EMERGING CONTAMINANTS MONITORING: WHERE DO WE START?

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ABSTRACT

Emerging contaminants, or perhaps more aptly, contaminants of emerging concern (CECs), are a growing consideration in in all aspects of the water cycle. This is not only due to human impacts on the water cycle and release of a large variety of new contaminants, or increases in the prevalence of naturally occurring contaminants due to climate change, but also due to the increased speculation of risk that comes with better analytical techniques and greater knowledge of a range of contaminants at "trace" concentrations that have likely gone undetected before now.

Watercare are currently investigating the potential for incorporating recycled water into their future source water portfolio, and as part of this piloting of a purified recycled water (potable) treatment plant will beundertaken to gather data and inform future planning decisions. To get on the front foot of addressing the growing considerations in the emerging contaminants space for their long-term recycled water plans, Watercare plan to include monitoring for CECs as part of the recycled water pilot plant study. By including this monitoring, the intent is to address concerns around CECs and provide evidence for what is in the catchment, and ultimately improve the understanding of source risks and the effectiveness of treatment processes.

However, the sheer number of potential CECs that may need to be considered in this kind of monitoring plan make this a daunting task. Particularly in the recycled water space, there are potentially thousands of CECs that could possibly be present in the various feed water sources, and it would certainly be an impressive monitoring budget that could sample for all of them at any sort of regular interval. Laboratory capability and capacity also needs to be considered. The question we had to ask ourselves was: 'how can a list of potentially thousands of contaminants be narrowed down to an affordable and manageable sampling program while still addressing the dangers and risks posed by all CECs? '.

After conducting a literature review to develop a long list of potential CECs to consider for monitoring, Watercare engaged Beca HunterH2O to help in narrowing down the long list to a much shorter one that still provides a risk-based approach to obtaining solid evidence on CECs, whilst not breaking the monitoring budget.

This case study provides an overview of the approach Watercare and Beca HunterH2O are taking to achieve this, presented in the format of a guidance note on how others can apply the same principles to developing their own monitoring approach for CECs. In other words, this is how we went from a very long

speculative list of emerging contaminants to an actual plan for collecting evidence, and how you can do it too!

KEYWORDS

Emerging contaminants, monitoring program, recycled water, water quality monitoring, pilot trial, indicator/representative compounds

PRESENTER PROFILES

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Clemence Carlinet: Clemence is now a senior wastewater planner after more than 10 years' experience as a process engineer with Watercare. After completing her studies in France and further training in Australia, she relocated to Auckland where she is now based.

Brendon Dockary: Brendon is the Recycled Water Lead at Watercare in Auckland. After 3 years as a dam technician, he is now working on pilot projects and regulatory changes to enhance our understanding of recycled water and normalizing it as a valued resource.

1. INTRODUCTION

Contaminants of emerging concern (CECs) are a growing consideration in in all aspects of the water cycle. This is not only due to human impacts on the water cycle and the release of a large variety of new contaminants, or increases in the prevalence of naturally occurring contaminants due to climate change, but also due to the increased speculation of risk that comes with better analytical techniques and greater knowledge of a range of contaminants at "trace" concentrations that have likely gone undetected before now (Leusch & Petterson, 2020).

Particularly, CECs are becoming highlighted as a concern for the increased uptake of recycled water schemes as the industry moves toward sustainable and climate resilient water sources, and the focus on circular economy solutions increases.

Watercare Services Limited (Watercare) are currently investigating the potential for incorporating recycled water into their future water source planning decisions, and as part of this a purified recycled water pilot plant study is being undertaken. Understanding the importance that consideration of CECs plays in this type of investigation, Watercare is looking to include regular monitoring for CECs as part of the pilot plant study.

Watercare initially developed a long list of potential CECs to be considered for monitoring, however limitations in laboratory analysis capability, such as resourcing and the unavailability of specialist equipment, as well as the cost of sampling meant that sampling all the possible CECs in the long list would be above what is reasonably achievable for ongoing monitoring during the pilot plant project.

Thus, a problem was presented that is common to almost anyone attempting to gather data-based evidence on CECs in their catchments, wastewater, recycled water, or potable water systems: there are too many possible CECs to monitor for them all, so where do we start? (Stewart et al., 2016) (Zhang et al., 2021).

Beca HunterH2O assisted Watercare to further develop the long list of CECs and provided guidance for developing a CEC monitoring plan based on experience and a review of approaches used both in New Zealand and internationally. A key objective of this work was to develop a short list of indicator compounds that could be used in an ongoing monitoring program to obtain solid evidence on the prevalence CECs, without breaking the monitoring budget.

This case study provides an overview of the approach Watercare and Beca HunterH2O are taking to achieve this, presented in the format of a guidance note on how others can apply the same principles to developing their own monitoring program for CECs. In other words, this is how we went from a very long speculative list of emerging contaminants to an actual plan for collecting evidence, and how you can do it too!

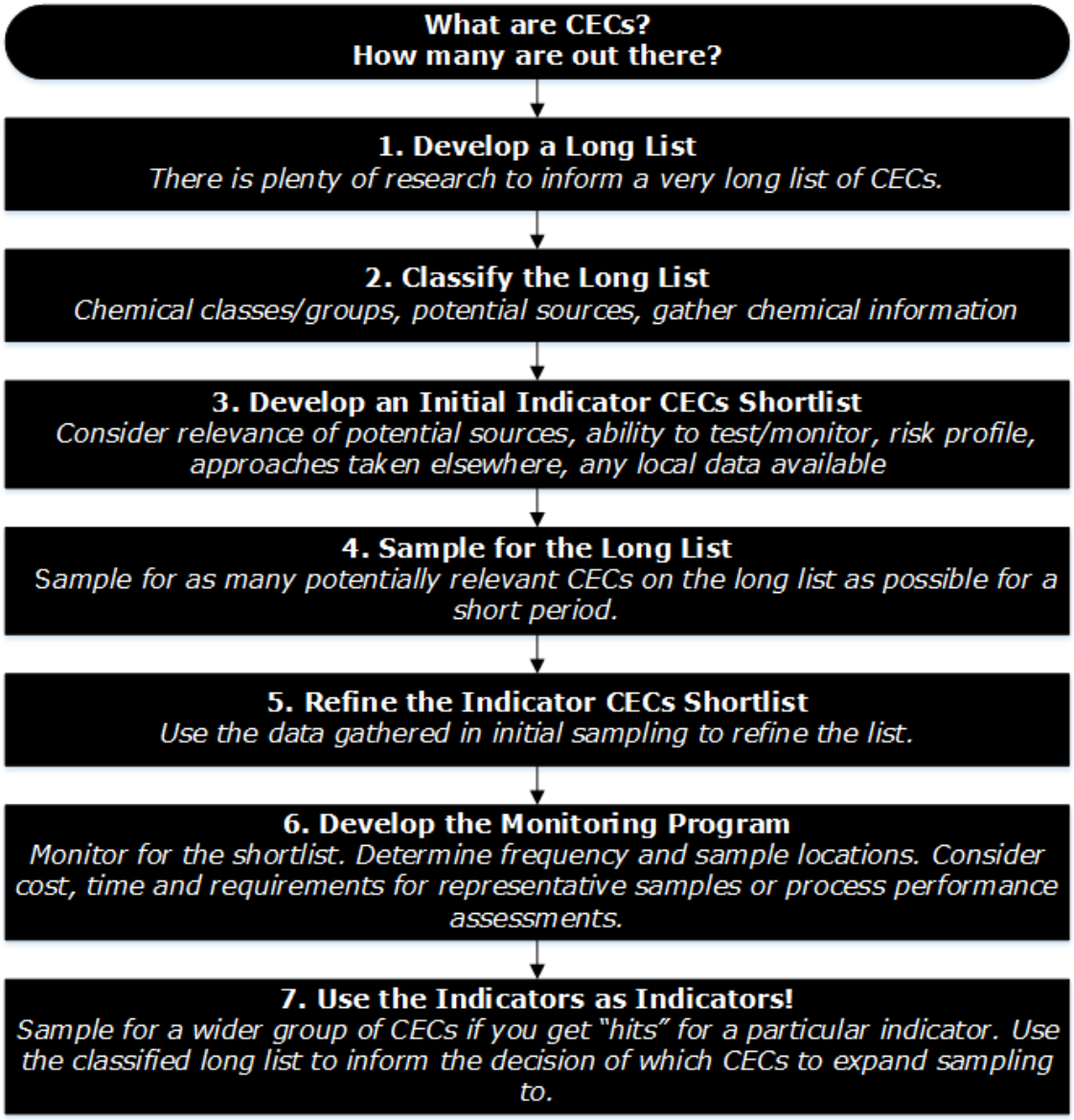
2. DISCUSSION

2.1 OVERALL METHODOLOGY: HOW DO WE GET THERE?

Moving from a starting point of speculation about CECs to implementing an effective CEC monitoring program can be a daunting journey. 'Figure 1: Methodology adopted for CEC monitoring' outlines the methodical approach adopted by Watercare for this journey as part of the pilot study.

At the time of writing Watercare are nearing the beginning of step 4 in the process, so there is still plenty of work to do, but a clear path has been developed for how to get there.

Figure 1: Methodology adopted for CEC monitoring.



The following sub-sections provide further detail on each of these steps.

2.2 DEVELOP A LONG LIST

The first step taken in Watercare's journey of gathering data on CECs was to compile a long list all the possible chemical and biological contaminants that fall under the umbrella of emerging contaminants and may potentially be relevant to the implementation of a recycled water scheme.

Watercare undertook a literature review in the early stages of the pilot study to compile an initial long list of CECs.

Whilst this may seem like a daunting task in itself, there is extensive literature available to enable production of a **very** long list of potentially concerning contaminants.

Potentially useful resources for this type of literature review include:

- The Emerging Chemicals Database for National Awareness (ECHIDNA) compiled by Water Research Australia (2022)
- The Aotearoa—New Zealand Strategy for Emerging Contaminants, prepared by the Aotearoa-NZ Emerging Contaminants Advisory Panel (n.d.)
- The Australian Guidelines for Water Recycling Phase 1 (Natural Resource Management Ministerial Council et al., 2006) and Phase 2 (Environment Protection and Heritage Council et al., 2008)
- Other international standards and guidance documents (depending on your geographical and legislative context)
- Published literature on CECs relevant to your geographical context (in Watercare's case this was literature concerning the Aotearoa-NZ context).

2.3 CLASSIFY THE LONG LIST

Developing a long list of CECs to consider was a very useful starting point for Watercare, but it would be much too expensive and impractical to monitor for all the compounds on the long list. To shorten the list into one that could be practically incorporated into a monitoring program, we first needed to compile more information about each compound such that they could be grouped and sorted in a meaningful way.

We initially reviewed the long list of CECs and added data for the following:

- **CEC class** – the major class that can be used to describe the CEC based on commonly used approaches in literature (e.g., disinfection by-products, endocrine disruptors, pesticides, personal use products etc.)
- **Chemical group** – a more specific chemical grouping that can be used to differentiate chemical types within a class (where applicable) (e.g., antibiotics, androgenic or estrogenic hormones, bisphenols, brominated flame retardants, trihalomethanes etc.)
- **Key source areas** – how the CEC is typically used/produced (as an indication of how it could potentially enter the recycled water system)
- **Links to further chemical information** – in this instance we primarily referred to the US Environmental Protection Agency's (EPA) 'CompTox' database (Williams et al., 2017)
- **Comments** – including other notable details where applicable, such as:
    - If the CEC is often referred to under another name
    - If there are specific limits or guideline values found for the CEC in a widely accepted guidance document (e.g. the AGWR Phase 1 or 2)

- Any other information deemed to be notable for inclusion in relation to the CEC.

Adding this information produced a classified CEC list that could then be used to sort the CECs into classes for further specific investigation, or even further into groups if required. This helps to expediate further review and management of the long list in ongoing CEC investigations.

The data provided for key source areas also provides a further method of classification that was useful to assess the applicability of CECs to the pilot plant feed water sources.

Including links to additional chemical information is also expected to be useful for ease of accessing further information on compounds.

2.4 DEVELOP AN INITIAL INDICATOR SHORTLIST

The proposed approach to monitoring for CECs in Watercare's pilot study is to use indicator compounds. The general theory behind this approach is to routinely sample for a short list of compounds that may act as "indicators" for other compounds that are likely to or may potentially be present along with the indicator compound.

This approach is already commonly used in potable water supply system monitoring, for example the monitoring of trihalomethanes (THMs) as an indicator for a wider range of disinfection by-products (DBPs). Although there have been approaches developed for CEC monitoring in countries such as the United States of America (Stephen et al., 2010) and Australia (Natural Resource Management Ministerial Council et al., 2006) (Environment Protection and Heritage Council et al., 2008), there is currently no common or widely accepted approach applicable to the Aotearoa-NZ context for assigning indicator compounds to monitor all classes of CECs (Stewart et al., 2016).

When assigning indicator compounds it is important to consider factors such as:

- **Relevance of potential sources** - i.e., is the indicator something that would be likely to be in the feed source if other similar compounds are present, or is there a reason it would not be present when other similar compounds are? For example, a particular pesticide may commonly be used as an indicator compound for water quality monitoring in Australia, but farmers in Aotearoa-NZ may not use this pesticide at all).
- **Ability to test / analyse** – the analytical methods for some compounds may be simpler, less costly, and more accurate than for others, and some CECs may not be practical to monitor regularly at all.
- **Risk profile** – although not generally considered in a true "indicator" monitoring approach, it can be worth considering the addition of CECs that may have a particularly high-risk profile to the shortlist to ensure they aren't missed.
- **Treatment effectiveness** – what compounds are known to be less effectively removed through commonly used advanced treatment processes, and whether these compounds need to be included alongside identified indicator compounds.

For this project, an initial shortlist of key indicator compounds was selected for each CEC class considering the factors above and an amalgamation of multiple approaches documented in the available literature for both the Aotearoa-NZ

context and internationally (the citation of references for particular decisions on inclusion of CECs in the list is included in Appendix A).

The initial CEC indicator compounds shortlist produced for the pilot study by Beca HunterH2O and Watercare is included in Appendix A.

This initial shorter list of indicator compounds is proposed to form the basis of the recommended parameters for Watercare's purified recycled water (potable) pilot plant monitoring program; however, it is important to note the limitations of the approach taken to develop the initial list, as there was minimal specific data available for the Aotearoa-NZ context. Further work is needed (in the form of "full sweep" sampling for the long list) to ensure the applicability of the indicator list for ongoing CEC monitoring, and a catchment specific survey should be undertaken as part of the development of an enhanced source control/risk management programme.

2.5 SAMPLE FOR THE LONG LIST

The initial indicator compounds shortlist prepared for the pilot study monitoring will be revised and/or supplemented by an initial "full sweep" of sampling for all the parameters in the long, classified CEC list. Watercare is planning to begin their sampling programme shortly at the time of writing.

This initial sweep will provide a more comprehensive understanding of which CECs may or may not be present in the feed, or otherwise relevant to the pilot study.

This aligns with the general approach recommended by most available guidance documents, i.e., undertaking "full sweep" monitoring to develop a baseline of the source/catchment, followed by a risk-based approach to decide on which compounds are included in an ongoing monitoring program (Stewart et al., 2016).

It is important that the full sweep testing is based on representative samples of the feed water source/catchment, and potential seasonal variations should be considered.

2.6 REFINE THE SHORTLIST

After undertaking the sampling for the long list, Watercare will analyse these results to help inform the final indicator CEC list that will be used in the monitoring program.

The initial shortlist will be revised or supplemented using a risk-based approach regarding the specific prevalence of CECs in the feed water source.

2.7 DEVELOP THE MONITORING PROGRAM

Once the final list of indicator CECs has been confirmed Watercare will incorporate the indicator compounds into an ongoing monitoring program to gather data on the occurrence of CECs in the WWTP influent and feedwater for the pilot plant, and their removal through the pilot plant treatment train and individual treatment processes.

Key considerations for development of the final CEC monitoring program will include:

- **Cost of sampling and the available budget for monitoring CECs:** Watercare have obtained a quote from their preferred laboratory for testing of the final CEC indicator list. This cost will then be used to determine how frequent sampling can be conducted within the allocated

budget for CEC monitoring at the pilot plant. It may also be preferable to analyze groups of CECs in 'suites', depending on the capabilities of the chosen laboratory.

- **Required frequency of sampling:** Initially, sampling is expected to be intensive (e.g., every 1-6 months) to develop a strong baseline and understanding of the prevalence of CECs in the source/feed water. Sampling frequency could then be decreased (e.g., 6 monthly to yearly, depending on potential seasonal variations) for most CECs, with more frequent monitoring potentially maintained if there is a specific area of concern, or if specific indicator compounds need to be used to assess process performance for the pilot plant.
- **Event-based sampling:** The sampling program should allow for "event-based" sampling where additional samples are taken when loads are elevated or when upstream processes feeding into the "catchment" are behaving abnormally. This would include during periods of high rainfall or flooding in the catchment, upstream process disturbance or equipment failure, or unexpected catchment processes.
- **Additional sampling based on indicator compound "hits":** as described in Section 2.7 below.
- **Pilot plant process performance assessment:** Initially sampling will be conducted on the pilot plant's feed water source and treated water to observe overall removal performance for CECs, however intra-process sample locations will also be selected to evaluate the performance of specific process units as required (noting verification of unit processes such as UV disinfection, membrane separation or advanced oxidation requires development of a detailed monitoring and assessment program, and assistance from an experienced party should be sought).

2.7 USE THE INDICATORS AS INDICATORS!

Once the monitoring program has been developed and is underway, it will be important not to lapse into the false assumption that the indicator compounds are the only CECs we need to be concerned about.

A critical feature of any monitoring approach using indicators is to make sure that they are used as true indicators! If the ongoing monitoring shows elevated concentrations of a particular indicator CEC, this should trigger consideration to undertake additional monitoring for other CECs that may be likely to be present with the indicator compound, such as CECs with similar chemical structures, or with a similar source. Such results may also highlight the need for source control in the relevant catchment, however this level of investigation would not be pursued during the pilot project.

Determination of how much additional monitoring to perform and which additional CECs to monitor for should be based on a risk-based approach. The classified long list of CECs (described in Section 2.3), and the information it contains, is expected to be a useful tool in this determination.

3. CONCLUSIONS/RECOMMENDATIONS

Watercare is currently developing a final plan for emerging contaminants monitoring as part of the pilot study, and further work is required to develop an effective and cost-efficient CEC monitoring program for assessing the performance of the pilot plant or future recycled water projects.

However, the work undertaken by Watercare and Beca HunterH2O to put forward an approach for developing this CEC monitoring program provides a useful framework that could be adopted by other parties interested in collecting more information about CECs.

Whilst the initial indicator CEC list developed as part of this work may be useful as an example for other applications in all aspects of the water cycle, it is important to consider specific local catchment risks and end use requirements for any application where CEC monitoring is required. Future regulatory frameworks may also require monitoring of specific CECs, which will dictate sampling programmes.

By definition, contaminants of emerging concern will always be an "emerging" field, and the authors of this paper would like to stress the importance of sharing knowledge on CECs, and encourage collaboration between researchers, water suppliers, and the wider water industry to support each other in monitoring emerging contaminants, to manage the risks together.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the critical and important research and work that has been undertaken in the field of emerging contaminants to-date, much of which this work heavily relied upon. We did not conduct ground-breaking research in this project, but rather we built on the valuable work of others to develop a framework for emerging contaminants monitoring.

We would also like to acknowledge the wider team from Watercare and Beca HunterH2O that contributed to this project, including Shannon Palmer, Mark Dawson, and Asher Beasley.

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APPENDIX A: INDICATOR COMPOUNDS SHORTLIST

'Table 1: Initial indicator compound shortlist for CEC classes' shows the initial indicator compound shortlist developed as part of Watercare's approach to developing a CEC monitoring program. This shortlist is still to be refined through further sampling and investigations.

Sources, references, and general justifications for inclusion of compounds in the shortlist are also provided in Table 1.

Table 1: Initial indicator compound shortlist for CEC classes.

CEC Class	Indicator Compound(s)	Source/Reference
Pathogens	Risk-based approach should be used to determine monitoring for specific opportunistic pathogens / pathogens of emerging concern.	Standard approaches recommended. 'Indicator' pathogens not typically used for this class of CECs. Note that this does not preclude monitoring that should be undertaken for more recognised pathogens using commonly accepted indicators (e.g. E. coli).
Cyanotoxins	To be confirmed if required/relevant to the feed water source.	A risk-based approach should be used to determine if/when regular monitoring for cyanotoxins is required.
Disinfection by-products	1. N-nitrosodimethylamine (NDMA) 2. Trichloromethane (chloroform)	1-2 identified as indicator compounds for recycled water operational performance monitoring in the AGWR Phase 2 (Environment Protection and Heritage Council et al., 2008).
Endocrine disruptors	1. Di(2-ethylhexyl)phthalate (DEHP) 2. Benzyl butyl phthalate (BBP) 3. Bisphenol A (BPA) 4. Nonylphenol 5. Estrone 6. Estradiol (17-beta)	1-5 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 5 also identified as an indicator compound for recycled water operational performance

CEC Class	Indicator Compound(s)	Source/Reference
	7. Cholesterol 8. Iopromide	monitoring in the AGWR Phase 2 (Environment Protection and Heritage Council et al., 2008). 6-8 suggested as indicator compounds in a US study by Zhang et al. (2021).
Flame retardants	1. Tetrabromodiphenyl ether (BDE-47) 2. Pentabromodiphenyl ether (BDE-99) 3. Decabromodiphenyl ether (BDE-209) 4. Tris(1,3-dichloro-2-propyl)phosphate (TDCP) 5. Triphenyl phosphate (TPP) 6. Tris(2-chloropropyl) phosphate (TCPP) 7. Tri(chloroethyl)phosphate (TCEP)	1-6 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 1-3 may be able to be monitored collectively as 'total polybromodiphenyl ethers (PBDEs)' if a suitable laboratory testing method is available. 7 suggested as an indicator compound in a US study by Zhang et al. (2021).
Herbicides and fungicides	1. Diuron 2. Isoproturon 3. Bentazone	1-2 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 3 was one of the four CECs found at the highest concentrations in Waikato region groundwater monitoring by Moreau et al. (2019).
Metals / metalloids / halides	1. Cyanide (total) 2. Iodide	These were all the metals/metalloids/halides included in the classified CECs list. Note that this does not preclude monitoring that should be undertaken for more recognised metals/metalloids/halides

CEC Class	Indicator Compound(s)	Source/Reference
		relevant to recycled water applications (e.g. boron).
Miscellaneous organics	1. Linear alkylbenzene sulphonate (LAS)	1 suggested as a 'marker' compound for initial CEC screening in NZ context by M Stewart et al. (2016). Additional miscellaneous organic compounds may need to be added based on results of initial long list screening.
Personal use products	1. Galaxolide (HHCB) 2. Tonalide (AHTN) 3. Triclosan 4. Methyl triclosan 5. Methylparaben 6. Benzotriazole 7. Benzophenone 8. N,N-Diethyl-meta-toluamide (DEET)	1-7 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 8 identified as an indicator compound for recycled water operational performance monitoring in the AGWR Phase 2 (Environment Protection and Heritage Council et al., 2008). 8 also suggested as an indicator compound in a US study by Zhang et al. (2021).
Pesticides and metabolites	1. Glyphosate 2. Imidacloprid 3. Bifenthrin 4. Permethrin 5. Chloridazon-desphenyl 6. Atrazine 7. Metolachlor	1-4 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 5 was one of the three CECs found at the highest concentrations in Waikato region groundwater monitoring by Moreau et al. (2019). 6-7 suggested as indicator compounds in a US study by Zhang et al. (2021).

CEC Class	Indicator Compound(s)	Source/Reference
PFAS	1. Perfluorooctane sulfonate (PFOS) 2. Perfluorooctanoic acid (PFOA) 3. Perfluorohexane sulfonate (PFHxS)	1-2 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 1-2 also suggested as indicator compounds in a US study by Zhang et al. (2021). 3 was found at the higher concentrations than typically reported in EU studies in Waikato region groundwater monitoring by Moreau et al. (2019).
Pharmaceuticals and metabolites	1. Acetaminophen (Paracetamol) 2. Diclofenac (Voltaren) 3. Ibuprofen (Nurofen) 4. Carbamazepine (Tegratol) 5. Acesulfame-K 6. Mefenamic acid 7. Levamisole 8. Caffeine 9. Meprobamate 10. Erythromycin (E-mycin) 11. Sulfamethoxazole (Trisul) 12. Trimethoprim 13. Diazepam (Valium) 14. Fluoxetine (Prozac) 15. Atenolol 16. Propanolol 17. Gemfibrozil (lopid) 18. Cotinine	1-4 suggested as 'marker' compounds for initial CEC screening in NZ context by M Stewart et al. (2016). 5 was one of the three CECs found at the highest concentrations in Waikato region groundwater monitoring by Moreau et al. (2019). 6 -7 were the pharmaceuticals found at highest concentration in Waikato region groundwater monitoring by Moreau et al. (2019). 8-9 identified as indicator compounds for recycled water operational performance monitoring in the AGWR Phase 2 (Environment Protection and Heritage Council et al., 2008). 1, 3, 4, 8 & 10-18 suggested as indicator compounds in a US study by Zhang et al. (2021).

CEC Class	Indicator Compound(s)	Source/Reference
		This list is likely to be shortened based on the findings of initial full-sweep screening tests.
Plastics and nanoparticles	1. Microplastics	Suitable techniques for analysis need to be considered (including microplastics definition, to allow comparison to other results and guidance documents).
Radionuclides	To be confirmed based on initial screening results.	Implementation of regular monitoring should be reviewed based on detection data from initial screening.