality (PBDEs and dithiocarbamates)	100 g
Hill Laboratories (Organic Biocides)	400 - 500 g
Hill Laboratories (Total metals)	10 g
Hill Laboratories (<63 μm metals)	10 g
CSIRO (EDCs)	2 x 200 g
Archive	Approximately 200 g

Archived samples of whole wet sediment were stored frozen (-20ºC).

Appendix C Analytical suites

AsureQuality

AsureQuality EOCs by LC-MS/MS (USEPA 1694)

Compound	Sediment LOR (µg/kg)	Compound	Sediment LOR (µg/kg)
Aspartame	20	Sulfamethizole	10
Acetaminophen	10	Sulfamethoxazole	10
Caffeine	10	Sulfanilamide	200
Carbamazepine	5	Sulfathiazole	50
Clarithromycin	10	Thiabendazole	10
Codeine	10	Triclocarban	10
Cotinine	5	Triclosan	20
Erythromycin	2	Trimethoprim	10
Ibuprofen	10	Tylosin	10
Lincomycin	10	Bisphenol A	250
Naproxen	20	4-nonylphenol	200
Sulfachloropyridazine	10	β-Estradiol	120
Sulfadiazine	10	Estriol	120
Sulfadimethoxine	10	Estrone	240
Sulfamerazine	10	Ethynyl estradiol	120
Sulfamethazine	10		

AsureQuality phthalates by GC-MS (USEPA 8270)

Compound	Sediment LOR (µg/kg)
Benzyl butyl phthalate	20
Bis(2-ethylhexyl)adipate	100
Bis(2-ethylhexyl)phthalate	100
Diethylphthalate	100
Dimethylphthalate	20
Di-n-butylphthalate	20
Di-n-octyl phthalate	100

AsureQuality PFCs by LC-MSMS (in-house method)

Compound	Sediment LOR (µg/kg)
Perfluoroalkylsulfonic acids	
Perfluorobutanesulfonic acid (PFBS)	1
Perfluorohexanesulfonic acid (PFHxS)	1
Perfluorooctanesulfonic acid (PFOS)	1
Perfluorodecanesulfonic acid (PFDS)	1
Perfluoroalkylcarboxylic acids	
Perfluorohexanoic acid (PFHxA)	1
Perfluoroheptanoic acid (PFHpA)	1
Perfluorooctanoic acid (PFOA)	2
Perfluorononanoic acid (PFNA)	1
Perfluorodecanoic acid (PFDA)	1
Perfluoroundecanoic acid (PFUnA)	2
Perfluorododecanoic acid (PFDoA)	1
Perfluorotridecanoic acid (PFTrDA)	1
Perfluorotetradecanoic acid (PFTeDA)	1
Other PFCs	
Perfluorooctane sulphonamide (PFOSA)	1
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	3
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	3
1H,1H,2H,2H-perfluorooctane sulfonic acid (6:2 FTS)	2
1H,1H,2H,2H-perfluorodecane sulfonic acid (8:2 FTS)	3

AsureQuality Brominated Flame Retardants by GC-HRMS (USEPA 1614)

BDEs	Sediment LOR (µg/kg)	BDEs	Sediment LOR (µg/kg)
BDE# 7	0.001-0.005	BDE# 153	0.002-0.02
BDE# 15	0.001-0.005	BDE# 154	0.002-0.02
BDE# 17	0.001-0.005	BDE# 156/169	0.002-0.02
BDE# 28/33	0.001-0.005	BDE# 171	0.002-0.02
BDE# 30	0.001-0.005	BDE# 180	0.002-0.02
BDE# 47	0.005-0.025	BDE# 183/175	0.002-0.02
BDE# 49	0.001-0.005	BDE# 184	0.002-0.02
BDE# 66	0.001-0.005	BDE# 191	0.002-0.02
BDE# 71	0.001-0.005	BDE# 196	0.01-0.05
BDE# 77	0.001-0.005	BDE# 197	0.01-0.05
BDE# 85	0.001-0.005	BDE# 201	0.01-0.05
BDE# 99	0.001-0.005	BDE# 203	0.01-0.05
BDE# 100	0.001-0.005	BDE# 204	0.01-0.05
BDE# 119/120	0.001-0.005	BDE# 205	0.01-0.05
BDE# 126	0.001-0.005	BDE# 206	0.01-0.05
BDE# 138/166	0.002-0.02	BDE# 207	0.01-0.05
BDE# 139	0.002-0.02	BDE# 208	0.01-0.05
BDE# 140	0.002-0.02	BDE# 209	0.1-1
Other BFRs			
BB-153	0.01-0.05		
Hexabromobenzene (HBB)	0.01-0.05		
Decabromodiphenylethane (DBDPE)	0.1-1		
Pentabromoethylbenzene (PBEB)	0.001-0.005		

AsureQuality Pesticides by GC-MS (in-house method)

Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)
acetochlor	100	dimepiperate	50	napropamide	50
alachlor	50	dimethenamid	50	nitrofen	50
aldrin	50	dimethoate	50	nitrothal-isopropyl	50
ametryn	50	dimethylvinphos	50	oxadiazon	50
anilofos	50	dioxabenzofos	50	oxadixyl	100
atrazine	50	diphenamid	50	oxyfluorfen	50
azaconazole	50	diphenylamine	50	paclobutrazol	50
azinphos-methyl	50	dithiopyr	50	parathion	50
azoxystrobin	50	endosulfan	50	parathion-	50

Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)
benalaxyl	100	endosulfan (alpha)	100	methyl penconazole	50
bendiocarb	50	endosulfan (beta)	50	pendimethalin	50
benfluralin	50	endosulfan sulphate	50	permethrin	200
benodanil	50	endrin	50	phenthoate	50
benoxacor	50	epoxiconazole	50	phorate	50
BHC (alpha)	50	EPTC	50	phosalone	50
BHC (beta)	50	esprocarb	50	phosmet	100
BHC (delta)	50	ethalfluralin	50	phosphhamidon	50
bifenox	50	ethion	50	picolinafen	50
bifenthrin	50	ethoprophos	50	piperonyl butoxide	50
bitertanol	100	etoxazole	50	piperophos	50
bromobutide	50	etridiazole	50	pirimicarb	50
bromophos-ethyl	50	etrimfos	50	pirimiphos-methyl	50
bromophos-methyl	50	famphur	100	pretilachlor	50
bromopropylate	50	fenarimol	50	procymidone	50
bupirimate	50	fenchlorphos	50	profenofos	50
buprofezin	100	fenitrothion	50	promecarb	50
butachlor	50	fenobucarb	50	prometryn	50
butamifos	50	fenoxaprop-ethyl	100	propachlor	50
cadusafos	50	fenoxycarb	100	propargite	50
carbaryl	100	fenpropathrin	50	propazine	50
carbofuran	50	fensulfothion	50	propetamphos	50
carfentrazone-ethyl	50	fenvalerate	50	propham	50
chlordane-cis	50	flamprop-methyl	50	propiconazole	50
chlordane-trans	50	fluacrypyrim	50	propoxur	50
chlorfenapyr	50	fluazifop-P-butyl	50	propyzamide	50
chlorfenvinphos	50	flumiclorac-pentyl	50	prothiofos	50
chlorobenzilate	50	flumioxazin	50	pyraflufen-ethyl	50
chlorothalonil	50	fluquinconazole	50	pyrazophos	50
chlorpropham	50	flusilazole	50	pyridaben	50
chlorpyrifos	50	flutolanil	50	pyridaphenthion	50

Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)
chlorpyrifos-methyl	50	fluvalinate	50	pyrimethanil	50
chlorthal-dimethyl	50	fonofos	50	pyrimidifen	50
chlozolinate	50	fosthiazate	50	pyriminobac-methyl(E)	50
clodinafop-propargyl	50	furalaxyl	50	pyriminobac-methyl(Z)	50
clomazone	50	furathiocarb	50	pyriproxyfen	50
cloquintocet-1-methylhexyl	50	haloxyfop-etotyl	50	quinalphos	50
coumaphos	50	haloxyfop-methyl	50	quinoxyfen	50
cyanazine	50	heptachlor	50	quintozene	50
cyanophos	50	heptachlor-endo-epoxide	50	quizalofop-ethyl	100
cyflufenamid	100	heptachlor-exo-epoxide	50	simazine	100
cyfluthrin	100	heptenophos	50	simeconazole	50
cyhalofop-butyl	50	hexachlorobenzene	50	simetryn	50
cyhalothrin	50	hexazinone	50	tebuconazole	50
cypermethrin	100	indoxacarb	100	tebufenpyrad	50
cyproconazole	50	iodofenphos	50	tecnazene	50
cyprodinil	50	iprobenfos	50	tefluthrin	50
DDD (o,p')	50	iprodione	50	terbacil	50
DDD (p,p')	50	iprovalicarb	100	terbufos	50
DDE (o,p')	50	isazofos	50	terbuthylazine	100
DDE (p,p')	50	isofenphos	50	terbutryne	50
DDT (o,p')	50	isoprocarb	50	tetrachlorvinphos	50
DDT (p,p')	50	isoprothiolane	50	tetraconazole	50
deltamethrin	50	kresoxim-methyl	100	tetradifon	50
diazinon	50	lactofen	50	thiobencarb	50
dichlobenil	50	leptophos	50	tolclofos-methyl	50
dichlofenthion	50	lindane	50	tolyfluanid	50
dichlofluanid	50	malathion	50	triadimefon	50
dichlorvos	50	metalaxyl	50	triadimenol	50
diclobutrazol	50	methacrifos	50	triallate	50
diclofop-methyl	50	methidathion	50	tribufos	50
dicloran	50	methiocarb	100	trifloxystrobin	50
dicrotophos	100	metolachlor	50	trifluralin	50

Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)	Compound	Soil LOR (µg/kg)
dieldrin	50	mevinphos	50	uniconizole-P	50
diethofencarb	50	molinate	50	vinclozolin	50
diflufenican	50	myclobutanil	50	XMC	50

Northcott Research Consultants / Plant and Food

EOC capability from NRC/Pand F with a range of estimated LOR for sediment.

Flame retardants (FRs) (1 - 20 µg/kg)	Brominated flame retardants (0.01 - 1.0 µg/kg)*
Alkylphosphate FRs	Suite of major PBDE congeners
Tri-isobutyl-phosphate (TiBP)	Bis(2,4,6-tribromophenoxy)ethane
Tri-n-butyl-phospahte (TBP)	decabromodiphenylethane
Tris-(2-chloroethyl)phospahte (TCEP)	2-ethylhexyl 2,3,4,5-tetrabromobenzoate
Tris-(2-chloroisopropyl)phosphate (TCPP)	(2-ethylhexyl)tetrabromophthalate
Tris-(2-chloro-1-(chloromethyl)ethyl)-phosphate (TDCP)	hexabromocyclododecanes
Tiphenyl phosphate (TPP)	**Insect repellents (1 - 10 µg/kg)**
Tris-(butoxyethyl)-phosphate (TBEP)	DEET
Tris-(2-ethylhexyl)-phosphate (TEHP)	Picaridin
Tri -ortho-cresyl-phosphate (ToCP)	**UV filters (1 - 20 µg/kg)***
Tri-meta-cresyl-phosphate (TmCP)	Benzophenone-1
Tri-para-cresyl-phosphate (TpCP)	Benzophenone-2
Tetrabromo-bisphenol-A	Benzophenone-3
Phthalates and plasticisers (1 - 20 µg/kg)	Benzophenone-8
Bis(2-chloroethoxy) methane	Avobenzone
Dimethyl phthalate	2-ethylhexyl-4-methoxycinnamate
Diethyl phthalate	2-ethylhexyl salicylate
4-chlorophenyl phenyl ether	3-(4-methylbenzylidene)camphor
4-bromophenyl phenyl ether	4-aminobenzoic acid
Dibutyl phthalate	cinoxate
Benzyl butyl phthalate	homosalate
Diethylhexyl phthalate	Octocrylene
Di-n-octyl phthalate	Padimate O
monomethyl phthlate	Menthyl anthranilate
monobutyl phthalate	
mono ethylhexyl phthalate	
Bisphenol-A	

EOC capability from NRC/Pand F with a range of estimated LOR for sediment

Pharmaceuticals[#] (0.1 - 1 µg/kg)	**Antimicrobials (0.05 - 5 µg/kg)**
Methyl salicylate	Chloroxylenol
Asprin (acetyl salicylic acid)	o-phenylphenol
Clofibric acid	Chlorphene
Caffeine	Triclosan
Ibuprofen	Methyl triclosan
Salicylic acid	2,4,5,6-tetrabromo-cresol
naproxen	Benzyl benzoate
acetominophen	Hexachlorphene
clotrimazole	p-chlorocresol
gemfibrozil	**Preservatives (0.1 - 10 µg/kg)**
metoprolol	Methyl paraben
propanolol	Ethyl paraben
ketoprofen	Propyl paraben
carbamazepine	Butyl paraben
Diclofenac	Benzyl paraben
meclofenamic acid	Phenoxy ethanol
Fenofibric acid	Butylated hydroxy toluene
Musks/fragrances (0.1 - 10 µg/kg)	Butylated hydroxy anisole
Nitro-musks	4-isopropyl-3-methylphenol
Musk Ambrette	
Musk ketone	
Musk mosken	
Musk Tibetene	
Musk xylene	
Polycyclic musks	
Cashmeran	
Celestolide	
Galaxolide	
Phantolide	
Traseolide	

[#] Nearing completion. *In development

EOC capability from NRC/Pand F with a range of estimated LOR for sediment

Phenolic xenoestrogens (0.1 - 10 µg/kg)	Steroid hormones (0.1 - 10 µg/kg)
4-tert-amylphenol	17-estradiol
4-n-amylphenol	17b-estradiol
4-tert-nonylphenol	Estrone
4-n-nonylphenol	Estradiol
4-tert-octylphenol	17a-ethinyl estradiol
4-n-octylphenol	Mestranol
4-tert-heptyphenol	19-nortestosterone
Technical nonylphenol equivalents	levonorgestrel
Nonylphenol monoethoxylates	norethisterone
Nonylphenol diethoxylates	androstenedione
2-(4-nonylphenoxy) acetic acid	ketotestosterone
	testosterone
	prednisolone

Hill Laboratories

Hill Laboratories-Phthalate plasticisers

Compound List	MDL (µg/kg)
Di(2-ethylhexyl)adipate	300
Bis(2-ethylhexyl)phthalate	500
Butylbenzylphthalate	500
Diethylphthalate	500
Dimethylphthalate	500
Di-n-butylphthalate	500
Di-n-octylphthalate	500

Hill Laboratories-Multi-residue pesticides

Compound List	Sediment MDL (µg/kg)	Compound List	Sediment MDL (µg/kg)
Acetochlor	6	Linuron	6
Alachlor	6	Malathion	6
Atrazine	6	Metalaxyl	6
Atrazine-desethyl	6	Methamidophos (including acephate)	30
Atrazine-desisopropyl	10	Metolachlor	6
Azaconazole	4	Metribuzin	6
Azinphos-methyl	10	Molinate	10
Benalaxyl	5	Myclobutanil	6
Bitertanol	10	Naled	30

Compound List	Sediment MDL (µg/kg)	Compound List	Sediment MDL (µg/kg)
Bromacil	6	Norflurazon	10
Bromopropylate	6	Oxadiazon	6
Butachlor	6	Oxyfluorfen	6
Captan	20	Paclobutrazol	8
Carbaryl	6	Parathion-ethyl	6
Carbofuran	6	Parathion-methyl	6
Chlorfluazuron	20	Pendimethalin	6
Chlorpyrifos	6	Permethrin	9
Chlorothalonil	6	Pirimicarb	8
Chlorpyrifos-methyl	6	Pirimiphos methyl	6
Chlorotoluron	20	Prochloraz	30
Cyanazine	6	Procymidone	6
Cyfluthrin	10	Prometryn	4
Cyhalothrin	10	Propachlor	6
Cypermethrin	10	Propanil	30
Deltamethrin	10	Propazine	4
Diazinon	6	Propiconazole	6
Dichlofluanid	6	Pyriproxifen	6
Dicloran	30	Quizalofop-p-ethyl	6
Dichlorvos	10	Simazine	6
Difenoconazole	10	Simetryn	6
Dimethoate	10	Sulfentrazone	60
Diphenylamine	10	TCMTB	10
Diuron	20	Tebuconazole	6
Fenpropimorph	20	Terbacil	6
Fluazifop-p-butyl	6	Terbufos	10
Fluometuron	6	Terbumeton	6
Flusilazole	6	Terbuthylazine	5
Fluvalinate	10	Terbuthylazine desethyl	6
Furalaxyl	10	Terbutryn	6
Haloxyfop-r-methyl	6	Thiabendazole	30
Hexaconazole	6	Thiobencarb	6
Hexazinone	3	Tolylfluanid	4
IPBC	30	Triazophos	7
Iprodione	6	Trifluralin	10
Kresoxim-methyl	6	Vinclozolin	6

Compound List	Sediment MDL (µg/kg)	Compound List	Sediment MDL (µg/kg)
Bendiocarb	6	Folpet	10
Benodanil	10	Hexythiazox	60
Bifenthrin	6	Imazalil	30
Bromophos-ethyl	6	Indoxacarb	6
Bupirimate	6	Iodofenphos	6
Buprofezin	6	Isazophos	6
Captafol	40	Isofenphos	6
Carbofenothion	6	Leptophos	6
Carboxin	6	Methacrifos	8
Chlorfenvinphos	6	Methidathion	6
Chlorpropham	10	Methiocarb	6
Chlozolinate	6	Mevinphos	20
Coumaphos	10	Nitrofen	10
Cyproconazole	8	Nitrothal-isopropyl	6
Cyprodinil	6	Omethoate	30
Demeton-S-methyl	10	Oxychlordane	3
Dichlobenil	6	Penconazole	6
Dichlofenthion	6	Phorate	10
Dicofol	30	Phosmet	6
Dicrotophos	20	Phosphamidon	20
Dinocap	70	Propetamphos	6
Disulfoton	7	Propham	6
EPN	6	Prothiofos	6
Ethion	6	Pyrazophos	6
Etrimfos	6	Pyrifenox	8
Famphur	6	Pyrimethanil	6
Fenamiphos	8	Quintozene	10
Fenarimol	6	Sulfotep	10
Fenitrothion	6	Tebufenpyrad	6
Fenpropathrin	7	Tetrachlorvinphos	6
Fensulfothion	6	Thiometon	10
Fenthion	6	Triadimefon	6
Fenvalerate	8		

Hill Laboratories-Glyphosate

Compound List	**Sediment MDL (µg/kg)**
Glyphosate	20
Glufosinate	10
AMPA (aminomethylphosphonic acid)	50

Hill Laboratories-Antifouling chemicals

Compound List	**Sediment MDL (µg/kg)**
Irgarol	5
Diuron	5
Isoproturon	10
Monobutyl tin (as Sn)	7
Dibutyl tin (as Sn)	4
Tributyl tin (as Sn)	3
Triphenyl tin (as Sn)	3

Watercare Laboratory Services

Watercare Laboratory Services - Plasticisers

Compound List	**MDL (µg/kg)**
Di(2-ethylhexyl)adipate	100
Bis(2-ethylhexyl)phthalate	100
Butylbenzylphthalate	100
Diethylphthalate	100
Dimethylphthalate	100
Di-n-butylphthalate	100
Di-n-octylphthalate	100