A critical control point approach to the removal of chemicals of concern from water for reuse

Scales, PJ, Wijekoon, K, Ladwig, C, Knight, A, Allinson, Mayumi, Allinson, Graeme, Zhang, Jianhua, Gray, Stephen, Packer, M, Northcott, K and Sheehan, D (2019) A critical control point approach to the removal of chemicals of concern from water for reuse. Water Research, 160. pp. 39-51. ISSN 0043-1354

A critical control point approach to the removal of chemicals of concern from water for reuse

Peter J. Scales, Kaushalya Wijekoon, Christian Ladwig, Adrian Knight, Mayumi Allinson, Graeme Allinson, Jianhua Zhang, Stephen Gray, Michael Packer, Kathy Northcott, David Sheehan

PII: S0043-1354(19)30423-3

DOI: https://doi.org/10.1016/j.watres.2019.05.035

Reference: WR 14684

To appear in: *Water Research*

Received Date: 26 September 2018

Revised Date: 8 May 2019

Accepted Date: 11 May 2019

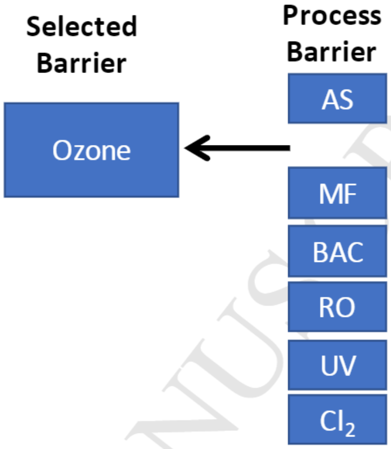
Please cite this article as: Scales, P.J., Wijekoon, K., Ladwig, C., Knight, A., Allinson, M., Allinson, G., Zhang, J., Gray, S., Packer, M., Northcott, K., Sheehan, D., A critical control point approach to the removal of chemicals of concern from water for reuse, *Water Research* (2019), doi: https://doi.org/10.1016/j.watres.2019.05.035.

EXAMPLE BARRIER CREDIT SYSTEM FOR CCP

CCP Surrogates	Feed Water
Residual >0.05 mg/L	DOC <10 mg/L
Dose >11.7 mg/L	
$CT_{10} > 14$ mg.min/L	
$T_{10} > 5$ min	

Pathogen Credits	LRV
Virus	2.0
Bacteria	2.0
Protozoa	0.0
Helminths	0.0

Chemical Credits	LRV
Ozone class 1	0.9
Ozone class 2	0.0
Ozone class 3	0.0
Ozone class 4	0.0



A Critical Control Point Approach to the Removal of Chemicals of Concern from Water for Reuse

Peter J Scales[1]*, Kaushalya Wijekoon[1], Christian Ladwig[2], Adrian Knight[1], Mayumi Allinson[1], Graeme Allinson[3], Jianhua Zhang[4], Stephen Gray[4], Michael Packer[5], Kathy Northcott[6] and David Sheehan[7]

[1] *Particulate Fluids Processing Centre, Department of Chemical Engineering, The University of Melbourne, 3010, Australia*

[2] *Department of Chemistry, Technical University Munich, Munich, Germany*

[3] *Centre for Environmental Sustainability and Remediation, School of Science, RMIT University, Melbourne, 3001, Australia*

[4] *Institute for Sustainable Industries and Liveable Cities, Victoria University, Werribee, 3030, Australia*

[5] *Australian Antarctic Division, Kingston, 7050, Australia*

[6] *Water Research Australia, Adelaide, 5000, Australia*

[7] *Coliban Water, Bendigo, 3550, Australia*

[*] *Author* for correspondence: Email: peterjs@unimelb.edu.au; Phone: +61 3 8344 6480

Abstract

The reuse of water in a range of potable and non-potable applications is an important factor in the augmentation of water supply and in improving water security and productivity worldwide. A key hindrance to the reuse of water is the cost of compliance testing and process validation associated with ensuring that pathogen and chemicals in the feedwater are removed to a level that ensures no acute or chronic health and/or environmental effects. The critical control point (CCP) approach is well established and widely adopted by water utilities to provide an operational and risk management framework for the removal of pathogens in the treatment system. The application of a CCP approach to barriers in a treatment system for the removal of chemicals is presented. The application exemplar is to a small community wastewater treatment system that aims to produce potable quality water from a secondary treated wastewater effluent, however, the concepts presented are generic. The example used seven treatment barriers, five of which were designed and operated as CCP barriers for pathogens. The work demonstrates a method and risk management framework by which three of the seven barriers could also include a CCP approach for the removal of chemicals. Analogous to a CCP approach for pathogens, the potential is to reduce the use of chemical analysis as a routine determinant of performance criteria. The operational deployment of a CCP approach for chemicals was augmented with the development of a decision tree encompassing the classification of chemicals and the total removal credits across the treatment train in terms of the mechanistic removal of chemicals for each barrier. Validation of the approach is shown for a activated sludge, ozone and reverse osmosis barrier.

Key Words

Chemical log reduction value, chemicals of concern, critical control point, advanced water treatment, water recycling

1 Introduction

The recycling of water from wastewater and stormwater for re-use in a range of potable and non-potable applications is an important factor in the augmentation of water supply and in improving water productivity worldwide (Grant *et al.* 2012). Along with demand management, the opportunity exists through recycle to more than double current water resources available for human use in urban environments, referenced by the fact that more than 80% of all urban water in the world is used only once and disposed to the environment at lower quality (UN_WWAP 2017). Recycling some or all of this water would not only reduce pressures on surface and ground water resources but invigorate the use of water sources deemed too contaminated for potable use. Barriers to reuse are significant nonetheless. Pathogen and chemical removal from wastewater and stormwater requires a multiple barrier approach, and the associated chemical and microbial analysis to achieve compliance means that the water is often costlier than traditional source protected surface and groundwater supplies. In addition, there is a social stigma to the planned direct or indirect reuse of wastewater for potable purposes. The outcome is that desalination of seawater is often chosen over wastewater reuse for potable augmentation despite the fact that energy costs are higher and brine disposal limits the opportunity to coastal environments. Cost effective and well-regulated processes for ensuring the quality of water in non-coastal and small communities are therefore critical to water resilience in water scarce environments.

A key hindrance to the reuse of water is the cost of compliance testing and process validation associated with ensuring that pathogen and chemicals in the feedwater are removed to a level that ensures no acute or chronic health and/or environmental effects from the reuse of the water. In the case of pathogens, compliance entities have validated a number of processes for the removal of pathogens to minimum levels. An example is the USEPA Long Term 2 Enhanced Surface Water Treatment Rule for the removal of *Cryptosporidium* (USEPA 2018). This validation is deemed compliant by regulatory bodies provided that the equipment associated with the barrier is operated in a consistent manner and continuous or semi-continuous monitoring of surrogates to ensure performance are maintained (Hunter_Water 2005, USEPA 2018). Examples of validated barriers include membrane bioreactors (MBR), UV, ozonation and chlorination as well as nano-filtration (NF) and reverse osmosis (RO) membrane systems (WaterSecure 2018). The process allows the barrier to be operated using, for example, conductivity measurement as a surrogate of barrier integrity in the case of a RO membrane. This process significantly reduces the need for regular (daily) compliance testing using microbial analysis since barrier integrity and compliance validation have already been linked. Less regular (i.e. weekly or monthly) compliance validation is then acceptable, significantly reducing the cost of fit for purpose water production.

1.1 Critical Control Point (CCP)

To define the operational boundaries of the key barriers in a water treatment process, the Critical Control Point (CCP) concept is often used. The CCP approach was first developed by the food and beverage industry as a preventative approach to food safety as distinct from reliance on final inspection. It focused on the removal of biological, chemical and physical hazards from food and the approach was used to determine the key points within the manufacturing process where contamination can occur and be prevented (Ropkins *et al.* 2003). The same approach was then adapted for water quality management and many water regulators now specify the use of the CCP approach as the risk management framework for water treatment systems for managing operation of plants (Hunter_Water 2005, NRMMC 2008). By using the CCP approach, water treatment plant operators and their contracted entities are able to focus resources on monitoring these critical points. These points provide the greatest information and benefit in being able to quickly correct any deviations from acceptable limits and through the risk management framework, significantly reduce the costs of microbial analysis (Laydon. 2011). Along with quantitative microbial risk assessment (QMRA) of the required level of pathogen removal (Barker *et al.* 2013) (usually quoted as a log reduction value (LRV)) to mitigate the risk of acute or chronic illness), the CCP approach can be used to design and operate a multi-barrier treatment process. The basic rules for a CCP are (NHMRC and NRMMC 2011, Barker *et al.* 2013):

- Operational parameters can be measured and critical limits can be set to define the operational effectiveness of the activity (e.g. a CT measured as a chlorine residual multiplied by a contact time for disinfection)
- Operational parameters can be monitored frequently enough to reveal any failures in a timely manner (online and continuous monitoring is preferable)
- Procedures for corrective action (including process shutdown) can be implemented in response to deviation from alert or critical limits.

It should be noted here that depending on the circumstances, the claimed LRV for pathogen removal may vary for a given barrier and for the surrogate of performance used to monitor performance. In some instances, a range of surrogate measures may be in place for a particular barrier and indeed, this is the case in one instance herein where a pressure decay test and a measure of residual conductivity are used as surrogates of performance of a reverse osmosis barrier. It is important operationally that neither can over-ride the other in terms of process shutdown. To avoid confusion and reduce the costs of CCP validation for a barrier, it is usual to use one surrogate of performance per barrier with other surrogates used as quality control points (advisory), unless an extra credit for a particular pathogen or chemical is necessary that is not already covered by the single CCP.

In addition to pathogens, there are a large number of chemicals that find their way into our waterways and wastewater, and the number and diversity is increasing year on year. Many national regulatory authorities now publish guidelines for the maximum recommended concentrations of chemicals of concern (CoC) deemed to have potential in causing acute or chronic illness. These guidelines usually classify the chemicals into end use categories and although there are in excess of three hundred CoC in for instance the Australian Guidelines for Water Recycling (NRMMC 2008), the list can never be comprehensive in an environment where in excess of 50,000 chemicals and their metabolites are common to many cities and communities. To try and circumvent the issue, regulatory authorities associated with water recycling for potable applications often use a surrogate list of CoC (NRMMC 2008).

In drawing an analogy to the highly successful CCP approach used to operationally mitigate the risk of pathogens in our water supply through a focus on risk assessment and barrier integrity, the surrogate list does not represent a route to significantly lowering the cost of treated water

compliance. Whilst useful, it still requires regular chemical analysis and is prohibitive in both cost and logistics for small and remote communities (i.e. regular sampling and transport of these samples to certified measurement laboratories) and restricts the likely uptake of water recycling by those that are often most in need of water resilience. An approach that allows chemicals to use the same CCP criteria as pathogens for a particular barrier using a decision tree that relates molecular characteristics to the mechanism of removal in the barrier would seem more appropriate. The basis for such an approach is already available through extensive work on CoC across various water treatment barriers although the classification has not been formalised, trialled and validated at scale.

1.2 Demographic effect

Further to the above concept, the difference between small and large communities needs consideration. In the case of pathogens, it has been demonstrated that the treatment needs of a small community are significantly greater than for a large municipal purified water recycling plant, since pathogens shed by a few people during a disease outbreak are diluted by the bulk flow for large plants but less so for small communities (Barker *et al.* 2013). Indeed, more stringent pathogen log reduction values (LRV) are required for small communities (between 3-6 log higher) to meet a DALY (Disability Adjusted Life Year) of less than 10^{-6}/person-yr (NRMMC 2008). In the case of CoC, a similar scenario ensues whereby any chemical spills in a small community will be exacerbated since the volumetric buffering capacity of the system is much reduced. As an example, a 100 person community adding 200 L/day/person to the collection system using a treatment process with a hydraulic residence time of six hours will have an effective dilution volume of 5,000 litres. In a community of 100,000 people, the same spill would be diluted to 5 ML, a factor of 1,000 different,

albeit there is an implicit assumption of perfect mixing, something that is unlikely.

For chemicals that are added as a result of standard domestic activities, for example, pharmaceuticals and personal care products (PPCPs) and their metabolites, there is little difference expected between a large municipal and small community, save for greater variability as a result of demographic, industrial and societal influences that are not homogenized within the small community. In this context, a study on small communities is representative of a worst-case scenario and yet, except for a chemical spill scenario, the feed to a large and small community wastewater treatment plant is expected to be very similar, save for industrial inputs. Testing of a treatment plant for a small community using a large community feed is thus considered viable since a spill scenario can be considered as part of the risk management framework and everyday product concentrations in wastewater feed will be similar.

1.3 Multiple barrier approach

A multiple barrier approach has been applied in the production of potable water for centuries. The selection of barriers seeks to optimise the removal capabilities of different steps in the treatment process. Typically, the barriers include five main functions, namely source water protection, coagulation/flocculation/sedimentation, filtration, disinfection and distribution system protection (Hunter_Water 2005). To monitor the key points in the water treatment chain, the CCP concept is often used. Various guideline document outline that the CCP method is one approach which can successfully assist in reviewing the preventative measures for potable water quality management (NRMMC 2008, Laydon. 2011). The approach also specifies within the preventative measures for recycled water management that CCP analysis can be used in managing effluent quality to ensure it is fit for purpose (DPI 2015). Guideline documents usually detail the criteria that a preventative measure must meet for selection as a CCP, inclusive of operational requirements (NHMRC and NRMMC 2011).

Feedwater quality, ozonation, microfiltration, reverse osmosis, ultraviolet radiation, and chlorination were identified as CCP locations for the treatment system designed herein for the case of pathogen removal. A minimum log reduction value (LRV) and the associated operational and risk criteria to achieve the LRV were then considered (Zhang *et al.* 2017). This barrier list is not intended to be exhaustive, just a necessary minimum to achieve potable water with an acceptable risk of pathogen exposure in a small community scenario (Barker *et al.* 2013). The testing and validation of the barriers to achieve pathogen compliance is detailed elsewhere (Zhang *et al.* 2016a, Zhang *et al.* 2016c). The surrogates of performance chosen and the LRV of pathogens associated with each of the barriers was based on pre-validation scenarios from around the world and limited additional validation (Zhang *et al.* 2016c) was performed as part of the activity. For the feed water type involved, the combinations of performance surrogate and claimed LRV are thus considered typical but clearly not exhaustive of the multiple operations across the globe.

Besides pathogens, water supplies may also be polluted with trace organic chemicals, metals, nutrients, radionuclides, radioactive tracers and disinfection by-products. The latter are a consequence of oxidation steps such as ozonation, advanced oxidation and chlorination. As many of these chemicals have a potential to cause harm to health and/or the environment, chemical residual concentrations are considered as problematic and are of concern. Since input sources vary, the removal of CoC from water to achieve a fit for purpose quality is very challenging. Published work on the removal performance of CoCs in wastewater mainly focus on specific types of chemicals or the behaviour of specific barriers, however, none of them has used the CCP concept as the approach to test the overall performance of the combined barriers. Also, classification of CoCs according to their end use or broad molecular description (NRMMC 2006, NRMMC 2008), whilst useful in determining the maximum guideline concentration in the product water and the likely route to a particular toxic effect, is not useful in defining whether a molecule would be removed by a particular barrier (Tadkaew *et al.* 2011).

1.4 Advanced water treatment plant (AWTP)

This study comprises the testing of the CCP concept for CoC removal using a small scale (20 m^3/day) semi-batch containerised advanced water treatment plant (AWTP) using the secondary effluent of a municipal (50,000 person equivalent) treatment plant as a feed. The AWTP was designed for installation into an Antarctic community of 150 persons (maximum), 20 persons (minimum) and was commissioned and then tested for nine months to determine the suitability for deployment. The variation in feed between summer (150 persons) and winter (20 persons) dictated a need for semi-batch operation. The logistics of regular (daily, weekly or even monthly) water quality monitoring using sophisticated chemical analysis across a broad spectrum of chemicals and surrogates was considered impossible since the community is isolated for at least 7 months per year. Simple on-site laboratory tests and passive sampling were considered achievable. A greater level of sophistication was available during the test period although the key consideration was always the remote operational status.

The Advanced Water Treatment Plant (AWTP) for Australian Antarctic Division's (AAD) Davis Station was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, Australia during the test period. Although only a low capacity plant, it was the actual plant that is now deployed in

Antarctica and was used as the testing device herein to demonstrate the performance and reliability in the reduction of CoC using the CCP approach. It was designed especially for potable water production for small communities. The plant consists of seven barriers including ozone, ceramic micro-filtration (CMF), biologically activated carbon (BAC), reverse osmosis (RO), ultra-violet radiation (UV), calcite dissolution and chlorination (Cl_2), and was preceded by a secondary effluent treatment plant (activated sludge (AS)). At the application site in Antarctica, the secondary treatment step also includes an MBR unit with a polymeric ultrafiltration configuration, although the secondary effluent or the results presented here was from a clarifier. Earlier work has shown that except for the calcite filter, which acts as a water stabilizer and the BAC, all the other barriers have LRV claims for pathogen removal and associated CCP criteria, indicating they are all functional barriers for pathogens. These claims are summarised in Table 1.

Table 1: Claimed LRVs for pathogens for the AWTP and CCPs for each barrier (Bartlett *et al.* 2015).

Barrier	**CCP**	**LRV***		
		Virus	**Bacteria**	**Protozoa**
Ozonation	CT	2	2	0
Ceramic MF	PDT	1	1	4
BAC	Turbidity	0	0	0
RO	Conductivity and PDT	1.5	1.5	2
UV	Measured dose	4	4	4
Calcite Filter	pH	0	0	0
Chlorination	CT	4	4	0
Total claimed LRVs		12.5	12.5	10

* The LRVs are credited based on the USEPA Long Term 2 Enhanced Surface Water Treatment Rule (USEPA 2018). CT = residual concentration x contact time, PDT = pressure decay test. For ozonation, the contact time was a T_{10}, namely the time at which 10% of a surrogate appeared in the effluent.

In the assessment of CoC removal, calcite dissolution is considered a water stabilization step and Cl_2 provides no obvious chemical removal (indeed, chemicals are added in both barriers) and molecular destruction by the UV barrier, whilst possible, was not able to be quantified to a particular class of chemicals. Therefore, these three barriers are not considered as functional barriers for CoC removal in this study. It is noted none the less that advanced oxidation (using UV peroxide, UV ozone, or UV hypochlorite) is often used as a key chemical removal step and there is an opportunity to develop protocols and claims for these barriers based on the principles outlined. This means that the seven-barrier process of the AWTP plus the AS, with six barriers functional for pathogen removal, can really only be considered a maximum five barrier process for the quantification of chemical removal.

Using a CCP approach and LRV assessment, the AS, ozone, CMF, BAC and RO barriers are investigated as functional barriers for CoC removal in this work. Given that a removal mechanism specific to a class of molecules could not be assigned to the CMF and BAC barriers, analysis of the AS, ozone and RO barriers is completed in detail here. The potential for MBR removal of chemicals is also considered although no validation data is presented since this barrier was not operational during testing. As a consequence of the CCP approach, the maximum feed concentrations of chemicals in the wastewater collection system that would have the potential to cause compliance breaches are also calculated. The results of this assessment are considered generalizable to direct potable water reuse. Also, a decision tree is established for the classification and assignment of total credits for any CoC. The decision tree takes into account the attributes of a particular molecule that would cause it to be removed or indeed generated at a treatment barrier. These attributes include mass, volume, water-oil partition characteristics, bond structure, bond type and charge. This is combined with the guideline limits for potable water to assess the effectiveness of the AWTP barriers.

The study aims to provide a case study for the use of the CCP approach for the removal of chemicals of concern from water for potable reuse. The case study chosen, that of a small plant associated with a small community, represents the worse-case scenario in risk management terms for the removal of chemicals, although the barriers analysed are generic to a wide range of recycle plants and the analysis of each of these barriers is independent of the scale of the plant. It is acknowledged that the barrier types and conditions are not comprehensive, but the barrier operational conditions chosen are considered applicable to a wide range of scenarios.

2 Experimental Section

2.1 AWTP operation

The AWTP was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, Australia. The AWTP had seven process units including ozonation, CMF, BAC, RO, UV disinfection, calcite filtration and chlorination (Cl_2). In its final application state, the AWTP is preceded by an MBR within the secondary treatment plant (AS plant with clarifier as tested here). There were two output streams of the AWTP, namely a RO concentrate and a product stream stored for potential potable use. A schematic of the process flowsheet is shown in Figure 1.

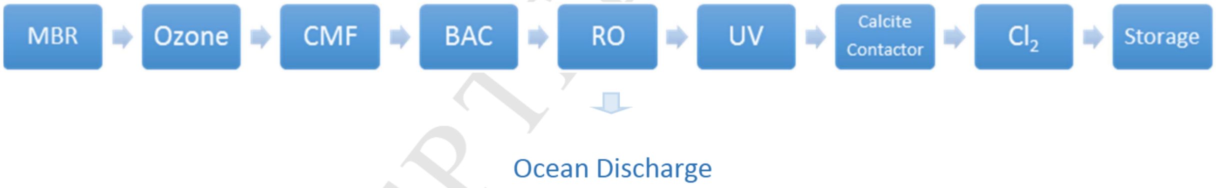


Figure 1: Schematic of the AWTP flowsheet

2.1.1 Ozone

A packaged ozone system (Wedeco OCS-GSO) and its operation are described elsewhere (Zhang *et al.* 2016a). The plant commenced operation with target, alert and critical limits for ozone residual or ozone dose as shown in Table 2. These were taken as critical control point (CCP) limits for the ozone barrier. The target ozone levels were chosen based on pathogen reduction requirements. The CoC reduction criteria and chemical classification, including the propensity of a particular chemical type to be destroyed by ozone (specified as a LRV), were chosen based on the description of Dickenson et al (Dickenson *et al.* 2009) and the feedwater characteristics. Of critical interest here was the concentration of total organic carbon (TOC) in the feed to the ozone barrier. Data from the literature in terms of ozone dose and residual to achieve a given LRV of a particular class of chemical, when compared to that required to achieve the pathogen credits of the barrier (see Table 1) were such that the pathogen based CCP criteria were considered adequate in this instance. Other surrogate and higher order criteria may be required if either a higher chemical or pathogen removal credit is deemed desirable.

Table 2: CCP values for the ozone barrier, with either ozone residual or an ozone dose as the target criteria

Key Control Measures	**Ozone residual (mg/L)**	**Ozone dose (mg/L)**
Target Criteria	0.25	14
Alert Limit	<0.1	<12
Critical Limit	<0.05	<11.7

2.1.2 Reverse Osmosis (RO)

The RO system consisted of five 10.2 cm (4”) BW30 (Dow Filmtec) membranes in series and is described elsewhere (Zhang *et al.* 2016a). A simple process flow diagram for the RO barrier is shown in Figure 2.

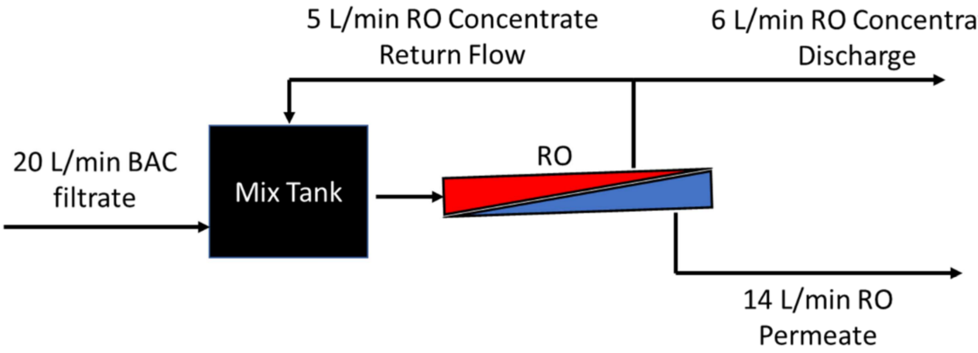


Figure 2: Process flow diagram for RO

2.2 Sampling and data analysis

Unfiltered water samples were collected from 8 locations in the AWTP. These locations were the feed (post AS), post ozone, post CMF, post BAC, RO concentrate, RO permeate, post UV and plant outlet (Figure 3). All outlets were flamed and then flushed before sampling. Additionally, a sample of feed water to the Selfs Point wastewater treatment plant was also taken.

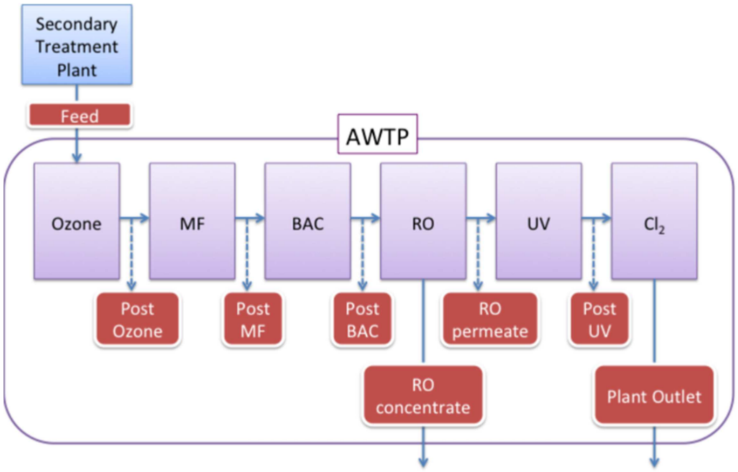


Figure 3: Summary of sampling locations in the AWTP

The samples were sent stored on ice to a laboratory in the School of Chemistry at the University of Melbourne. The analytical analysis of all samples and the subsequent data analysis is described in detail in Allinson et al. (Allinson *et al.* 2018).

The Limit of Reporting (LOR) were determined according to Method 1030C in Standard Methods for the Analysis of Water and Wastewater (Eaton *et al.* 2005). Where statistical comparisons required all data to have a numerical value, then concentrations less than the LOR values were set at 0.5 times the LOR value.

3 Results and discussion

3.1 Critical Control Point identification and LRV credits

3.1.1 Feed assessment and the role of secondary (activated sludge) treatment

The final installation of the AWTP is inclusive of a membrane bioreactor, which is expected to show better performance for the removal of micropollutants compared to a more conventional activated sludge treatment process inclusive of clarification (Clara *et al.* 2005a, Reif *et al.* 2008, Radjenović *et al.* 2009), since the membrane acts as a more complete physical barrier to the passage of particulate/suspended solids. The membrane also acts as a barrier to dissolved organic species through adsorption and entrapment in the fouling layer (Steinle-Darling *et al.* 2007, Fujioka *et al.* 2013, Fujioka *et al.* 2017). The extended solids residence time (SRT) of an MBR enhances the growth of slow growing microorganisms and prolongs biodegradation of micropollutants (Clara *et al.* 2005a, Clara *et al.* 2005b). None the less, a standard activated sludge (AS) process was used during this testing and as with all such processes, including those with an MBR, adsorption of micropollutants onto sludge and/or biodegradation (Clara *et al.* 2005a, Wijekoon *et al.* 2013b) are expected to be the most important micro-pollutant removal mechanisms. Molecules that do not adsorb on to sludge (hydrophilic or less hydrophobic) or that are not readily biodegradable within the hydraulic residence time of the activated sludge process will have a propensity to pass through the barrier.

There are few systematic studies of the mechanistic removal of organic pollutants by activated sludge treatment. Tadkaew et al. (Tadkaew *et al.* 2011) used a range of challenge additions of organic COCs including endocrine disrupting chemicals (EDCs), pesticides, and pharmaceutically active chemicals (PhACs) to a synthetic wastewater to test a 40nm pore sized MBR. Three molecular features were identified as directly connected to the removal efficiency (Isma *et al.* 2014) and a classification is designated as:

AS Class 1: Hydrophobicity: all molecules with a hydrophobicity greater than log D@pH 8 of 3.2 showed >85% removal (LRV>0.8) where D is the partition coefficient between a hydrophilic and a lyophilic phase, relative to octanol=8.0

AS Class 2: Non-Class 1 chemicals with electron withdrawing groups: molecules with electron withdrawing groups such as chlorine, fluorine, bromine or amide are observed to be recalcitrant to removal with <20% removal.

AS Class 3: Non-Class 1 molecules with electron donating groups: these chemicals are more easily attacked and showed good removal in many cases. This includes a very wide variety of functional groups, exclusive of those in AS Class 2.

Kovalova et al. (Kovalova *et al.* 2012), in their study on micropollutant removal from hospital wastewater provided consistent results to Tadkaew et al. (Tadkaew *et al.* 2011). Based on a range of literature reviewed in Kovalova (Kovalova *et al.* 2012) and the Tadkaew (Tadkaew *et al.* 2011) studies, it was concluded that the only claim that could be made for the removal of CoC that was consistent across all literature for a standard secondary activated sludge process or for an MBR system was for the class of chemicals determined to be hydrophobic (Log D @ pH 8>3.2) (**AS Class 1**). This chemical grouping was expected to be consistently removed to better than 85% (LRV>0.8) (Tadkaew *et al.* 2011, Kovalova *et al.* 2012) and the main removal mechanism for this chemical grouping was adsorption to the biomass that in turn assisted prolonged biodegradation or transformation (Clara *et al.* 2005a, Radjenović *et al.* 2009, Wijekoon *et al.* 2013b). A key difficulty with a AS with clarifier or an MBR system is to define an operational surrogate that can be used to set alert and critical control points in a CCP system. It is usual to set multiple criteria in this instance. Examples include turbidity of the clarified overflow (since AS Class 1 molecules are adsorbed to the biomass) and a combined measure of the reduction of either DOC or nitrogen. The latter is a performance surrogate in terms of hydraulic residence time and biological activity.

Although no MBR was operational during testing, the CoC removal mechanism was tested assuming that the clarification system was a worst-case scenario mimic of an MBR whereby feedwater turbidity was taken as a CCP. In cases where the turbidity exceeded 5 NTU, the plant was not operated. Samples of the feed to the Selfs Point plant (primary wastewater) were filtered through standard Whatman filter papers and analysis completed using the AIQS-DB methodology. Many of the semi volatile chemicals in the feed sample to the plant saturated the GC-MS detector and non-volatile compound levels were so high that they saturated the LC-MS column completely, which negated further work. As a result, 34 chemicals that were within the measurement range in the primary influent were chosen for further analysis. Dilution of the feed to the GC-MS and LC-MS was not performed to rectify the saturation issue as the initial detection analysis is quite time consuming for the AIQS-DB method and the saturation was not confirmed until more than a month after the initial run. Among the 34 chemicals, the K_{ow} (LogD) data for 21 chemicals is available from the on-line "ChemSpider" database (Royal Society of Chemistry 2019). For a further 11 straight chain alkane chemicals, the K_{ow} was assumed (based on chemical structure) to be greater than 10. Only 3 chemicals had a K_{ow} less than 3.2. The removal efficiency across the secondary waste water treatment plant was then assessed through sampling of the secondary waste water clarifier (feed to the AWTP). Samples were taken under high and low flow conditions although the hydraulic residence time was not significantly different across any 24-hour period. The data and associated analysis are shown in the supplementary information (Table S1) for one primary feed sampling event. It should be noted that the clarifier overflow of the secondary treatment plant (feed to the AWTP) was sampled weekly for a period of nine months as well as specifically for high and low flow periods of operation (as detailed in Table S1).

Although only 3 of the 34 chemicals considered here had a Log D value below 3.2, a minimum LRV of 1.25 was measured for all chemicals across the secondary (AS) treatment process that was the feed to the AWTP. Therefore, the operational data indicate this minimum LRV was not restricted to chemicals with a Log D >3.2, as chemicals with a Log D < 3.2 were also removed to similar extent (Tadkaew *et al.* 2011). However, the removal mechanism for the Log D < 3.2 chemicals is not singular or well defined. Other characteristics such as the presence of electron donating or withdrawing groups and their strengths (Tadkaew *et al.* 2011, Wijekoon *et al.* 2013b), and the extent to which the molecule is assimilable makes assessment difficult. Molecules of LogD <3.2 with strong electron donating groups tend to biodegrade easily while molecules with strong electron withdrawing groups would be expected to be retained in the clarifier overflow. The data here is limited, since the number of molecules in the feed analysis was limited. Indeed, over seventy chemicals were detected regularly in the feed to the AWTP and many of these were beyond the saturation limit of the detector in the sampling associated with the feed to the Selfs Point plant. Taking both the consistency of the analysis data in this study and the literature data into account, it would seem that a claim of an LRV of 0.8 for organic chemicals with a Log D >3.2 is justified, since the main mechanism of removal is associated with particle attachment and this is enhanced for an

MBR. The operational CCP for the MBR in Antarctica is <0.1 NTU with a critical limit of 0.2 NTU to achieve pathogen removal requirements. The CoC removal criteria should be easily achieved at this operational state.

Other chemicals of interest include nitrogen and radiolytic compounds. Since total nitrogen (TN) is a feed water quality control parameter of the AWTP, it was monitored on-line in the feedwater. Removal to an LRV of greater than 1 was observed across the 9 months of operation. Radiolytic compounds such as particulate radioactive tracers were not measured and although good removal would be expected, no data is available from this study.

A conservative LRV of 0.8 for AS Class 1 chemicals and 1.0 for TN for a AS system is supported based on the data from the Selfs Point Waste Water Treatment Plant and previous literature. This will be considered further later and although not validated, is an important consideration in the treatment of chemical spills to small community wastewater treatment plants where the water is being re-used.

3.1.2 Ozone

Using the experimental results and protocols developed by WaterVal for pathogen control (WaterSecure 2017a), protocols for chemical control for ozonation were formulated and validated. The WaterVal procedure provides a recommended approach to validation that is based on the following nine elements (originally written for pathogens but reformulated here),

1. Identification of the mechanisms of chemical removal by the treatment process unit,

2. Identification of target chemicals and or surrogates that are the subject of the validation study,
3. Identification of factors that affect the efficacy of the treatment process unit in reducing the target chemical,
4. Identification of operational monitoring parameters that can be measured continually and are related to the reduction of the target chemical,
5. Identification of the validation method to demonstrate the capability of the treatment process unit,
6. Description of a method to collect and analyse data to formulate evidence-based conclusions,
7. Description of a method to determine the critical limits, as well as an operational monitoring and control strategy,
8. Description of a method to determine the LRV for each chemical group in each specific treatment process unit performing within defined critical limits,
9. Provision of a means for revalidation or additional onsite validation where proposed modifications are inconsistent with the previous validation test conditions

Data for the removal of organic CoC across the AWTP barriers, as measured by GC-MS and LC-MS (Kadokami *et al.* 2005) according to the AIQS-DB methodology as a composite of monthly data (for 9 months) is reported in detail in an earlier publication (Allinson *et al.* 2018) as well as removal of

DOC and TN across barriers for an average of 30 weekly sampling events (Zhang *et al.* 2016b, Zhang *et al.* 2017).

From the operational data of the AWTP (Allinson *et al.* 2018), an overall 60% reduction in CoC was achieved across the ozone barrier. However, for chemicals inclusive of TN and total DOC in solution, ozone showed little or no effect (Zhang *et al.* 2017). This is expected since mechanistically it is difficult to envisage mineralisation of organic chemicals, but it is expected that there should be significant fragmentation. Assimilable organic carbon is produced during ozonation hence DOC reduction is not expected, however, following ozonation, barriers such as activated carbon, biologically activated carbon, membranes and sand filtration have been used to reduce the concentration of assimilable organic carbon (Hollender *et al.* 2009, Zhang *et al.* 2016a).

Ozonation has been identified as an effective process of removing a wide spectrum of CoC both in wastewater treatment and water treatment (Ternes *et al.* 2003, Snyder *et al.* 2006, Broséus *et al.* 2009, Margot *et al.* 2013). Effective removal is mainly attributed to the high oxidation potential of OH radicals. Huber et al. (Huber *et al.* 2005), reported between 90-99 % removal of eleven commonly found pharmaceutical and personal care products (PPCPs) in a pilot scale wastewater treatment system, at an ozone dose 2-5 mg O_3/L. This dose level is significantly below the critical limit of the ozone barrier of the AWTP but it has been shown that the absolute dose is not a preferred criterion since the dose should reflect the initial ozone demand (IOD) in the feed water (Dickenson *et al.* 2009, Wert *et al.* 2009). A CCP criteria that includes both a dose relative to the IOD and a CT may be indicated.

In the presence of an excess of ozone and a sufficient reaction time, chemicals with tertiary amino groups and aniline moieties (e.g., diclofenac and sulfanamides) and chemicals with an activated aromatic ring and double bonds (e.g., carbamazepine and trimethoprim) can be significantly reduced during ozonation at a relatively low ozone dose of as little as 2-3 mg O_3/L (Hollender *et al.* 2009). The efficiency of ozonation, especially at low ozone dose, is attributed to the high rate constants for the reaction of those chemicals with ozone, low DOC concentration (<5 mg/L), an absence of competitors such as nitrite (~0.05 mg/L) and a neutral pH, which leads to high ozone stability (Hollender *et al.* 2009). The target ozone dose for the AWTP was 14 mg/L. This was designed to be high relative to the TN and DOC concentration so as to ensure the presence of OH radicals, not just ozone, for the destruction of CoC.

Analysis showed that nitrosamines including NDMA, NDEA and 9 other new molecules were produced after ozone oxidation, mainly aliphatic chemicals (6 aliphatic, 3 aromatic). The occurrence of reactive inorganic nitrogenous intermediates such as hydroxylamine and dinitrogen tetroxide (N_2O_4) are mainly attributed to the formation of nitrosamines during ozonation (Lei *et al.* 2009). NDMA is a known disinfection by-product of ozonation (Gerrity *et al.* 2015) and was under continuous concentration detection through each barrier. NDMA can be effectively removed by biodegradation due to the presence of an electron-donating group (i.e. dimethyl amine) (Krauss *et al.* 2009, Wijekoon *et al.* 2013a). The data is presented in an earlier publication (Allinson *et al.* 2018) and shows that a small reduction in NDMA was achieved after the biological activated carbon barrier but that the RO membrane system was critical in the reduction to non-detectable levels.

As noted, literature data for molecular changes solely across ozone barriers under operational conditions are very limited. The data is usually for combined ozone-BAC scenarios (Hubner *et al.*

2015) although the study of Lee *et al.* looks at removal both before and after BAC and provides

detailed information on the ozone dose to DOC ratio in an operational plant (Lee *et al.* 2012). In addition, ozone dose and contact time reported in literature are for their own specific cases and are often not reported and/or are very different from the operational scenario of the AWTP. Ozonation efficiency for the removal of CoC is significantly affected by the instantaneous ozone demand (IOD), wherein a higher ozone dose than the IOD assures occurrence of OH radicals to oxidize recalcitrant chemicals. Whilst an ozone dose below the IOD destroys molecules susceptible to ozone oxidation, it is hard to quantify removal unless there is an excess of OH radicals. At an O_3 dose equal or higher than the IOD, significant OH formation takes place. As indicated earlier, the organic concentration strongly influences the available OH radical concentration. At an ozone:TOC ratio of 0.6 or higher, substantial OH formation can always be assumed (Dickenson *et al.* 2009, Wert *et al.* 2009). For higher ratios, almost all organic molecules, not depending on their structure, are removed efficiently, often below the detection limit. With increasing ozone contact time, the chemical removal increases and typically the reaction completes after a few seconds to minutes (EPA 2011).

In Dickenson et al.'s pilot study (Dickenson *et al.* 2009), the ozone dose was varied across a range of 2.1 to 7.0 mg/L to give an ozone/TOC ratio from 0.3 to 1.0 mg/mg with data reported predominately (Snyder *et al.* 2006, Wert *et al.* 2009) for the 0.6 to 1.0 range. The contact time varied from 2 to 18 minutes. Using the extended integrated method based on the ozone residual concentration at outlet and T_{10} in the reactor, the calculated ozone CT_{10} value was between 4 and 11 mg.min/L (Rakness *et al.* 2005). The T_{10} in the reactor was measured using tracer studies. No CT_{10} value is given for the study by Lee et al. but contact times between 5 and 15 minutes and ozone/TOC ratios of 0.4 to 2 are reported (Lee *et al.* 2012). In the AWTP, the ozone dose was such that the ozone/TOC ratio was always >1.0 and the CT_{10} was >14 mg.min/L at a minimum contact time > 5 minutes for all operational times where an ozone residual was detected. There was a period of operation where this was not the case although no change in performance against pathogen or chemical LRV's was noted in this period. In the pilot study of Dickenson *et al.* (Dickenson *et al.* 2009), they investigated the response to ozone of different molecular types. By assuming the instantaneous ozone demand (IOD) had been exceeded, they categorized the ozonation potential of chemicals into four key molecular groups. The groupings are outlined in Table 6.

Table 3: Molecular categories for ozonation

Class	**RE (%)**	**Molecular Characteristics**	**Other indicators**
Ozone 1	>90	Electron rich aromatic systems with hydroxyl, amino, acylamino, alkoxy or alkyl groups Deprotonated amines Nonaromatic alkenes	Ozone second order reaction rate >103 M^{-1} s^{-1}
Ozone 2	>50 <90	aliphatic alkane, ketone, alcohol, acid, ether, and amide or and nitro aromatic chemicals	
Ozone 3	>25 <50	Nitrosamines	Formation and removal are competitive.
Ozone 4	<25	Halogen containing aliphatic and aromatic chemicals	Strong electron withdrawing groups (EWG's)

An analysis was completed on the nine data sets accumulated over the monthly sampling events in the AWTP using GC-MS and LC-MS analysis as well as a separate nitrosamine study. The feed and post ozone data were compared and categorized using the Dickenson *et al.* classification. The detailed results are provided in Table S2 of the supplementary information. A summary of the data is shown in Table 4.

516 Table 4: Removal data across the ozone barrier by class of compound

Class	**RE (%)**	**Removal observations**	**Exceptions**
Ozone 1	>90	N=24 chemicals >90 % N=20 50-90% N=1 increased N=3	50-90% - 4-Methyl-2,6-di-t-butylphenol(BHT) Increased – Fenubucarb, Dimethyl phthalate, Benzyl alcohol
Ozone 2	50-90	N=19 chemicals >90% N=7 50-90% N=2 25-50% N=3 <25% N=2 increased N=5	25-50% - Cholestanol, 24-Ethyl coprostanol, Stigmastanol <25% - Methyl myristate, beta-Sitosterol Increased Tris(1,3-dichloro-2-propyl) phosphate, Octanol, 9Z)-9-Tetradecenoic acid, methyl ester, Coprostanone,
Ozone 3	25-50	N=2 chemicals Increased N=2	Increased - NDMA, NDEA
Ozone 4	<25	N=10 chemicals >90% N=8 25-50% N=1 increased N=1	Increased - Tris(2-chloroethyl) phosphate

Chemicals in the Class 1 categorisation (Table 4), nominally electron rich aromatic molecules and non-aromatic alkenes, were removed very effectively by ozone, often to the point of non-detection and all were well below guideline values associated with the Australian Drinking Water Guidelines (ADWG) and the Australian Guidelines for Water Recycle (AGWR) (tabulated information is shown in the supplementary information). The three chemicals that increased in concentration were still well below guideline values and can be classed as either an ozone by-product in the case of dimethyl phthalate and as possible anomalies in the other two cases since these were not observed in the feed and detected only once in the effluent in nine samplings. The concentrations in each case were close to the LOR. Therefore, 21 out of 24 chemicals in Class 1 were reduced in concentration and all to substantially below guideline values. The latter is not a criterion for operation of a CCP, just a necessary outcome if no other barriers exist for chemical removal. The average removal efficiency of the 21 chemicals was >98.6% with a range of 86.6-100%. This was consistent with literature expectations for the role of ozone at doses greater than the IOD and with a high CT_{10} as measured by the extended integration method (Kadokami *et al.* 2005). Therefore, the data is consistent with the claim that the ozone barrier, operated under CCP criteria to remove pathogens, could be operated under the same criteria to remove chemicals where the classification is systematic with the Class 1 designation of Dickenson *et al.* Under these conditions, an LRV for electron rich aromatic chemicals of 0.9 is indicated for this barrier. The performance of the barrier for the other classes of compound was also consistent with literature and the mechanistic removal/formation classification, but the LRV is too low and inconsistent to make a claim for LRV credits under CCP operational conditions.

3.1.3 Reverse Osmosis (RO)

Using experimental results and protocols developed by WaterVal (WaterSecure 2017b) for pathogen control, protocols for chemical control for reverse osmosis were formulated and validated. The nine elements of the WaterVal validation protocol were listed earlier.

The operational data from the AWTP shows a good rejection of both organic (Allinson *et al.* 2018) and inorganic species including DOC, TN and NDMA (Zhang *et al.* 2016a) across the RO barrier. The general mechanisms of RO rejection of chemicals are size exclusion and steric hindrance for all kinds of molecules and electrostatic interaction and rejection for ionic species (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010). To a lesser extent, adsorption to the membrane and hydrophobic-hydrophobic interactions take place and influence the rejection rate (Kiso *et al.* 2001, Bellona *et al.* 2004a, Nghiem *et al.* 2004). For uncharged molecules, size exclusion is the most important rejection mechanism. Electrostatic interactions lead to high rejection, even for very small ions (Kimura *et al.* 2004).

Despite the myriad of possible mechanisms, the principal mechanism to remove chemicals with a molecular weight greater than the molecular weight cut off (MWCO) of the membrane is size exclusion. The MWCO of RO membranes is typically in the range of 100–300 Dalton (Da) for organic molecules with a rejection of 96.5 % (LRV 1.5) and up to 99 % (LRV 2.0) or greater for inorganic ionic solutes (Ahrens *et al.* 2010). However, the MWCO provides an estimate of the sieving effect only and does not take into account the hydrophobicity, charge and geometry of the molecule, temperature and flux effects, all of which can also affect rejection (Kiso *et al.* 2001, Bellona *et al.* 2004b).

Several studies indicate that the molecular weight and consequentially derived molecular weight cut-offs are not particularly reliable predictors for chemical rejection (Drewes *et al.* 2003, Agenson and Urase 2007, Alturki *et al.* 2010, Doederer *et al.* 2014). Only at a certain molecular weight significantly higher than the MWCO do molecules seem to be always rejected by the membrane due to size exclusion. A better predictor of exclusion is the molecular diameter or width, which was successfully used by Alturki *et al.*(Alturki A.A. *et al.* 2010) and Doederer *et al.* (Doederer *et al.* 2014) to predict rejection. However, this information is not directly available in common databases and has to be calculated. A good surrogate appears to be the molar volume which can be obtained in databases for every chemical (i.e. http://www.chemspider.com/).

Charged molecules possess a hydration shell, which makes the combination of actual ion and hydration shell too bulky to pass the membrane. Therefore, all charged molecules are rejected efficiently, albeit there are indications that positively and negatively charged chemicals can behave differently, possibly due to adsorption. Alturki *et al.* (Alturki A.A. *et al.* 2010) demonstrated that rejection of hydrophobic molecules by RO is not as effective as ionic and hydrophilic species, but a combination of 40 TrOCs ranging in partition coefficient (1.21 to 6.19@pH 8) and size (151 to 454 MW) were removed to below detection limits from an initial dose of 2 g/L. This represents a LRV>2 for a Limit of Reporting (LOR) of 0.005 g/L.

Conductivity across the process was used for on-line verification in the AWTP and was a CCP monitoring parameter for pathogen reduction. Typical operational LRV data for ionic species (predominately inorganic salts) is reported elsewhere (Zhang *et al.* 2016a).

The data for operation of the AWTP indicated that the DOC in the feed to the RO was reduced from

an average value across all samplings of 6.27 mg/L to a value of <0.26 mg/L, a reduction of 95.8% or LRV of 1.38. For TN, the average feed concentration was 6.89 mg/L. This was reduced to an average of 0.28 mg/L (n= 30 weeks of readings), a reduction of 95.9% or LRV of 1.39.

The classification of CoC varies across the world, but commonly, the classification is based on end use and the human response of the molecules. One example is the classification used in the the AGWR (NRMMC 2008) where molecules are classified as: inorganic chemicals; disinfection by-products; pesticides; fragrances; pharmaceuticals and metabolites; fire retardants; dioxins and dioxin like chemicals; miscellaneous organic chemicals – PCB's, PAH's, phthalates, organotins, etc.; radiological; and chelating agents .

Based on the operational data from the AWTP over nine-months of operation along with literature analysis (NRMMC 2006, Snyder *et al.* 2006), the classification of molecules used in the AGWR is not considered useful in determining whether a molecule would be removed by a particular barrier, as there was often a range of molecular attributes within a particular class. A new classification based on the mechanistic propensity of a particular compound to be removed by the RO barrier is suggested. Similar to the designation of hydrophobicity as a key determinant of removal for the activated sludge barrier and the presence of an electron rich moiety for removal by ozone, a set of criteria were considered for RO. This classification was for polyamide (PA) based RO membranes with a NaCl rejection of greater than 96.5 % (as was used here).

RO Class 1: Organic ionic species. Mechanism of removal: (a) electrostatic interactions between charged solute and the negatively charged membrane surface (Bellona *et al.* 2004a, Alturki A.A. *et al.* 2010) and (b) electrostatic repulsion of negatively charged hydrophilic solutes (Kimura *et al.*

2004, Alturki A.A. *et al.* 2010). The pH must be at least one above or below the pK_a or pK_b of the molecule respectively.

RO Class 2: Organic neutral molecules, molar volume > 120 cm^3, Mechanism of removal: size exclusion and steric hindrance (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010)

RO Class 3: Organic neutral molecules, molar volume < 120 cm^3, electron withdrawing groups, Mechanism of removal: not reliable due to small size (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010)

RO Class 4: Organic neutral molecules, molar volume < 120 cm^3, only electron donating groups or electron donating and electron withdrawing groups. Mechanism of removal: not reliable due to small size (Bellona *et al.* 2004a, Kimura *et al.* 2004, Alturki A.A. *et al.* 2010)

RO Class 5: Inorganic ionic species, Mechanism of removal: (a) electrostatic interactions between charged solute and negatively charged membrane surface (Bellona *et al.* 2004a, Alturki A.A. *et al.* 2010) and (b) electrostatic repulsion of negatively charged hydrophilic solutes (Bellona *et al.* 2004a, Kimura *et al.* 2004)

RO Class 6: Inorganic non-ionic species. Mechanism of removal: poorly removed due to extremely small size and hydrophilicity (Kezia *et al.* 2013)

RO Class 7: Particulate radioactive tracers. Mechanism of removal: size exclusion, similar to the removal of viruses and particulates

Literature data is now presented alongside data from the AWTP. As noted earlier, in excess of seventy organic molecules were found regularly in the feed to the AWTP across the 9 month test period. Many of these were removed in the first three barriers to below the LOR. The cumulative

DOC removal was consistently in the range 55-60% across the ozone, CMF and BAC barriers.

Figure 4 shows data from previous literature (Comerton *et al.* 2008, Alturki *et al.* 2010, Appleman *et al.* 2014, Fujioka *et al.* 2015, Zhang *et al.* 2017) for RO Class 1 chemicals (organic ionic). The literature data was for similar RO membranes in terms of surface layer and MWCO (polyamide, rejection >96.5%). A minimum LRV = 1 is observed for all chemicals of this group, with most rejected to a considerably higher level. There is no data from the AWTP here as although there were RO Class 1 chemicals in the feed (Allinson *et al.* 2018), , they were not detected in the permeate of the RO membrane and their concentration in the feed was not greater than 5x the LOR. Under these circumstances, any LRV calculation would be an underestimate of the actual LRV and may imply a poor rejection. This would be inaccurate.

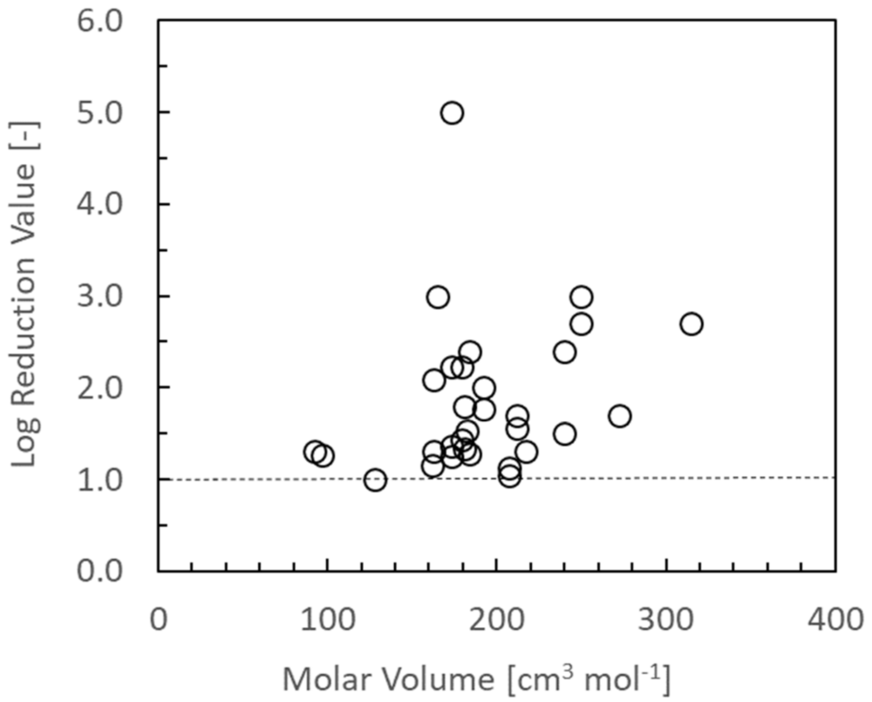


Figure 4: Performance of rejection of Class 1 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

Data for RO Class 2 molecules is shown in Figure 5. They have a molar volume above the limit of 120 cm^3 mol^{-1} and although one might expect rejection rate to improve with molar volume, the literature (Comerton *et al.* 2008, Alturki *et al.* 2010, Appleman *et al.* 2014, Doederer *et al.* 2014, Altalyan *et al.* 2016) is not supportive of this expectation. However, a large number of the molecules in the literature were rejected to the extent that they could not be detected in the RO permeate. A lack of knowledge of the LOR in these systems meant that an LRV could not be determined in many cases. For the AWTP data, a rejection of between 90-99 % is observed, regardless of molar volume, however the criteria for inclusion in the data set was, as for the Class 1 molecules, not met. This is an issue with results where the input concentration is not controlled and reflects a dilemma of all field scale work where spiking of chemicals is not an option for a wide range of pollutants. It is noted that wherever the criteria for LRV determination was met, an LRV of > 1 was observed for all chemicals in this class except for one data point (LRV=0.84) for bisphenol A from the laboratory scale work of Alturki *et al*. (Alturki *et al.* 2010).

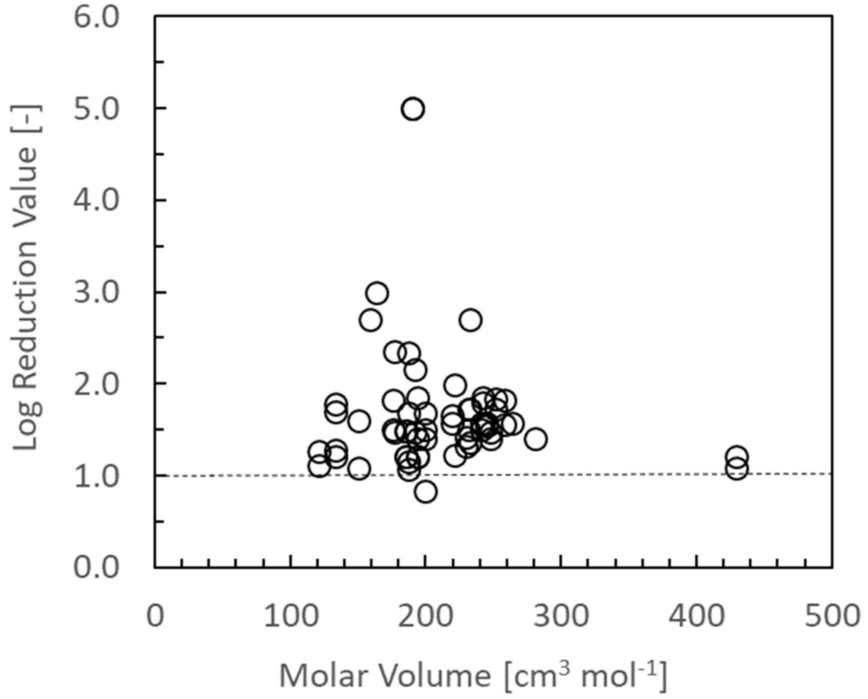


Figure 5: Performance of rejection of Class 2 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

Data for RO Class 3 molecules are shown in Figure 6. The data (Doederer *et al.* 2014, Altalyan *et al.* 2016, Allinson *et al.* 2018) confirms, including that from the AWTP, that most chemicals in this class are rejected to some extent but once the molar volume decreases significantly below 120 cm^3 mol^{-1}, for molecules that do not have a negatively polarised centre (caused by the presence of an electron withdrawing group), neither a reliable minimum removal nor a mechanism for rejection can be claimed. There is also evidence that rejection of some molecules in this class is increased by fouling and others where fouling is detrimental to removal. Operating the barrier according to the protocols defined earlier ensured that cleaning was always performed once the trans membrane pressure reached a fixed value. As such, the data reported here is for unfouled or weakly fouled

membranes.

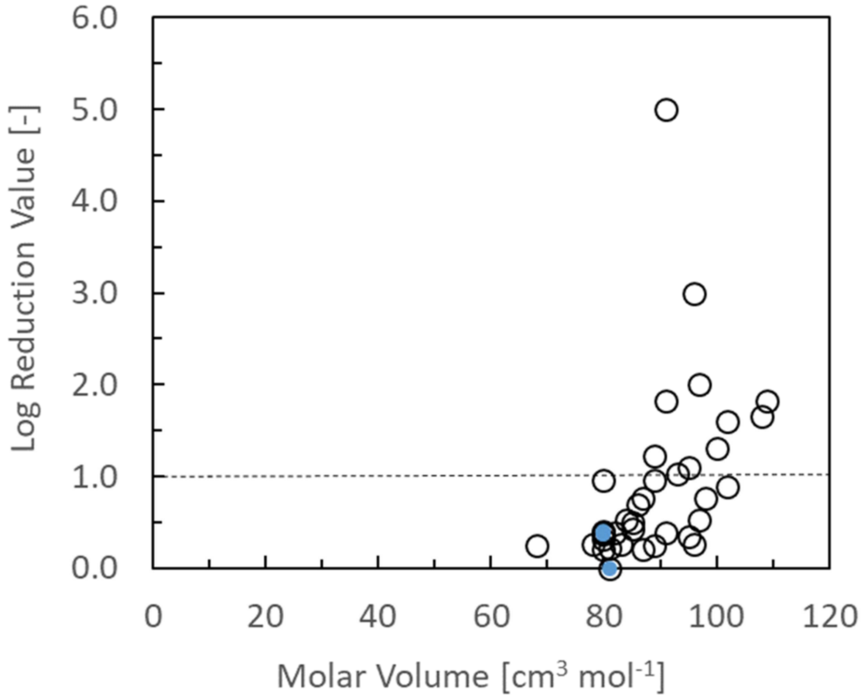


Figure 6: Performance of rejection of RO Class 3 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5). Filled data points are from the AWTP.

Data for RO Class 4 molecules is shown in Figure 7. The list of molecules in this class, for which data is available, is not extensive and includes halo-methanes and halo-ethanes amongst others. The rejection of molecules of this type would need to be specifically validated and preferably by the supplier of the RO unit (i.e. pre-commissioning) since many are harmful to health. An LRV of 0.5 is deemed possible with appropriate validation. The results of all validated data found in the literature (Altalyan *et al.* 2016) are from one source. There was no data from the AWTP in this class.

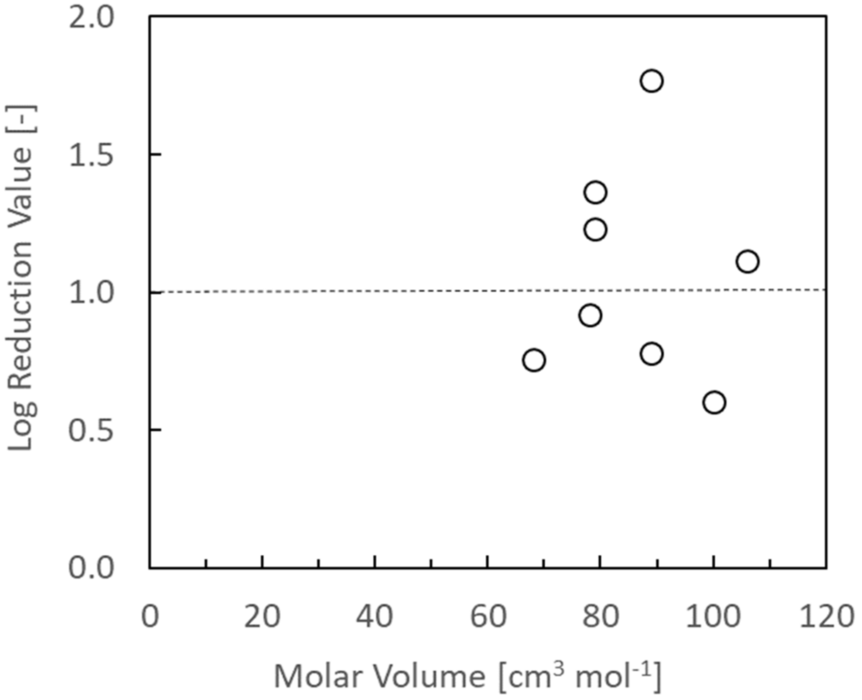


Figure 7: Performance of rejection of RO Class 4 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

The performance for RO Class 5 molecules is shown in Figure 8. The data indicates that all inorganic ions are rejected to an LRV>1 and most to an LRV>1.5. Only the smallest positively charged species are removed to less than an LRV of 1.5, although the study that reported the data (Malamis *et al.* 2012) for sodium, potassium, magnesium and manganese is at odds with the standard validation of most RO membranes using seawater and NaCl rejection as the criteria for operation. In general, an LRV of > 1.5 is achieved. The results of all data found in the literature (Ozaki *et al.* 2002, Ipek 2005, Mohsen-Nia *et al.* 2007, Malamis *et al.* 2012, Zhang *et al.* 2015) are shown in Figure 8. Since a CCP using conductance as the surrogate of performance across the RO barrier of the AWTP (Zhang *et al.*

2016a) showed greater than LRV 1.5 performance for the entire operation, the AWTP data is consistent with a proposed credit for RO Class 5 molecules and ions of LRV 1.5. The data from the AWTP was for bromate, bromide and iodide.

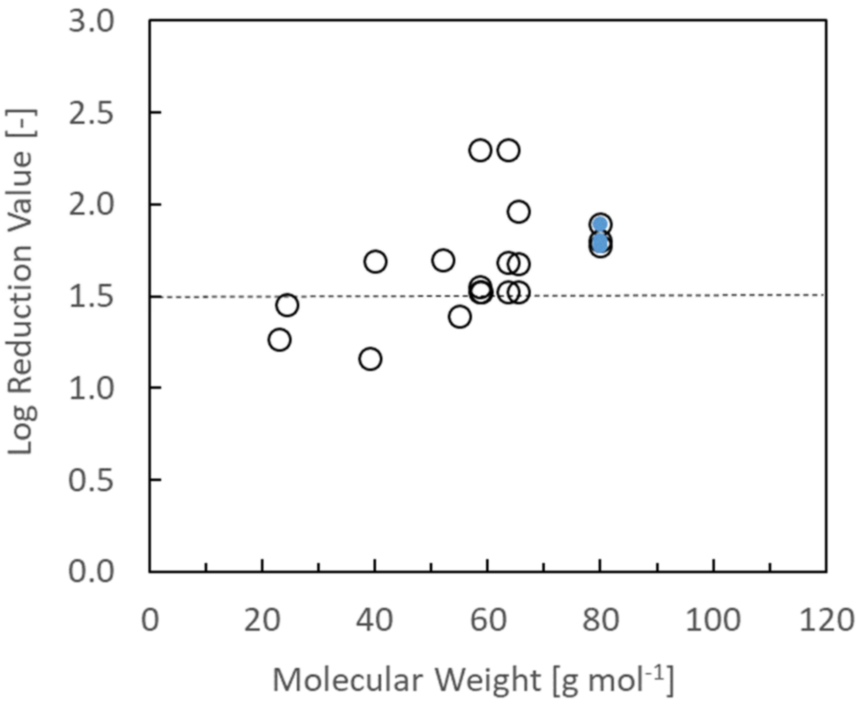


Figure 8: Performance of rejection of RO Class 5 molecules for an RO barrier of the type used in the AWTP and operated such that NaCl rejection was >96.5% (LRV 1.5).

RO Class 6 is a for water soluble uncharged inorganic ions. Boron is the obvious member of this class. Because of its extremely small size and strong hydrophilicity it can neither be rejected due to size exclusion nor due to adsorption. It is poorly rejected (Kezia *et al.* 2013) and no LRV claim would seem appropriate. RO Class 7 is for particulate radioactive tracers. Qualitative data shows good rejection since the systems of interest are the same or greater in size to viruses and as such, a similar rejection is assumed. Validation with a particulate surrogate would be required, albeit with a sub-micron sized particle. Other radionuclides fall into the other classes depending on their molecular or atomic structure.

As the result of mechanistic studies and literature research, along with the data from the AWTP, a range LRVs (shown in Table 5) would be deemed achievable under CCP operational conditions for a polyamide RO membrane operating with a NaCl rejection >96.5% (LRV 1.5). Given that the highest claim is for inorganic ionic species (RO Class 5) and this class is of itself validated continuously with on-line conductivity measurement, it is expected that these figures are robust to non-membrane failures (o-ring or glue line leaks) since such leaks should be detected with sufficient sensitivity to identify when the CCP was close to alert or alarm levels.

Table 5: Proposed achievable LRV for RO Class 1-7 molecules, ions, atoms and particulate radioactive tracers based on literature data and new data presented herein.

RO Class	**LRV**
1: Organic ionic species	1.0
2: Organic neutral species, MV > 120 cm³/mol	1.0
3: Organic neutral species, MV < 120cm³/mol, EWG	0.0
4: Organic neutral species, MV < 120 cm³/mol, EDG/other	0.5
5: Inorganic ionic species	1.5
6: Inorganic non-ionic species	0.0
7: Particulate radioactive tracers	1.5

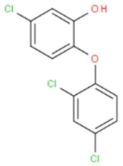
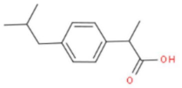
3.2 LRV calculation examples and decision tree for chemical removal

Triclosan and ibuprofen, two common molecules that fall into the category of Pharmaceutical and Personal Care Products (PPCP) found in the discharge in the secondary effluent of wastewater treatment processes, were taken as examples to exemplify how a barrier credit process or decision tree for achieving a total credits for a particular molecule would work in an analogous manner to the allocated credits for pathogens (as per Table 1). A summary of the credits allocated to each barrier chemical classification is shown in Table 6. A comparison on their characteristics and the proposed credits is shown in Table 7, along with the calculated value for the maximum concentration in the feed and the maximum spill volume. The characteristics (sometimes multiple) of each molecule in terms of its mechanism of removal has been associated to a classification and the associated removal credit for each barrier (i.e. a decision tree system) in Table 7. For example, the charge state, hydrophobicity, molecular size and the electron withdrawing or donating nature are critical to the classification across the RO, AS, RO and ozone barriers respectively since they are directly related to the dominant mechanism of removal.

Table 6: Overview of LRV credits proposed for each class of chemical across each of the AS, ozone and RO barriers. NB: Each classification is not the same for each barrier. Refer to earlier sections.

Chemical Class	BARRIER	LRV	BARRIER	LRV	BARRIER	LRV
1	AS	0.8	OZONE	1.0	RO	1.0
2	AS	0.0	OZONE	0.0	RO	1.0
3	AS	0.0	OZONE	0.0	RO	0.0
4			OZONE	0.0	RO	0.5
5					RO	1.5
6					RO	0.0
7					RO	1.5

Table 7: Proposed classification and LRV credits and comparison of Triclosan and Ibuprofen

Name	Triclosan	Ibuprofen
Structure		
General Classification	Aromatic (EWG)	Aromatic (EDG)
pKa and charge at pH 8	7.9 (neutral)	5.2 (negative)
MW	289.542	206.281
Kow	4.76 (hydrophobic)	2.23 (hydrophilic)
AGWR max value (µg/L)	0.35	400
AS Class and (LRV)	1 (0.8)	3 (0.0)
Ozone Class and (LRV)	4 (0.0)	1 (0.9)
RO Class and (LRV)	2 (1.0)	1 (1.0)
Total LRV	1.8	1.9
Maximum WWTP feed concentration (∝g/L)	22.1	31,773

In addition to the LRV credit for each barrier, the influence of a spill into the small wastewater treatment system can be predicted and a dilution factor into the waste treatment system calculated. This can be added to the LRV value in terms of the management of risk. For additions that are ubiquitous and part of normally daily activities, this is not appropriate. In this scenario, the process allows a calculation of the maximum allowable concentration in the feed, a parameter that is easier to measure than in product waters where the concentrations are quite often close to the

LOR (Allinson *et al.* 2018). These values are shown in Table 7 and can be nominally calculated for any chemical where a prescribed guideline limit is known or where a human health value can be calculated (Allinson *et al.* 2018).

For a spill, any calculation needs to consider the hydraulic residence and volume of the system. For the AWTP, this was 6 hours and 5,000 L at a person equivalent of 140 L per day for 150 people. The small volume of the system and lower than typical water use represents a worse-case scenario relative to larger treatment systems. A dilution factor or equivalent LRV can be assigned based on the concentration per litre in the spill and the spill volume relative to the volume of the treatment system.

Triclosan is a commonly used additive in disinfectants, soaps, toothpastes and mouthwashes at a concentration of 0.1-1%, typically 0.5%. A 2 mL triclosan based disinfectant and/or toothpaste use per person per day would supply around 0.01 g of triclosan per person to the wastewater system. At 140 L of water use per day, this would result in a feed concentration of 71 ∝g/L. This is more than triple the maximum calculated value in Table 7. Alternatively, a spill of 20 mL of triclosan disinfectant solution into the waste water system (5 g/L equivalent concentration), would see a dilution factor of 250,000 based on the hydraulic residence time and system volume for a small community model (5000 L wastewater holding volume). This would result in a concentration in the feed of 20 ∝g/L. This is in line with the maximum calculated value for removal to guideline limit values. In both scenarios, source control is indicated. The data from the AWTP study reflects a higher removal rate than (LRV 1.8) but from a regulatory perspective, operation of a CCP barrier model for chemicals suggests that without specific validation for chemicals of concern (too expensive for small communities), that source control and extra barrier measures are indicated. As an example of performance, the data in the supplementary information section shows that

triclosan was actually removed quite effectively by the ozone barrier with an LRV of 1.24 (as against a claim of 0.0). This is not unexpected for such a barrier operating at ozone dose levels well above the IOD whereby it is expected that the presence of the OH radical will result in indiscriminate molecular destruction.

Ibuprofen is a drug used for treating pain, fever, and inflammation. It is typically supplied as tablets containing 200mg active ingredient. The calculated value in Table 7 to achieve regulatory guideline limits is 31,773 ∝g/L. With ubiquitous use of say 5 tablets per person per day (close to the recommended maximum daily dose) and no metabolic destruction in-vivo, the feed concentration to the waste water treatment plant would still only be 7200 ∝g/L. Indeed, it would take over 1000 tablets solubilised into the waste collection system to cause an issue (5000L wastewater holding volume), which was unlikely to happen. In this instance, source control is not indicated, although measurements of the feed concentration at periodic intervals would be required to identify a maximum concentration for the barrier system for removal of this chemical. Indeed, the suitability of a particular single or multiple barrier system operating to CCP principles could be evaluated for any chemical to a maximum desirable discharge concentration.

4 Conclusions

A detailed investigation of barrier performance and CCP classification of chemicals around a activated sludge, ozone and reverse osmosis barrier has been performed using the operational data from an Advanced Water Treatment Plant (AWTP) operated at Self Point Wastewater Treatment Plant in Tasmania, Australia as well as (predominately) data from published literature.

The seven barriers associated with the AWTP were evaluated as well as an activated sludge process

that preceded the AWTP. No credible chemical removal was associated with five of the seven AWTP barriers, although the microfiltration (MF), biologically activated carbon (BAC) and to a lesser extent, UV barriers, were observed to be effective in the reduction of trace organic chemicals. However, the mechanism of removal of trace organic chemicals for these barriers was not well defined and the data did not allow classification of the removal to a particular class that would likely satisfy a regulatory authority that there was a known and systematic relationship between mechanism of removal, a specific molecular attribute (i.e. molar volume, state of charge, hydrophobicity, etc.), operating conditions and the removal achieved. The BAC was effective in the removal of assimilable organic carbon (AOC).

The individual chemical classifications developed for each of the activated sludge, ozone and reverse osmosis barriers were reflective of the molecular mechanisms of removal of a particular chemical by the barrier in the scenario considered herein. The classification is nominally generic and not based on the end use of the chemical. On this basis, the study is considered a first demonstration of the use of a multi-barrier chemical decision-tree based approach to the classification of the removal of a chemical by a treatment plant under CCP constraints. It is acknowledged none the less that further testing across a broader set of conditions (i.e. temperature, different water hardness) is essential to establishing the efficacy of the approach, including limitations across a broad set of water conditions.

A log reduction value for the removal of each chemical class of each barrier was then assigned based on operational data for the barrier operating to a CCP condition for the water type and CCP conditions considered here. This approach allows an operational plant to be designed with a clear knowledge of the likely removal of a particular chemical to a regulatory standard such as a maximum permissible guideline limit, based only on a knowledge of feed concentrations. It is envisaged that after validation across a broader set of water and operational conditions, the implementation of this process will substantially reduce the need for chemical analysis on product water from treatment plants since a plant operated to CCP limits for each barrier should then only need periodic verification of barrier performance.

5 Acknowledgements

Funding from the Australian Antarctic Division of the Australian Government and from the Australian Water Recycle Centre of Excellence is gratefully acknowledged. NDMA analyses associated with the work were performed by Stuart Khan and James McDonald at the University of New South Wales Water Research Centre. Their input is gratefully acknowledged.

6 References

Agenson, K. O. and T. Urase (2007). Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications. Great Britain, Elsevier Science B.V., Amsterdam.**:** 147.

Ahrens, S., S. Taniyasu, L. Yeung, N. Yamashita, P. Lam and R. Einghaus (2010). "Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. ." Chemosphere, **79**: 266-272.

Allinson, M., K. Kadokami, S. Shiraishi, D. Nakajima, J. Zhang, A. Knight, S. Gray, P. Scales and G. Allinson (2018). "Wastewater recycling in Antarctica: Performance assessment of an advanced water treatment plant in removing trace organic chemicals." Journal of Environmental Management **224**: 122-129.

Altalyan, H., B. Jones, J. Bradd, L. Nghiem and Y. Alyazichi (2016). " Removal of volatile organic compounds (VOCs) from groundwater by reverse osmosis and nanofiltration." Journal of Water Process Engineering **9**: 9-21.

Alturki A.A., T. Nichanan, J. A. McDonald, S. J. Khan, W. E. Price and L. D. Nghiem (2010). "Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications." Journal of Membrane Science **365**(1-2): 206-215.

Alturki, A. A., N. Tadkaew, J. A. McDonald, S. J. Khan, W. E. Price and L. D. Nghiem (2010). "Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications." Journal of Membrane Science **365**: 206-215.

Appleman, T. D., C. P. Higgins, O. Quiñones, B. J. Vanderford, C. Kolstad, J. C. Zeigler-Holady and E. R. V. Dickenson (2014). "Treatment of poly- and perfluoroalkyl substances in U.S. full-scale water treatment systems." Water Research **51**: 246-255.

Barker, S. F., M. Packer, P. J. Scales, S. Gray, I. Snape and A. J. Hamilton (2013). "Pathogen reduction requirements for direct potable reuse in Antarctica: Evaluating human health risks in small communities." Science of The Total Environment **461**(Supplement C): 723-733.

Bartlett, S., K. Northcott, P. J. Scales, D. Sheehan and S. Gray (2015). Demonstration of robust water recycling: Hazard analysis and critical control point report., Demonstration of robust water recycling (Project number 3170), Australian Water Recycling Centre of Excellence, ISBN 978-1-922202-57-4.

Bellona, C., Drewes J.E., P. Xu and G. Amy (2004a). "Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review." Water Research **38**(12): 2795-2809.

Bellona, C., J. E. Drewes, P. Xu and G. Amy (2004b). "Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review." Water Research **38**(12): 2795-2809.

Broséus, R., S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauvé, B. Barbeau and M. Prévost (2009). "Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment." Water Research **43**(18): 4707-4717.

Clara, M., N. Kreuzinger, B. Strenn, O. Gans and H. Kroiss (2005a). "The solids retention time—a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants." Water Research **39**(1): 97-106.

Clara, M., B. Strenn, O. Gans, E. Martinez, N. Kreuzinger and H. Kroiss (2005b). "Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants." Water Research **39**(19): 4797-4807.

Comerton, A. M., R. C. Andrews, D. M. Bagley and C. Hao (2008). "The rejection of endocrine disrupting and pharmaceutically active compounds by NF and RO membranes as a function of compound and water matrix properties." Journal of Membrane Science **313**(1-2): 323-335.

Dickenson, E. R. V., J. E. Drewes, D. L. Sedlak, E. C. Wert and S. A. Snyder (2009). "Applying Surrogates and Indicators to Assess Removal Efficiency of Trace Organic Chemicals during Chemical Oxidation of Wastewaters." Environmental Science & Technology **43**(16): 6242-6247.

Doederer, K., M. Farré, M. Pidou, H. Weinberg and W. Gernjak (2014). "Rejection of disinfection by-products by RO and NF membranes: Influence of solute properties and operational parameters." Journal of Membrane Science **467**: 195-205.

DPI (2015). Recyled Water: Information Sheet Number 4, Critical Control Points Department of Primary Industries, New South Wales Government, Sydney, Australia.

Drewes, J. E., M. Reinhard and P. Fox (2003). "Comparing microfiltration-reverse osmosis and soil-aquifer treatment for indirect potable reuse of water." Water Research **37**(15): 3612-3621.

Eaton, A. D., E. W. Rice and R. B. Baird (2005). Standard Methods for the Examination of Water and Wastewater. Washington, American Public Health Association.

EPA (2011). Water Treatment Manual : Disinfection The Environmental Protection Agency , Ireland

Fujioka, T., S. Khan, J. McDonald and L. Nghiem (2015). "Validating the rejection of trace organic chemicals by reverse osmosis membranes using a pilot-scale system." Desalination **358**: 18-26.

Fujioka, T., S. J. Khan, J. A. McDonald, R. K. Henderson, Y. Poussade, J. E. Drewes and L. D. Nghiem (2013). "Effects of membrane fouling on N-nitrosamine rejection by nanofiltration and reverse osmosis membranes." Journal of Membrane Science **427**: 311-319.

Fujioka, T., H. Kodamatani, H. Aizawa, S. Gray, K. P. Ishida and L. D. Nghiem (2017). "Role of membrane fouling substances on the rejection of N-nitrosamines by reverse osmosis." Water Research **118**: 187-195.

Gerrity, D., A. N. Pisarenko, E. Marti, R. A. Trenholm, F. Gerringer, J. Reungoat and E. Dickenson (2015). "Nitrosamines in pilot-scale and full-scale wastewater treatment plants with ozonation." Water Research **72**(Supplement C): 251-261.

Grant, S. B., J.-D. Saphores, D. L. Feldman, A. J. Hamilton, T. D. Fletcher, P. L. M. Cook, M. Stewardson, B. F. Sanders, L. A. Levin, R. F. Ambrose, A. Deletic, R. Brown, S. C. Jiang, D. Rosso, W. J. Cooper and I. Marusic (2012). "Taking the 'waste' out of 'wastewater' for human water security and ecosystem sustainability." Science **337**(6095): 681-686.

Hollender, J., S. G. Zimmermann, S. Koepke, M. Krauss, C. S. McArdell, C. Ort, H. Singer, U. von Gunten and H. Siegrist (2009). "Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration." Environmental Science & Technology **43**(20): 7862-7869.

Huber, M. M., A. Göbel, A. Joss, N. Hermann, D. Löffler, C. S. McArdell, A. Ried, H. Siegrist, T. A. Ternes and U. von Gunten (2005). "Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study." Environmental Science and Technology **39**(11): 4290-4299.

Hubner, U., U. von Gunten and M. Jekel (2015). "Evaluation of the persistence of transformation products from ozonation of trace organic compounds - a critical review." Water Res **68**: 150-170.

Hunter_Water (2005). Water Quality Management: A multiple barrier approach. Hunter Water, Newcastle, Australia.

Ipek, U. (2005). "Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis." Desalination **174**: 161-169.

Isma, M. I. A., A. Idris, R. Omar and A. R. P. Razreena (2014). "Effects of SRT and HRT on Treatment Performance of MBR and Membrane Fouling." International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering **8**(6): 488-492.

Kadokami, K., K. Tanada, K. Taneda and K. Nakagawa (2005). "Novel gas chromatography–mass spectrometry database for automatic identification and quantification of micropollutants." Journal of Chromatography A **1089**(1): 219-226.

Kezia, K., J. Lee, A. J. Hill and S. E. Kentish (2013). "Convective transport of boron through a brackish water reverse osmosis membrane." Journal of Membrane Science **445**(Supplement C): 160-169.

Kimura, K., S. Toshima, G. Amy and Y. Watanabe (2004). "Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes." Journal of Membrane Science **245**(1-2): 71-78.

Kiso, Y., Y. Sugiura, T. Kitao and K. Nishimura (2001). "Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes." Journal of Membrane Science **192**(1–2): 1-10.

Kovalova, L., H. Siegrist, H. Singer, A. Wittmer and C. S. McArdell (2012). "Hospital Wastewater Treatment by Membrane Bioreactor: Performance and Efficiency for Organic Micropollutant Elimination." Environmental Science & Technology **46**(3): 1536-1545.

Krauss, M., P. Longrée, F. Dorusch, C. Ort and J. Hollender (2009). "Occurrence and removal of N-nitrosamines in wastewater treatment plants." Water Research **43**(17): 4381-4391.

Laydon., C. (2011). Critical control point analysis: the operational benefits. 36th Annual Qld Water Industry Operations Workshop. Toowoomba Queensland Water Industry Operators Association Australia 73-79.

Lee, C. O., K. J. Howe and B. M. Thomson (2012). "Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater." Water Research **46**: 1005-1014.

Lei, Y., C. Zhonglin, S. Jimin, X. U. Zhenzhen, L. Heng, T. Jiayu, B. E. N. Yue, Z. Xu, S. H. I. Wenxin and L. I. Guibai (2009). "Reinvestigation of the nitrosamine-formation mechanism during ozonation." Environmental Science and Technology **43**(14): 5481-5487.

Malamis, S., E. Katsou, K. Takopoulos, P. Demetriou and M. Loizidou (2012). "Assessment of metal removal, biomass activity and RO concentrate treatment in an MBR–RO system." Journal of Hazardous Materials **209-210**: 1-8.

Margot, J., C. Kienle, A. Magnet, M. Weil, L. Rossi, L. F. de Alencastro, C. Abegglen, D. Thonney, N. Chèvre, M. Schärer and D. A. Barry (2013). "Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon?" Science of The Total Environment **461**(Supplement C): 480-498.

Mohsen-Nia, M., P. Montazeri and H. Modarress (2007). "Removal of Cu2+ and Ni2+ from wastewater with a chelating agent and reverse osmosis processes." Desalination **217**: 276-281.

Nghiem, L. D., A. I. Schäfer and M. Elimelech (2004). "Removal of Natural Hormones by Nanofiltration Membranes: Measurement, Modeling, and Mechanisms." Environmental Science & Technology **38**(6): 1888-1896.

NHMRC and NRMMC (2011). Australian Drinking Water Guidelines. N. H. a. M. R. Council. Australia

NRMMC (2006). National Guidelines for Water Recycling: Managing Health and Environmental Risks National Resource Management Ministerial Council, Australian Health Ministers Conference Canberra, Australia.

NRMMC (2008). Australian guidelines for water recycling: Managing health and environmental risks (Phase 2). Augmentation of drinking water supplies. Canberra, Australia, Environment Protection and Heritage Council, the National Health and Medical Research Council and the Natural Resource Management Ministerial Council.

Ozaki, H., K. Sharma and W. Saktaywin (2002). "Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters." Desalination **144**: 287-294.

Radjenović, J., M. Petrović and D. Barceló (2009). "Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment." Water Research **43**(3): 831-841.

Rakness, K. L., I. Najm, M. Elovitz, D. Rexing and S. Via (2005). "Cryptosporidium Log-inactivation with Ozone Using Effluent CT10, Geometric Mean CT10, Extended Integrated CT10 and Extended CSTR Calculations." Ozone: Science & Engineering **27**(5): 335-350.

Reif, R., S. Suárez, F. Omil and J. M. Lema (2008). "Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage." Desalination **221**(1): 511-517.

Ropkins, K., A. Ferguson and A. J. Beck (2003). "Development of hazard analysis by critical control points (HACCP) procedures to control organic chemical hazards in the agricultural production of raw food commodities." Critical Reviews in Food Science and Nutrition **43**(3): 287-316.

Royal Society of Chemistry. (2019). ""chemspider.com," " Retrieved 5/02/2019, 2019, from http://www.chemspider.com/.

Snyder, S. A., E. C. Wert, D. J. Rexing, R. E. Zegers and D. D. Drury (2006). "Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater." Ozone: Science & Engineering **28**(6): 445-460.

Steinle-Darling, E., M. Zedda, M. H. Plumlee, H. F. Ridgway and M. Reinhard (2007). "Evaluating the impacts of membrane type, coating, fouling, chemical properties and water chemistry on reverse osmosis rejection of seven nitrosoalklyamines, including NDMA." Water Research **41**: 3959-3967.

Tadkaew, N., F. I. Hai, J. A. McDonald, S. J. Khan and L. D. Nghiem (2011). "Removal of trace organics by MBR treatment: The role of molecular properties." Water Research **45**(8): 2439-2451.

Ternes, T. A., J. Stüber, N. Herrmann, D. McDowell, A. Ried, M. Kampmann and B. Teiser (2003). "Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater?" Water Research **37**(8): 1976-1982.

UN_WWAP (2017). The United Nations World Water Development Report 2017, Wastewater, the untapped resource. Paris, UNESCO: pp. 198.

USEPA. (2018). "Long Term 2 Enhanced Surface Water Treatment Rule Documents." Drinking Water Requirements for States and Public Water Systems Retrieved 10/08/2018, 2018, from https://www.epa.gov/dwreginfo/long-term-2-enhanced-surface-water-treatment-rule-documents.

WaterSecure (2017a). Ozone disinfection: WaterVal validation protocol Australian WaterSecure Innovations Ltd, Brisbane, Australia.

WaterSecure (2017b). Reverse osmosis and nanofiltration, WaterVal validation protocol Australian WaterSecure Innovations Ltd, Brisbane, Australia.

WaterSecure. (2018). "WaterVal validation protocols." Retrieved 10/08/2018, from https://www.waterra.com.au/research/waterval/.

Wert, E. C., F. L. Rosario-Ortiz and S. A. Snyder (2009). "Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater." Water Research **43**(4): 1005-1014.

Wijekoon, K. C., T. Fujioka, J. A. McDonald, S. J. Khan, F. I. Hai, W. E. Price and L. D. Nghiem (2013a). "Removal of N-nitrosamines by an aerobic membrane bioreactor." Bioresource Technology **141**(Supplement C): 41-45.

Wijekoon, K. C., F. I. Hai, J. Kang, W. E. Price, W. Guo, H. H. Ngo and L. D. Nghiem (2013b). "The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment." Bioresource Technology **144**(Supplement C): 247-254.

Zhang, J., M. C. Duke, K. Northcott, M. Packer, M. Allinson, G. Allinson, K. Kadokami, J. Tan, S. Allard, J.-P. Croue, A. Knight, P. J. Scales and S. R. Gray (2017). "Small scale direct potable reuse (DPR) project for a remote area." Water **9**(94): 1-25.

Zhang, J., A. Knight, M. Duke, K. Northcott, M. Packer, P. J. Scales and S. R. Gray (2016a). "A new integrated potable reuse process for a small remote community in Antarctica." Safety Process and Environment Protection **104**: 196-208.

Zhang, J., A. Knight, P. Scales, M. Packer, K. Northcott, J.-P. Croué, S. Allard, J. Tan and S. Gray (2015). Demonstration of robust water recycling: Operating performance and water quality report, Demonstration of robust water recycling (Project number 3170), Australian Water Recycling Centre of Excellence, ISBN 978-1-922202-58-1.

Zhang, J., K. Northcott, M. Duke, P. J. Scales and S. R. Gray (2016b). "Influence of pre-treatment combinations on RO membrane fouling." Desalination **393**: 120-126.

Zhang, J. H., M. Cran, K. Northcott, M. Packer, M. Duke, N. Milne, P. Scales, A. Knight and S. R. Gray (2016c). "Assessment of pressure decay test for RO protozoa removal validation in remote operations." Desalination **386**: 19-24.

Highlights

- A critical control point approach for the removal of chemicals in water recycle is presented
- The critical control point approach is detailed for three barriers
- A combined chemical log reduction value credits approach is demonstrated for a multi-barrier plant

Editor

Water Research

Dear Editor

I confirm that the authors do not have a conflict of interest in presenting the work and that it is not been submitted elsewhere for publication.

Yours sincerely

Peter Scales