Australian Water Recycling
Centre of Excellence

Demonstration of robust water recycling:

Risk Assessment of the Removal of Chemicals of Concern in the Davis Station Advanced Water Treatment Plant

A report of a study funded by the
Australian Water Recycling Centre of Excellence

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Demonstration of robust water recycling: Risk assessment of the removal of chemicals of concern in the Davis Station Advanced Water Treatment Plant

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About the Australian Water Recycling Centre of Excellence

The mission of the Australian Water Recycling Centre of Excellence is to enhance management and use of water recycling through industry partnerships, build capacity and capability within the recycled water industry, and promote water recycling as a socially, environmentally and economically sustainable option for future water security.

The Australian Government has provided $20 million to the Centre through its National Urban Water and Desalination Plan to support applied research and development projects which meet water recycling challenges for Australia's irrigation, urban development, food processing, heavy industry and water utility sectors. This funding has levered an additional $40 million investment from more than 80 private and public organisations, in Australia and overseas.

ISBN: 978-1-922202-55-0

Citation:

P.J. Scales, A. Knight, M. Allinson, G. Allinson, S. Gray, J. Zhang, M. Packer, K. Northcott, and D. Sheehan (2015). Demonstration of robust water recycling: Risk assessment of the removal of chemicals of concern in the Davis Station Advanced Water Treatment Plant, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

Date of publication: July, 2015

Publisher:
Australian Water Recycling Centre of Excellence
Level 5, 200 Creek St, Brisbane, Queensland 4000
www.australianwaterrecycling.com.au

This report was funded by the Australian Water Recycling Centre of Excellence through the Australian Government's National Urban Water and Desalination Plan.

Executive Summary

The Advanced Water Treatment Plant (AWTP) for Australian Antarctic Division's (AAD) Davis Station was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, to demonstrate its performance and reliability. This report outlines the risk of chemicals of concern (CoCs) being found in the product water. The AWTP will have seven functional barriers including ozone, microfiltration (MF), bacteria activated carbon (BAC), reverse osmosis (RO), UV, calcite filtration and chlorination (Cl_2) and be preceded by an MBR. The conclusions from the work are based on demonstrated results from the trial, an analysis of likely differences between the trial case and when the plant is located at Davis Station as well as comparative data from the literature. It does not cover measurement of micro-contaminants or pathogen rejection in the AWTP as these are presented in other Australian Water Recycling Centre of Excellence reports. The report seeks to identify critical control points (CCPs) for chemicals of concern and the maximum concentrations of chemicals in the wastewater collection system at Davis Station that will cause potential CCP breaches.

The main outcomes from this report are:

- A LRV of 1.0 is claimed for Total N and a LRV of 0.8 for hydrophobic organic chemicals for the MBR barrier with CCP requirements.
- A LRV of 1.0 is claimed for the ozone barrier for electron rich aromatic compounds and alkenes with CCP requirements.
- A LRV of 1.0 is claimed for the RO barrier for all compounds except neutral hydrophilic molecules with a MW<200 and neutral hydrophobic molecules with a MW<400, with CCP requirements.
- A LRV of 0.5 is claimed for the RO barrier for neutral hydrophilic molecules with a MW<200 and neutral hydrophobic molecules with a MW<400, with CCP requirements.
- The MF and BAC barriers were observed to be important functional barriers for the removal of organic compounds to aid both the quality of the environmental discharge from the AWTP and reduce fouling of the RO barrier. No LRV or CCP requirements are claimed for these barriers.
- The UV, calcite filter and Cl_2 barriers were given no status in the removal of CoC's from the product water.
- CoC compounds were classified according to three broad classes, namely aromatics, aliphatics and inorganics. A range of sub-classes and subordinate classes were designated in each of the classes.
- Classification of compounds according to their end use or broad molecular description as is outlined in the Australian Guidelines for Water Recycling was found to be useful in determining the maximum guideline concentration in the product water but was not useful in defining whether a molecule would be removed by a particular barrier.
- Table 11 provides an overview of the maximum concentrations of chemicals that should be introduced into the wastewater collection system such that there is no risk of CCP performance breaches.
- The data from Table 11 demonstrates the explicit need for three CCP barriers and source control measures to ensure product water quality and highlights the importance of dilution in the collection system in the removal of CoC's to safe levels.

TABLE OF CONTENTS

Nomenclature

AAD	Australian Antarctic Division
ADWG	Australia Drinking Water Guidelines
AGWR	Australian Guidelines for Water Recycling
AWTP	Advanced water treatment process
AWRCoE	Australian Water Recycling Centre of Excellence
BAC	Biological activated carbon
BDOC	Biodegradable organic carbon
BNR	Biological nitrogen removal
CCP	Critical control point
CoC	Chemical of concern
DBP	Disinfection by-product
EWG	Electron withdrawing group
EDG	Electron donating group
DOC	Dissolved organic carbon
HACCP	Hazard analysis and critical control point
HRT	Hydraulic residence time
IOD	Initial ozone dose
LRV	Log removal value
MBR	Membrane bioreactor
MF	Microfiltration
PDT	Pressure decay test
QMRA	Quantitative microbial risk assessment
QCP	Quality control point
RO	Reverse osmosis
RWQMP	Recycled water quality management plan
SCADA	Supervisory control and data acquisition
SEM	Scanning electron microscopy
SPWWTP	Selfs Point wastewater treatment plant
TDS	Total dissolved solids
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TrOC	Trace organic chemical
TSS	Total suspended solids
UV	Ultra-violet disinfection

Introduction

Trace organic chemicals (TrOC's), metals, nutrients, radio-nucleotides and disinfection bi-products are often unwanted in water supplies as many have the propensity to cause detrimental health and environmental effects. The residual concentrations at which these so called chemicals of concern (CoC) are considered problematic is of interest herein, since the removal to a level where the water is fit for purpose is often difficult to establish because of the large number of potential chemical inputs from a range of sources. There are well developed guidelines for the quality of water deemed fit for potable use in Australia and these are outlined in the Australian Drinking Water Guidelines [1]. In the reclamation of wastewater, it is common to use secondary treated wastewater effluent as a feed to a further treatment process (i.e. advanced water treatment process (AWTP) to produce a reclaimed water having a quality commensurate with the intended use. The AWTP looks to purify the water for re-use whereby the level of treatment required depends critically on the re-use option. This is brought into sharp focus when the water is for potable use through either indirect or direct re-use schemes. At the core of the risk assessment process is the level of treatment required to ensure that use of the water causes no acute or chronic health effects, as well as the robustness of the treatment process to variations in performance. Providing robust solutions has both a social and technical dimension and it is the latter that is the focus herein.

The difficulty in defining a robust, all encompassing, AWTP option depends on our ability to ensure that the limits of the composition of the feed to the process are well defined. This for example, may be that a particular pathogen or chemical of concern never exceeds a certain value. In the case of pathogens, a quantitative microbial risk assessment (QMRA) study [2] provides an example that this can be achieved quite well for large treatment facilities serving large populace areas. If the treatment includes a secondary treatment process such as biological nitrogen removal (BNR) and it is operated to a defined standard, since the level of dilution of point input sources into the treatment process is high (i.e. in the case of a large city with a centralised collection system and population greater than 200,000 persons), the maximum likely pathogen loads to any AWTP can be defined. The next step is to use an appropriate risk matrix and calculate the required log removal values (LRV's) of these pathogens. The removal requirements for a range of pathogen types in water re-cycle are outlined in the Australian Guidelines for Water Recycle (AGWR) [3]. Design of advanced treatment systems with an appropriate barrier configuration and controls can then be used to ensure the risk of pathogens in product water is extremely low.

In the case of small communities (i.e. less than 1000 persons), our earlier work indicated that the guideline values for pathogen reduction for large populace areas may be insufficient and a higher LRV is required to achieve the same level of risk reduction [2]. The changes required were significant (up to 4 LRV for virus) and pointed to the fact that source control of pathogens is difficult since wastewater is the capture point for the output of acute illness (i.e. norovirus infection) and more importantly, a high level of dilution cannot be assumed for small communities. This is exacerbated by the expected secondary infection rate as a percentage of the total community. In the case of a viral infection such as norovirus, there is the potential for a large proportion of the community to be sick at the same time (e.g. 40%) [2]. This led to the conclusion that the AGWR may underestimate requirements for small communities [4] and although the higher LRV's may not be required for the majority of the time, uncontrolled acute illness could raise pathogen risk in a product water. The role of the wastewater treatment plant in mitigating peak pathogen loads is poorly understood and as such, claims for pathogen removal of this barrier were related to the physical barrier provided by the membrane only.

This document provides an assessment of the source and barrier controls required for the removal of CoC's from a treatment system consisting of a secondary wastewater treatment effluent (presumed to be from a membrane bioreactor (MBR)) that is then used as a feed to a multi-barrier AWTP. Two output streams are considered, one being a hypo-saline waste and the other a product treated to potable standard. The assessment assumes some barriers in the multi-barrier process will operate as critical control points (CCP's) for both chemicals and pathogens, some will operate as CCP's for just pathogens and the remainder will operate to quality control point (QCP) standards. The AWTP was designed and built, commissioned and tested on secondary treated wastewater effluent at Selfs Point Wastewater Treatment Plant (SPWWTP) in Hobart, Tasmania.

Removal of Chemicals of Concern

Many of the risks associated with being able to control the composition of the feed to an advanced water treatment plant (AWTP) for pathogens are also applicable to chemicals. In a large city, a range of chemicals are able to enter the collection system, with the mix being highly variable depending on the ratio of industrial to domestic inputs. Large populace areas with uncontrolled collection often show an industry to domestic split of the order 30:70, although this clearly depends on the city and the industry distribution in the sewer catchment. In any case, the dilution in large sewer catchments for isolated spills to the system is high (relative to a small community) and changes to the average composition of the wastewater entering the treatment facility are usually not large. As with the pathogen case, making the assumption that the BNR process is operating effectively, the maximum likely dissolved organic, nutrient and metal loads can be defined, assuming there are no once off and very large industrial inputs (spills). The latter is usually mitigated by source control measures such as EPA licensing of loads and concentrations or the requirement to treat such potential discharges locally. It is desirable to avoid large chemical spills entering the wastewater collection system to avoid spikes in CoC's in the treatment process.

The risk of spikes in chemicals in the influent to the treatment process is once again exacerbated for small communities. The QMRA study conducted for pathogens can be used as an analogue here, although two factors significantly change the risk profile relative to the pathogen case. The first of these is that highly concentrated chemical inputs (i.e. a single chemical spill) may induce a toxic effect in the biomass used to achieve secondary treatment and second, the number of barriers designed specifically for chemical removal in AWTP's is usually far fewer than that for pathogens. As such, the ability to achieve an overall LRV through multiple barriers is far more restricted than for pathogens. In short, the need for source control is heightened in a small community although it is not well documented what level of source control is required to ensure a reproducible feed for an AWTP in a small community. As with the pathogen analogy, a 1 kg spill of a highly toxic chemical into the sewer collection system of a city of 1 million people will be diluted by a factor of 10,000 relative to a community of 100. However, in the absence of source control in the small community, the base chemical load from household chemicals such as disinfectants, cleaners, personal care products and pharmaceuticals is likely to be similar. Therefore, it is the spill situation that is of greatest concern.

An example of the case for a small community is typified by the design of the AWTP for Davis Station that is the subject of the work herein. The plant is a seven barrier process with ozone, micro-filtration (MF), biologically activated carbon (BAC), reverse osmosis (RO), ultra-violet radiation (UV), calcite dissolution and chlorination (Cl_2). The feed to the AWTP once installed at Davis Station, passes through 2 x 4 kL tanks that are used for flow equalisation across the day before biological treatment with BNR incorporated with a flat sheet membrane bio-reactor (MBR). Phosphate levels will be controlled by the addition of iron salts to the MBR, if required. Two of the barriers (UV and Cl_2) are for pathogen removal from RO permeate and calcite dissolution is a water stabilisation step. All three of these steps will not be considered further here, as they provide little or no removal of CoCs or in the case of UV, any CoC removal is not specific to a particular molecular class.

The MF and BAC are expected to remove some chemicals though capture in a fouling layer and adsorption/bacterial metabolism respectively. There is some removal of inorganic species such as Fe and Mn through these barriers but it is mechanistically not well described and not able to be quantified in a systematic way. For organic molecules, removal by these barriers is important, particularly in reducing the load of assimiliable organic carbon (AOC) sent to the environment and in mitigating fouling in the RO barrier. The particular molecular species that are removed by these barriers and the parameters that describe how continuity of performance would be maintained are not well described in literature. None the less, conservative estimates of removal can be made. This means that the seven barrier process of the AWTP, with six barriers functional for pathogen removal, can really only be considered a four and possibly a three barrier process for the quantification of chemical removal. Despite the lower number of functional barriers, the LRV of chemicals to achieve compliance with ADWG and AGWR is assumed to be less than that for pathogens.

A further issue is that not all of the organic chemicals, metals, nutrients, radio-nucleotides and disinfection bi-products have the propensity to cause health and environmental risks. Indeed, only a small proportion are expected to cause acute and/or long-term health and environmental issues.

These CoC's are predominately synthetic and some, as is the case of disinfection by-products, are created through oxidation processes (i.e. ozone). Controlling synthetic inputs to the feed of the water treatment process is therefore an important starting point in reducing risk. This is aided by the fact that there are a range of common chemicals found in the effluent of secondary treatment plants that are either limited or not permitted at Davis Station. These include pesticides, herbicides and dioxins as well as some personal care products that show poor biodegradation. In addition, the population is healthy by community standards, with persons with chronic illness such as diabetes and heart disease being excluded from making the trip to Antarctica. However, medications for these ailments are not excluded and there is a finite risk of all pharmaceuticals and metabolites that are common to a large city being present in the wastewater.

Source Control

The feed to the AWTP at Davis Station is planned to be from a flat sheet ultra-filtration MBR system. The specification of the feed water quality to the plant, as established in the functional design, is given in Table 1. The data are considered highly conservative for an ultra-filtration MBR unit and expected data based on typical industrial observations of an MBR are also shown.

Day to day operations at Davis Station includes typical domestic inputs into the MBR system inclusive of grey and black water from accommodation and food preparation, but there are also inputs from laboratory and machinery operations. Unlike many large cities with large manufacturing and a range of commercial activities, Davis Station can be nominally considered as a waste stream dominated by domestic activities. Health related/clinical activities, hydroponic food growth and laboratory activities are the main non-domestic inputs. The AWTP feed water requirements shown in Table 1 detail only the requirements for the key nutrients of N and P and the product of the reduction of organic wastes, namely suspended and dissolved organic molecules from bacterial metabolism. The latter is expected to be predominately proteins, polysaccharides, nucleic acids and phospholipids [5] but will also include synthetic organic and inorganic chemicals that are not assimilated by or adsorbed to the biomass in the MBR reactor. CoC's not able to be easily assimilated to the biomass or that are of a concentration that will significantly influence the numbers in Table 1 are therefore of interest here. These include highly soluble organic chemicals that are poorly biodegradable and weakly adsorbing, toxic metals, radio-nucleotides, acids and bases and metal salts.

In making the assessment, a starting point is to look at the likely removal of inputs across the MBR reactor. This facility includes screening followed by a BNR reactor with an integrated flat sheet membrane system and control of phosphate with dosing of ferric salts. Domestic wastewaters are generally considered biodegradable and the relatively low water use per person (< 150 l/day) at Davis Station means that the wastewater will be considered moderately to highly concentrated. Infiltration and exfiltration is unlikely and wastewater is held locally in a building sump prior to being pumped to the wastewater treatment plant. Each sump is evacuated on a high level switch but can be over-ridden in the event of a spill. The wastewater entering the combined primary treatment and MBR reactor will be buffered in two holding tanks with a total capacity of 8,000 litres and a typical operational volume of 5,000 litres. In the event of an unwanted discharge to the waste collection system, there exists the possibility to isolate the discharge from the treatment train.

Using COD values for moderate to highly concentrated wastewater and a BOD/COD ratio of 0.47 [6], Table 2 shows the expected characteristics of the feed to the wastewater treatment plant and the expected reduction in the key variables across the MBR based on the data from Table 1.

A simple calculation suggests that for the numbers in Table 2, a spill or sudden release of a highly soluble organic chemical to the wastewater collection system whereby the effluent TOC doubled would require an input of 1.6 kg. This is based on the initial dilution into the holding tank of the collection system (5000 L), a value for the maximum TOC in the effluent of 10 mg/L and a typical log reduction value for the removal of organic compounds in the secondary wastewater treatment system (LRV=1.5). Since a LRV of 1.5 is equivalent to a multiplier of 32 ($10^{\wedge 1.5}$ = 32), then 5000x32x10/1,000,000 = 1.6 kg, where the denominator converts mg to kg. The true reduction in the concentration of the compound across the MBR is expected to be higher than indicated by the LRV since molecules are assimilated into the biomass and weakly associated cellular exudate compounds are released. In short, the TOC that enters the wastewater treatment plant is not the predominate

TOC that leaves. However, literature studies show that there are some molecules for which this is not the case and an alternative approach that considers the specific molecular characteristics is required.

Studies of the effluent of a series of large city wastewater treatment plants show that despite a large number of chemicals (1,000's) in the influent, a substantially lower number of chemicals are actually detected in the effluent, often less than 100 in number. In addition, the concentrations of those detected compounds is generally at the μg/L level, indicative that these compounds in total mass, are often only a small proportion (of order of 0.1%) of the effluent TOC [7]. This is consistent with the statement that most of the MBR effluent TOC is bacterial in origin although the large dilution in these sites will not be present at Davis Station.

A study of organic CoC's in the aqueous phase of the influent of the SPWWTP using a GC multi-residue mass spectrometric technique [8] was conducted and compared to the effluent on the same day (26 March 2014). Fifty seven CoC's were identified by GC-MS in the influent. Of these chemicals, ten were above the limit of detection and twelve saturated the detector. Thirty seven were not detected in the effluent. Using the forty seven chemicals for which there was a reading (10 saturated the detector) and using the limit of detection of the instrument as a substitute for the concentration in the effluent where none was detected, an average LRV across the SPWWTP of 2.45 was observed. This is higher than the figure in Tables 1 and 2, however, the data therein was calculated using an approximate LRV value based on the expected (not actual) influent characteristics and the required, as distinct from measured, effluent characteristics.

The actual site analytical data is encouraging in that it implies that the spill of a highly biodegradable and non-toxic substance at Davis Station into the waste collection system is not likely to be problematic unless it is at the tens of kg level. However, for those chemicals listed as having the potential to cause health or environmental issues (CoC's), the approach is clearly inadequate and does not take into account the maximum guideline value that is allowed in the product water nor their specific biodegradability, and a more detailed approach that considers the role of each barrier is required.

In particular, an understanding of the mechanism of removal of molecules across each barrier of the plant is necessary and although it is common to think for instance that the biodegradability of a molecule will be important to its removal in an activated sludge system, the more relevant removal mechanisms in the MBR and AWTP are adsorption to a solid phase, oxidative degradation and physical removal. This is a consequence of the short hydraulic residence time across each barrier. Oxidative degradation is likely to be associated with barriers that include the likes of ozone or UV and physical removal to be associated with membranes. The adsorption mechanism does not rule out biodegradation but if for instance a molecule does not adsorb in the BAC barrier, it is unlikely to be removed to a significant level in the hydraulic timescales associated with treatment. Thus, adsorption allows enough time for the secondary processes of assimilation and biodegradation. Understanding which mechanism(s) is dominant for a particular CoC is paramount to understanding the likelihood of removal.

Table 1: Davis station AWTP feedwater requirements as specified in the functional design (value), the expected value (taken from full scale studies of MBR systems) and the observed range of values during the operational trial at Selfs Point Wastewater Treatment Plant (SPWWTP). It should be noted that SPWWTP did not operate an MBR.

Parameter	Functional Design Value	Expected MBR value	Monitored Range (SPWWTP)
Biochemical Oxygen Demand (BOD_5)	<20mg/L	<5 mg/L	2.5-25
Suspended Solids (SS)	<10mg/L	<5 mg/L	1.9-6.0
Total Nitrogen (TN)	<10mg/L	<5 mg/L	1.2-15.2
Turbidity	Max: 1 NTU	<0.5 NTU	1-3
pH	Min: 6 Max: 8		
Ammonia#	<5mg/L	<5mg/L	0.1-13.1
Phosphorous#	<5mg/L	<2mg/L	0.7-2.7
Bromide#	<0.6 mg/L		0.18
True colour#	<10HU		57-79
TOC / DOC#	<10mg/L	<5mg/L	7.4-9.4

required values

Table 2: Expected wastewater influent composition for Davis Station (MBR reactor feed) and likely effluent LRV on each component (based on Table 1)

Parameter	Value	LRV
COD total	1000 mg/L	
BOD_5	466 mg/L	>1.4
Total Nitrogen (TN)	83 mg/L	>0.9
TOC	350 mg/L	>1.5
pH	6-8	
Ammonia as N	63 mg/L	>1.1
Phosphorous as P	21 mg/L	>0.6

Chemical classification

The classification of CoC's varies across nations and although it is common to use classifications such as those laid out in the AGWR, this in itself is more on the basis of end use and in some instances, the response of the molecule in humans. The expected response of a molecule to a treatment process would require a different classification. The AGWR uses the following classifications:

- inorganic chemicals
- disinfection byproducts
- pesticides
- fragrances
- pharmaceuticals and metabolites
- fire retardants
- dioxins and dioxin like compounds
- miscellaneous organic chemicals – PCB's, PAH's, phthalates, organotins, etc.
- radiological
- chelating agents

In looking at the guideline values in each of these classifications, Table 3 lists compounds with low guideline values in each class of the ADWG or AGWR. Typical data for the discharge of wastewater treatment plants for some of these chemicals is also shown [9] as well as the maximum observed values as given in AGWR (Table 4.4). The guideline limit data indicate that disinfection by-products, pesticides, fragrances, pharmaceuticals and metabolites, some miscellaneous organic chemicals and dioxin like compounds are the only classifications with guideline values below 1 μg/L. Each of these is a factor of 10^4 lower than the TOC level of the effluent from the MBR, although many of the chemicals in Table 3 are restricted from entry to Davis Station. Despite this restriction, the indicative TOC LRV and the 10^4 factor difference would indicate a significant requirement of the barriers within the AWTP to produce water that is able to consistently meet the maximum guideline concentrations in the ADWG and AGWR. Literature data on the concentration of organic compounds in wastewater effluents, predominately in north America [7, 9] suggests that levels of order tens of μg/L are rarely exceeded in secondary treatment effluents. However, the data is for large communities where any one-off spill would be highly diluted in the wastewater collection system. As such, the wastewater plant influent in these literature examples is highly diluted (relative to a small community) and influent chemical concentrations are lowered by this dilution accordingly. The very limited dilution at Davis Station is thus a significant issue in the assessment of the potential of the AWTP and associated MBR to remove CoC's.

Therefore, the data of Table 2 for the LRV removal of organic chemicals is seen as an under-estimate of the ability of the MBR to assimilate non-toxic, hydrophobic and readily biodegradable organic chemicals. Using the LRV from Table 2 to calculate spill volumes of non-toxic chemicals is therefore indicated to be highly conservative. A source control strategy that looks to ensure that organic chemicals never exceed one off spills in excess of 1.6 kg is therefore considered adequate to ensure that the ability to produce an MBR effluent with a requirement of <10 mg/L TOC. However, as already noted, this in itself does not ensure product water safety.

On this basis, a waste disposal or 'spill' decision tree can be developed. In the case of Davis Station, certain classes of chemical are restricted from entry and although this makes the evaluation easier, a generic decision tree is appropriate. The decision tree needs to take into account the mass, solubility, biodegradability and chemical type as well as the guideline limits for drinking water and effectiveness of the MBR and AWTP barriers. The evaluation then allows designation of the maximum pack size for a particular chemical to ensure that guideline values are never exceeded in the product water of the AWTP through accidental spills or regular disposal to the wastewater collection system. The chemical manifest for Davis Station, including individual compounds and commercial products (not including pharmaceuticals and medical treatment chemicals) is shown in Appendix 2.

Table 3: Overview of some example compounds with the lowest ADWG or AGWR threshold values in each class as compared to observed median or maximum concentrations in the effluent of wastewater treatment plants as reported by Dickenson et al. [9] and Table 4.4 in AGWR. Values are in μg/L. Maximum values are marked with an asterisk (*). Where the ADWG and AGWR differ, the lower of the guideline values is used.

Classification	Compound	ADWG or AGWR(μg/L)	Observed (μg/L)
Inorganic Chemicals	Arsenic	7	15*
	Antimony	3	6*
	Lead	10	60*
Disinfection by-products	NDMA	0.10	0.55*
	NDEA	0.10	0.003*
	Bromo-acetic acid	0.35	0.4*
Pesticides	Demeton-S	0.15	3*
	Fenthion	0.50	2.4*
Fragrances	Musk tibetene	0.35	0.40
Pharmaceuticals & Metabolites	Penicillin V	1.5	0.21*
	Diclofenac	1.8	0.04
	17α-ethinyl estradiol	0.0015	0.270*
	Bisoprolol	0.63	0.37*
	Carazolol	0.35	0.12*
	Alprazolam	0.25	0.62*
Fire Retardants	(tri(dichlorisopropyl) phosphate)	1	0.2*
Dioxins and dioxin like compounds	Octachlorodibenzo-p-dioxin (OCDD)	0.00016	0.0001*
Miscellaneous organic chemicals	Dibutyltin (DBT)	2	0.034*
	4 tert-octyl-phenol	50	0.014*
	Triclosan	0.35	0.30
	Caffeine	0.35	44*
Radiological	Alpha particles	0.5 Bq/L	1.2 Bq/L*
Chelating agents	EDTA	250	11.8

Control of CoC's through the AWTP

Data from the operational phase (Table 1) of the AWTP at SPWWTP in Tasmania, without the benefit of an upfront MBR system, shows that the monitored values of various compounds and parameters to the plant often exceeded the requirements as laid out in the functional design specification for BOD_5, total nitrogen, ammonia and colour. This was due to both the absence of an MBR in the treatment train and service issues with the operation of SPWWTP during the study period. However, the DOC levels were very consistent (8.4±0.1mg/L) (30 weeks of readings) and in the required range. Data for the removal of organic CoC's across the AWTP barriers, as measured by GC and LC mass spectrometry, is shown in Figure 1. These data are the average of monthly sampling across nine sampling events. Data for DOC and TN across the barriers is shown in Figure 2. These are the average of 30 weekly readings. It should be noted that the vertical abscissa is a log scale to aid viewing of the post-RO data. It should also be noted that the DOC and TN data is on a mg/L scale and the CoC data on a μg/L scale such that the total mass of CoC's/L was 0.13% of the total DOC. The usefulness of this figure is questionable since the analytical methods used herein, whilst able to detect approximately 1250 semi-volatile and non-volatile chemicals, only quantify 180 of the almost 300 chemicals listed in the ADWG and AGWR. This is still far more comprehensive than the often cited work from Drewes et al. [7], where only 29 chemicals overlap the same guidelines. To be fair on the latter none the less, the list of Drewes et al. is aimed at producing appropriate surrogates for a range of chemical classifications rather than being comprehensive. Therefore, the method used here is deemed on this basis to be representative of the CoC's likely observed in the feed to the AWTP but is by no means comprehensive. The risk that CoC's were present at more than 0.5% of the total DOC in the feed is considered low.

Data across a range of operational facilities shows generally lower TSS, BOD and DOC and significantly lower turbidity for MBR as compared to plants where biomass separation is via clarification [6]. Therefore, the data for operations at SPWWTP in terms of a feed to the AWTP is considered a more difficult operational scenario than would be expected at Davis Station. This is particularly the case for total nitrogen, ammonia and BOD_5 where specific control measures will be present to reduce the values in the feed to the AWTP.

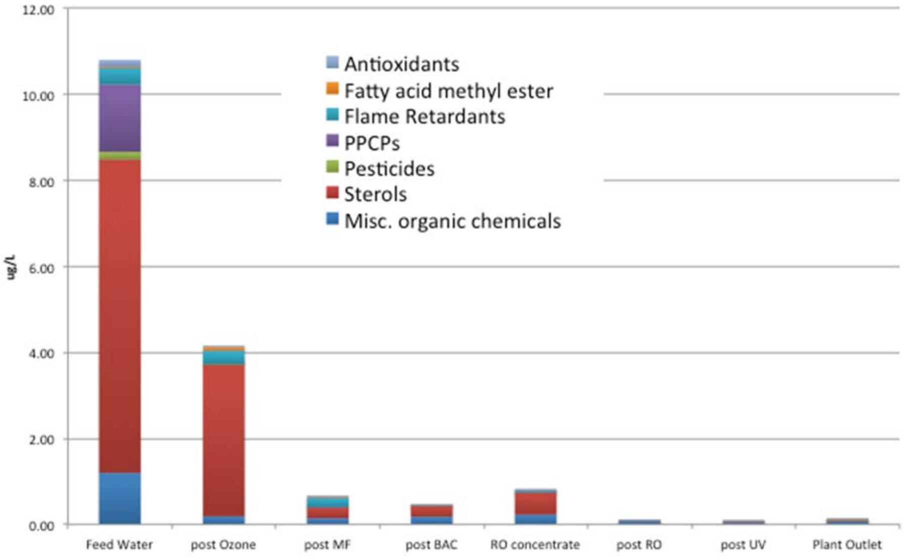

Figure 1: Overview of organic CoC's across the AWTP operated at SPWWTP. Data taken from Allinson et al. [10]

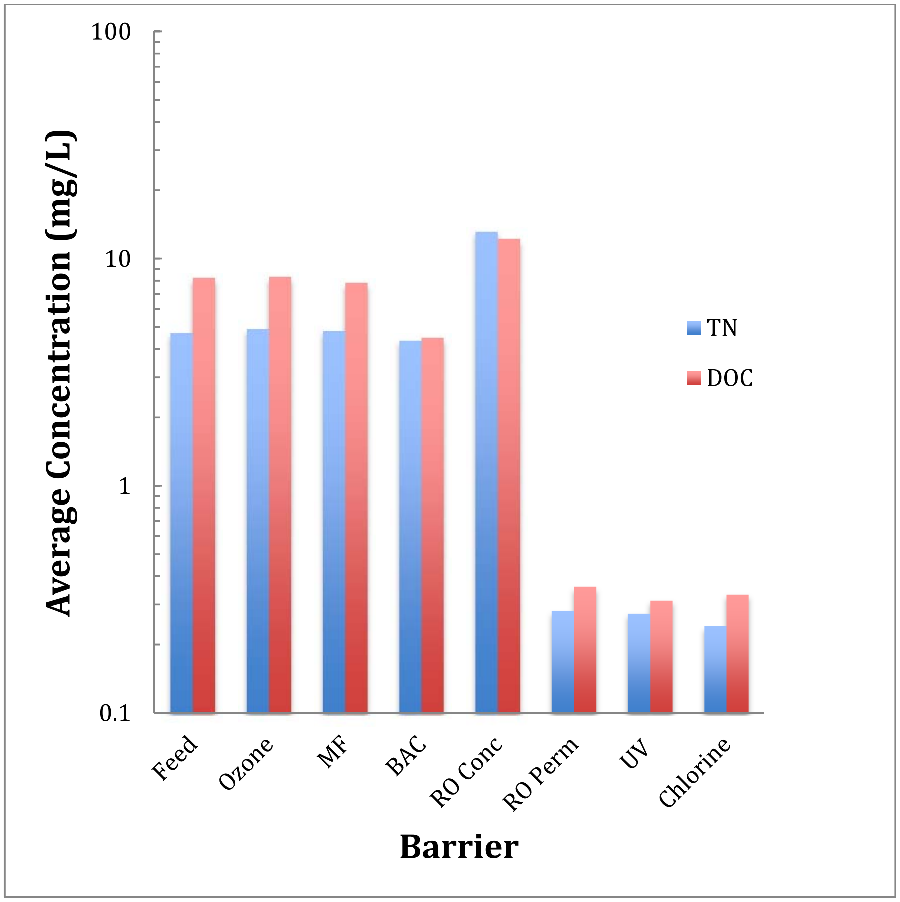

Figure 2: Average values of TN and DOC across each of the barriers of the AWTP for the test period.

Risk assessment of each AWTP barrier

Membrane Bioreactor (MBR)

MBR Design and Specifications

Supplier - Martin Membrane Systems
Membrane type – flat sheet, 150,000 MWCO polyether sulfone (PES) ultrafiltration membrane on a non-woven polypropylene support (nominal pores size is 35 nm and the maximum pore size is 0.1 μm)
pH range – 2.0 – 10.0
CIP pH – 1.5 – 11.5
Max. TMP – 0.6 bar
Intensive Cleaning – 1,500 ppm free chlorine, pH 10.5 or 4,000 ppm H_2O_2, pH 3-7 all at ≤25˚C
Maintenance cleaning - 500 ppm free chlorine, pH 10.5 or 2,000 ppm H_2O_2, pH 3-7 all at ≤25˚C
No backwashing but has continuous air scouring and relaxation periods.
Flux – 17 L/m^2.h (75 m^2 membrane area for 1200 L/hr flow)
Monitoring on filtrate - pH, conductivity, ammonia, nitrate and phosphate

Removal Mechanisms

The membrane acts as a physical barrier to the passage of particulate/suspended solids. The pore size of the membrane is nominally 35 nm, which is far greater in size than the majority of suspended particulates. The membrane also acts as a barrier to dissolved organic and inorganic species through adsorption and entrapment in the fouling layer. This then allows predation by the biomass. Total nitrogen, including ammonia, nitrates and nitrite is removed through a biological nitrogen removal process and total phosphate is reduced through the dosing of ferric salts. Organic chemicals all have to be assimilated by the biomass prior to utilisation. This requires adsorption to the biomass in the MBR with subsequent assimilation and biodegradation. Molecules that do not adsorb or that cannot be readily biodegraded in the time frame of the hydraulic residence time (HRT) of the MBR will pass through the barrier. The HRT is around 4 hours. The biomass is separated from the liquour through physical separation at the membrane and adsorbed molecules have between 15 and 25 days to be either biodegraded or removed with the solids fraction, where the time scale is representative of the solids residence time in the reactor.

Reported LRV for MBRs

There are a range of reports of the removal of suspended and dissolved organic carbon compounds as well as reductions in total nitrogen and phosphorus through MBR's relative to conventional activated sludge processes. Adsorption to the sludge biomass is seen as a key determinant of removal performance and the higher mixed liquour suspended solids concentration and SRT of MBR's tends to favour this mechanism. The pore size is not observed to be overly important other than in the removal of suspended solids, which may contain adsorbed CoC's. Therefore, molecular structure is observed to be critical to performance whereby in the absence of adsorption, intrinsic biodegradability is then an issue. As an example, Tadkaew et al. [11] used a range of challenge additions of common pesticides, pharmaceuticals and endocrine disrupting chemicals to a synthetic wastewater to test a 40 nm pore sized MBR (similar to the design of the AAD case) and compared their results to literature. Three molecular characteristics were found to be important:

-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, standardized to octanol=3.0. Some literature uses Log (D) at a particular pH, some log (P), where P is the partition coefficient and some K_{ow}, or $\log_{10}$ of the oil-water partition coefficient. For neutral molecules, all of these parameters are identical.

-Electron withdrawing groups: molecules with electron withdrawing groups such as chlorine or amide were observed to be recalcitrant to removal with <20% removal. This is consistent with an inability of bacteria to attack the molecule and has also been observed in a range of other literature. These literature are summarized in the paper of Tadkaew et al. (Table 1) [11]

-Electron donating groups: these compounds are more easily attacked and showed good removal in many cases, however the response was variable and once again, consistent with previous observations in the literature [11].

A similar study by Kovalova et al. [12] on hospital wastes showed slight variations but were consistent with the Tadkaew et al. study as are a range of literature reviewed in the article by Kovalova et al. It is concluded that the only claim that can be made for the removal of CoC's that is consistent across all literature for ultrafiltration MBR systems is for the class of chemicals determined to be hydrophobic. This condition is defined by Log(D)@pH 8>3.2. This chemical grouping is expected to be consistently removed to better than 85% by a properly functioning MBR [11, 12]. This is equivalent to a LRV>0.8.

Testing of the claim on the data from SPWWTP is a little difficult as only one sampling run was conducted on the primary influent due to analytical difficulties. As noted earlier, many of the semi-volatile compounds in the feed sample to the plant (screened at 0.45 μm to remove particulates) saturated the detector of the GC-MS and non-volatile compound levels were so high as to completely saturate the LC-MS column and negate further work. Taking the data for which there was a non-saturated reading in the primary influent, only 21 of the 34 compounds had a listed K_{ow} although many of the unknowns were straight chain alkanes with an assumed K_{ow} >10. Only 3 compounds had a K_{ow}

less than 3.2. Despite this, no chemical showed a LRV across the system of <1.25. The data and associated analysis is shown in Table 4.

The data analysis in Table 4 requires that where no compound is detected in the effluent, that either a zero value, the limit of detection of the method (LOD) or the limit of reporting (LOR) of the compound is used. In calculating a LRV for the system, zero values are problematic and 0.5xLOR is used here since this is the most common method used in the analytical reporting of compounds. LRV* is thus the log removal value for the compound where non-detects are replaced with 0.5xLOR. RE* is the removal efficiency. As before, 0.5xLOR replaced any non-detects. The removal efficiency is calculated as:

$$RE\ (\%) = \left(\frac{F-E}{F}\right) x\ 100 \qquad [1]$$

where F and E are the feed and effluent concentrations respectively. In some studies, a detection ratio (DR) is also used whereby all data with a median (influent) concentration that is not at least a factor of 5 greater than the LOD is excluded from removal efficiency analysis [9]. This was not required for any of the influent concentrations in this instance.

Table 4: Calculated LRV for GC-MS detected compounds between the influent and effluent of the SPWWTP. Only those compounds where analytical integrity was achieved are shown. All concentrations are in µg/L. K_{ow} values were taken from the on-line 'ChemSpider' database.

Chemical Names	K_{ow}	Round 1 (26th March 2014)				
		Primary	Secondary Low flow	Secondary High flow	LRV*	RE*
Benzyl alcohol	1.1	6.26			3.10	99.92
2-Ethyl-1-hexanol	2.72	6.31			3.10	99.92
L-Menthol	3.3	17.1			3.54	99.97
1,4-Dichlorobenzene	3.44	0.88			2.25	99.43
Triclosan	4.76	2.49	0.091	0.111	1.39	95.94
4-tert-Octylphenol	5.28	0.71	0.022	0.029	1.44	96.34
4-Nonylphenol	5.76	6.83			3.14	99.93
Stigmasterol	9.43	8.49	0.25	0.33	1.46	96.54
Squalane	12.19	3.49	0.11	0.11	1.50	96.83
n-C13H28	>10	0.74			2.17	99.32
n-C14H30	>10	1.03			2.31	99.51
n-C15H32	>10	1.06	0.059		1.25	93.92
n-C17H36	>10	2.12			2.63	99.76
n-C23H48	>10	0.98			2.29	99.49
n-C25H52	>10	1.21			2.38	99.59
n-C26H54	>10	1.00			2.30	99.50
n-C27H56	>10	2.55			2.71	99.80
n-C28H58	>10	0.91			2.26	99.45
n-C29H60	>10	2.44			2.69	99.79
n-C30H62	>10	0.75			2.17	99.33
Phenylethyl alcohol	1.50	2.18			2.64	99.77
4-Methyl-2,6-di-t-butylphenol	5.07	0.60			2.08	99.16
Methyl octanoate	3.37	2.24			2.65	99.78
Methyl pentadecanoate	7.18	2.37			2.68	99.79
Butyl benzyl pthalate	4.67	1.297	0.008	0.019	1.98	98.96
Piperonyl butoxide	3.99	0.48			1.98	98.96
24-Ethyl coprostanol		26.9	0.16	0.18	2.19	99.36
Cholestanol	8.94	13.2	0.46	0.48	1.45	96.45
Coprostanol		61.0	1.84	1.86	1.52	96.97
beta-Sitosterol	9.38	35.5	0.45	0.63	1.82	98.48
Campesterol	8.93	26.1	0.13	0.17	2.24	99.43
4-Cymene	4.13	1.27			2.40	99.61
Acetophenone	1.58	0.95			2.28	99.47
Benzothiazole	2.09	0.85			2.23	99.41

The operational data, although not for a MBR, show removal of all compounds to better than an LRV=0.8 with a minimum LRV of 1.25 and not just compounds with a K_{ow} >3.2. Based on literature data and the consistency of the outcome for the analysis conducted in the present study, an LRV of 0.8 is claimed for compounds with a K_{ow} >3.2. Compounds with a K_{ow} <3.2 will also be removed, often to a similar extent, but not according to a well defined and singular mechanism.

In the case of TN, data from the influent to SPWWTP were not obtained but based on expected feed characteristics of the wastewater at Davis Station, the BNR process in the MBR, a LRV for TN of 1.0 is claimed. In the case of radiolytic compounds able to emit a range of alpha, beta or gamma radiation, since these compounds are associated with particulates, a LRV of 1.0 is claimed due to size exclusion. It may be reasonable to claim a far higher value if the particulate was known to be greater than 3 μm in size. The size is unknown here but likely greater than 100 nm based on coagulation alone. The nominal pore size of the MBR membrane is 35 nm with maximum pore size of 100 nm.

Required Operating Parameters

Suspended solids in the MBR will be excluded from the filtrate by size exclusion. Hydrophobic molecules will adsorb to the biomass and will be removed from the product water through this mechanism. Normal operating conditions whereby the turbidity of the effluent is low and the biomass in the MBR is working optimally are critical parameters in hydrophobic CoC removal.

Therefore the operating conditions chosen for the removal of pathogens, which nominally assume membrane integrity and optimal biomass activity, are chosen as appropriate for the MBR to be credited with 0.8 LRV for hydrophobic CoC molecules with a Log(D)@pH8>3.2. The details of these operational conditions are [13]:

- pH between 6 – 8 (outside of this range would indicate the biological process is not operating in a typical manner).
- temperature > 13˚C (listed as a CCP as it affects the biological process and the TMP for the MBR)
- Flux <32 LMH (listed as a CCP since high flux may lower the LRV from size exclusion)
- TMP ≤ 85 kPa (listed as a CCP since high TMP indicates fouling that would increase the LRV. A TMP greater than 85 kPa does indicate unusual operating conditions)
- Turbidity ≤0.5 NTU (i.e. not >0.5 NTU for more than 10 minutes (2 consecutive readings).

Design parameters for the MBR

Summer: MLSS = 14,000 mg/L (not < 5000 mg/L) and SRT = 15 days (not <10 days)

Winter: MLSS = 5,000 mg/L (not <3000 mg/L) and SRT = 25 days (not <15 days)

The plant will have a MLSS and an ammonia sensor. These sensors will be used to indicate any deviation from normal plant operation.

Ozone

Ozone design and specifications

Supplier – Wedeco, OCS-GSO 10; Maximum ozone production = 30 g/h; continuous with internal recycle; HRT_{10} = HRT when 10% of the flow has exited the ozone system (flow-rate = 20 L/min) = 5.0 min (4.8 and 5.2 min measured for HRT_{10} using Rhodamine WT).

Removal Mechanisms

Chemicals are oxidised in contact with ozone and by OH radicals generated in the presence of ozone. The main role of ozone in AWTP for organic chemicals of concern is to breakdown compounds with double or multiple bonds and aromatic molecules, producing assimilable organic carbon (AOC). Some of these ‘new’ compounds will be less soluble and precipitate or be adsorbed to other particulates, making them susceptible to removal by filtration. Others will become more susceptible to bacterial action [14].

Ozone is very effective in the degradation of molecules with electron donor groups such as C=C double bonds or aromatic rings with certain functional groups. Compounds with electron-withdrawing groups (EWG's) are poorly active to ozone [15]. Meanwhile, ozonation is also known to produce OH radicals. The OH radical is shown to be indiscriminate in oxidization reactions [16]. Therefore, having an excess of ozone where the OH radicals are not scavenged quickly is important to the breakdown of molecules that are recalcitrant to ozone oxidation [16].

Reported LRV for ozone

The data in Figure 1 for the operation of the AWTP at SPWWTP shows a reduction in CoC's of over 60% across the ozone barrier. The data in Figure 2 show there to be little or no effect of ozone on inorganic compounds inclusive of TN and little effect on total DOC in solution. It is concluded based on the DOC data that there is very little or no mineralisation of organic compounds, just attack on and fragmentation of molecules. In addition, true colour decreased from an average of 67 HU in the feed to 9.7 HU after ozone treatment, a reduction of 85.5 %. The production of new molecules was observed including NDMA, NDEA and 9 other, mainly aliphatic compounds (6 aliphatic, 3 aromatic). The data for NDMA is shown in Figure 3. NDMA is a known disinfection by-product of ozonation. AOC was not measured in this work although samples (n=4) were taken for Biodegradable DOC (BDOC) analysis. BDOC was observed to increase from an average value of 2.6±0.2 to 4.6±0.3 mg/L, an increase from 31% to 55% of the total DOC. The reduction in CoC's observed in Figure 1 is greater than what might have been expected based on the BDOC data but reflects that not all molecular fragments produced through ozonation are expected to be biodegradable. BDOC data across the barriers is shown in Table 5.

There is limited data in the literature for molecular changes across ozone barriers on their own. Frequently, the data is combined for ozone-BAC scenarios. In addition, what data is available is often at a substantially different dose and contact time than the case herein. The laboratory and field study data of Dickenson et al. [17] is relevant none the less. In their pilot study, they investigated the response to ozone of different molecular types and varied the ozone dose from 2.1 to 7.0 mg/L to give a ozone/TOC ratio from 0.3 to 1.0 mg/mg with data reported predominately for the 0.6 to 1.0 range. The contact time varied from 2 to 18 minutes. Based on the ozone residual at outlet and hydraulic residence time in the reactor, they calculated an ozone contact time (CT_{10}) value of between 4 and 11 mg.min/L using the extended integrated method [18].

The dose employed in the AWTP, varied from 11.7 to 14 mg/L ozone to give a ozone/DOC ratio of between 1.3 and 1.7. This is a higher initial ozone dose than the literature studies [17, 19] but the DOC levels are also higher and Wert et al. [19] demonstrated that even for large variations in ozone dose, quoting of the data on a ozone/DOC or ozone/TOC ratio is appropriate as many disparate scenarios normalize on this basis. The hydraulic residence time ($HDT_{10} = HDTxT_{10}/T$) for the reactor, taking short-circuiting into account was 4.8 minutes based on dye testing. The CT_{10} for the AWTP based on this HDT_{10} value using a conventional approach varies between 0 and around 5 mg.min/L since the residual ozone at the outlet of the reactor varied considerably across the period of the trial (0 to 1.1 mg/L, although it was almost always above zero and often above 0.5 mg/L). Use of an extended integrated method is more appropriate since this considers the rate of decay within the reactor but without access to such decay data within the reactor, this was not possible. The case study of Dickenson et al. would calculate a CT_{10} of <1 using a conventional approach as against a value of 11 mg.min/L for 18 minutes of contact using the extended integrated method. Rakness et al.[18] introduced the extended integrated contact time (CT_{10}) method to take better account of the decay rate and contact time within the reactor but comparisons in the literature but given that this method is not available to this work, comparisons will need to be made on the basis that a ozone/DOC ratio >1 was utilised and the HDT_{10} of 4.8 minutes would likely achieve a CT_{10} by an extended integrated method that was similar to the work of Dickenson et al. [17]

Table 5: DOC and BDOC data across unit processes

Sample	9 Oct 2014		28 Jan 2015		25 March 2015	
	DOC (mg/L)	BDOC (mg/L)	DOC (mg/L)	BDOC (mg/L)	DOC (mg/L)	BDOC (mg/L)
Plant Feed	8.5	2.7	8.9	2.6	8.7	2.4
Post Ozone	7.5	4.4	8.7	4.9	8.1	4.5
MF filtrate	6.8	3.8	8.2	4.4	7.6	4.0
Post BAC	3.9	1.9	4.0	1.5	3.6	1.1

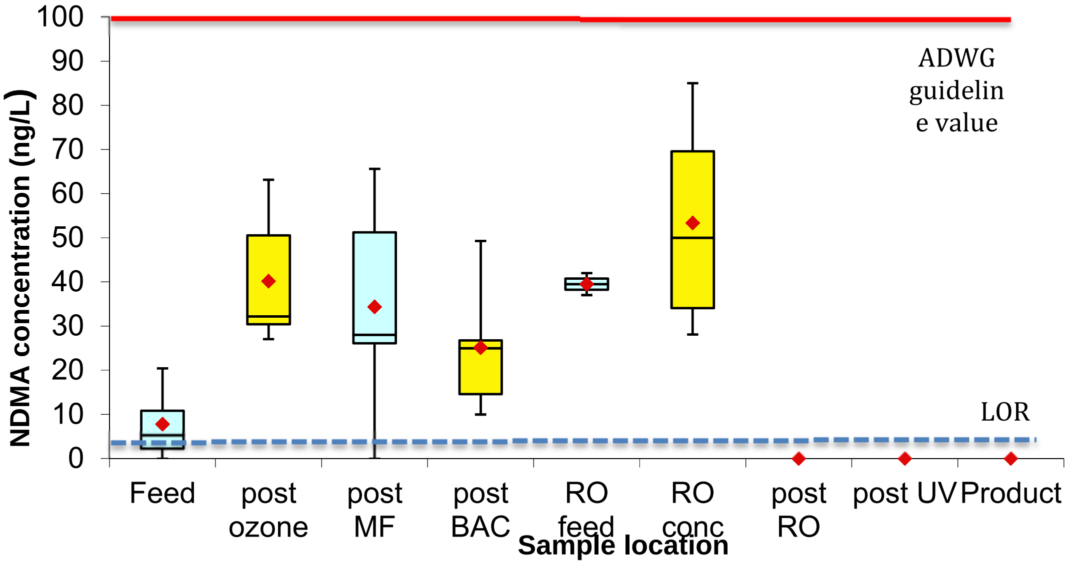

Figure 3: NDMA as measured across the AWTP at SPWWTP for the sampling period.

Dickenson categorised the ozonation potential of compounds into four key molecular groupings, assuming that a parameter called the instantaneous ozone demand (IOD) had been exceeded [17]. These groupings are outlined in Table 6. The IOD is the ozone utilisation during the first 30 seconds of exposure where the predominate reaction is that of O_3 and not the formation of OH radicals. Wert et al. [19] show that the reaction of ozone with some compounds leads to the production of OH radicals and once the excess of O_3 is sufficient to lead to OH radical formation, the IOD is exceeded. It is important that OH radicals are produced to improve the indiscriminate breakdown of CoC's. An ozone/DOC ratio in excess of 1.0 was assumed to have achieved this condition since once the uptake of ozone by nitrate was taken into account, ozone to TOC ratios of greater than 0.5 generally achieved significant OH radical formation after 30 seconds exposure times. This is the basis for the criteria that an O_3/TOC ratio of >1.0 is assumed to have exceeded the IOD of the system. The destruction of recalcitrant indicator (probe) compounds such as para-chlorobenzoic acid, an electron withdrawing aromatic compound, were used in the work of Wert et al. [19] to indicate the presence of OH radicals. An overview of the Dickenson et al. classification, based on their work and the work of Wert et al. [19] is summarised in Table 5. The work used O_3/TOC ratios of 0.3, 0.5 and 1.0 corresponding to 2, 3 and 7 mg/L of O_3 and contact times of 2, 6 and 18 minutes.

In the trial period at SPWWTP, an analysis was completed on data over 9 sampling events using GC-MS and LC-MS analysis as well as a separate nitrosamine study. Data comparing the feed data to that post ozone and categorized as per the Dickenson et al. classification is shown in Table 7. The analysis of data was the same as for the MBR in that when a compound was not detected in either the feed or post-ozone, a value of 0.5xLOR was used. However, in this instance, in cases where there was no detection post ozone of the compound over the 9 sampling events, the removal efficiency was set to 100%. The calculated LRV for these compounds was then considered as a minimum only. Despite this, data for some compounds was at such low concentrations across the sampling events that a critical analysis was difficult. This is consistent with the DR concept discussed earlier [17]. For compounds where there was no data above the LOR, analysis was not completed. These included Bisphenol A, 2,4,6-Tribromophenol, Dimethylterephthalate, Methyl decanoate and Methyl dodecanoate. Ten compounds (inclusive of the NDMA data shown in Figure 3 and NDEA) were observed to either increase in concentration across the ozone barrier or were not detected in the feed but were detected post-ozone.

Table 6: Molecular categories for ozonation based on the classification of Dickenson et al. using their own and other work in the literature [17, 20]. The removal extent (RE) is given by equation 1.

Group	RE (%)	Molecular Characteristics	Other indicators
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}
2	>50 <90	aliphatic alkane, ketone, alcohol, acid, ether, and amide or and nitro aromatic compounds	
3	>25 <50	Nitrosamines	Formation and removal are competitive.
4	<25	Halogen containing aliphatic and aromatic compounds	Strong electron withdrawing groups (EWG's)

Each molecule in Table 7 is designated to a group according to the classification of Dickenson et al. [17]. Each grouping is coloured according to group 1 (green), group 2 (white), group 4 (yellow). There were no group 3 compounds detected by the GC-MS and LC-MS methodology. Compounds that increased in concentration across the barrier are highlighted in grey. All compounds for which the DR value was <5 are shown in pink. The DR concept [17] was introduced to avoid issues whereby if the concentration of a molecule in the feed was close in concentration to the limit of detection, the efficacy of the LRV assessment would be considered marginal and a good basis for rejection.

Table 7: Overview of the change in concentration of all compounds detected in the feed by GC-MS and LC-MS across the ozone barrier during the trial period at SPWWTP.

Name	GROUP	Feed (N)	Feed (µg/L)	Post ozone (N)	Post-ozone (µg/L)	RE (%)	LRV
1,4-Dichlorobenzene	4	6	0.0776	1	0.0053	93.21	1.17
1,2-Dichlorobenzene	4	2	0.0466	0	0.0050	100	0.97
trans-Decahydronaphthalene	2	1	0.0143	0	0.0125	100	0.06
Dibenzyl ether	1	3	0.0578	0	0.0125	100	0.66
3-&4-Methylphenol	1	1	0.0112	0	0.0100	100	0.05
2-Methoxyphenol	1	4	0.0353	0	0.0125	100	0.45
2-tert-Butyl-4-methoxyphenol	1	1	0.0511	0	0.0050	100	1.01
4-Methyl-2,6-di-t-butylphenol (BHT)	1	5	0.1089	1	0.0146	86.60	0.87
4-tert-Octylphenol	1	5	0.0527	0	0.0050	100	1.02
4-Nonylphenol	1	2	0.1003	0	0.0050	100	1.30
2,5-Dichlorophenol	4	2	0.0119	0	0.0050	100	0.38
2,6-Dichlorophenol	4	3	0.0230	0	0.0050	100	0.66
2,4,5-Trichlorophenol	4	2	0.0166	0	0.0050	100	0.52
Triclosan	4	4	0.0863	0	0.0050	100	1.24
Dimethyl phthalate	1	1	0.0140	5	0.0668		
(9Z)-9-Tetradecenoic acid, methyl ester	2	0		3	0.0808		
Bis(2-ethylhexyl)phthalate (DEHP)	1	3	0.3274	0	0.0050	100	1.82
Methyl myristate	2	1	0.0101	1	0.0094	6.52	0.03
Methyl palmitate	2	1	0.0635	0	0.0750	100	
Elaidic acid methyl ester	2	1	0.0134	0	0.0050	100	0.43
Benzyl alcohol	1	0		1	0.0052		
Octanol	2	0		3	0.0644		
Phenylethyl alcohol	1	1	0.0105	0	0.0050	100	0.32
1-Nonanol	2	0		2	0.0169		
alpha-Terpineol	2	1	0.0308	0	0.0125	100	0.39
Coprostanol	2	6	2.2307	6	0.9834	55.91	0.36

Epicoprostanol	2	6	0.6612	5	0.2420	63.41	0.44
Cholesterol	1	6	1.4979	2	0.1355	90.96	1.04
Coprostanone	2	6	0.3626	5	1.6532		
Cholestanol	2	5	0.6163	4	0.3992	35.23	0.19
Ergosterol	2	6	0.9275	1	0.0655	92.94	1.15
Campesterol	2	4	0.1145	0	0.0050	100	1.36
Stigmasterol	2	4	0.2453	0	0.0500	100	0.69
24-Ethyl coprostanol	2	3	0.3365	4	0.2177	35.30	0.19
beta-Sitosterol	2	4	0.3123	2	0.2442	21.79	0.11
Stigmastanol	2	4	0.1114	2	0.0741	33.42	0.18
3,4-Dichloroaniline	4	1	0.0215	0	0.0125	100	0.24
2,6-Dinitrotoluene	1	1	0.1370	0	0.0050	100	1.44
e-Caprolactam	2	3	0.0730	2	0.1277		
2-(Methylthio)-benzothiazol	1	6	0.3433	0	0.0125	100	1.44
2(3H)-Benzothiazolone	1	1	0.0092	0	0.0050	100	0.26
Tributyl phosphate	4	3	0.0617	3	0.0073	88.15	0.93
Tris(2-chloroethyl) phosphate	4	4	0.2193	5	0.2305		
Tris(1,3-dichloro-2-propyl) phosphate	4	4	0.1150	4	0.0773	32.76	0.17
L-Menthol	1	1	0.0091	0	0.0050	100	0.26
Diethyltoluamide	1	6	0.2191	5	0.0142	93.53	1.19
Ibuprofen	1	2	0.0826	0	0.0050	100	1.22
Caffeine	1	2	0.0287	0	0.0050	100	0.76
Carbamazepine	1	6	1.1545	0	0.0050	100	2.36
Fenobucarb	1	0		1	0.0211		
Piperonyl butoxide	1	1	0.0093	0	0.0050	100	0.27
Bifenthrin	1	1	0.0822	0	0.0050	100	1.22
Simetryn	1	1	0.0154	0	0.0050	100	0.49

Table 8: Summary of analysis of the removal data by class of compound using the categorisation of Dickenson et al. [17].

Group	RE (%)	Removal observations	Exceptions
1	>90	N=24 compounds >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
2	50-90	N=19 compounds >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,
3	25-50	N=2 compounds Increased N=2	Increased - NDMA, NDEA
4	<25	N=10 compounds >90% N=8 25-50% N=1 increased N=1	Increased - Tris(2-chloroethyl) phosphate

In all, 71 CoC's were detected either in the influent or effluent of the ozone barrier. Of the 65 compounds included in the analysis, 36 were removed to >90%. A summary is shown in Table 8.

Compounds in the Group 1 categorisation, nominally electron rich aromatic compounds and nonaromatic alkenes, were removed very effectively by ozone, often to the point of non-detection and all to well below guideline values for ADWG and AGWR (some of the compounds are not listed in the Australian guidelines). The three compounds 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, 21/24 compounds in Group 1 were reduced to substantially below guideline values and the average removal efficiency was >98.6% with a range of 86.6-100%. This is consistent with literature expectations for the role of ozone at doses of greater than the IOD and with a high CT_{10} as measured by the extended integration method [17]. Therefore, a LRV for electron rich aromatic compounds of 1.0 is claimed for this barrier when operated under conditions consistent with the trial period, nominally at ozone/DOC ratio of greater than 1 and preferably, a CT_{10} value (calculated using the conventional method) of greater than 2 mg.min/L.

The Group 2 compounds showed a more varied result, with 5/19 compounds observed to increase in concentration across the barrier and 10/19 compounds below the expected literature performance of the barrier. These are almost certainly molecular fragments in a number of cases (i.e. Octanol and 1-Nonanol). Many compounds were removed to below LOR although there is no obvious trends in the data.

The Group 3 nitrosamines data was not consistent with the tabulated data of Dickenson et al. [17] although there is ample evidence in the literature for the formation of nitrosamines such as NDMA and NDEA through ozone treatment. Indeed, this grouping seems odd and based on literature it should be associated with formation rather than removal [21].

The Group 4 data for molecules with strong electron withdrawing groups appears consistent with literature expectations although a number of compounds were completely removed by the ozone. This is almost certainly due to the random attack of OH radicals but as for Group 2, no trends were obvious.

Required Operating Parameters

Flowrate = 20±10% L/min (T_{10} = 4.8 min)

Residual concentration >0.05 after a hydraulic residence time (10%) of 4.8 minutes

Or

Flowrate = 20±10% L/min (T_{10} = 4.8 min)

ozone dose > 13.5 mg/L, ratio of mg O_3/ mg DOC >1.0 and a CT_{10} of ozone of >2 mg.min/L.

Ceramic Microfiltration (CMF)

CMF design and specifications

Supplier - Metawater
Membrane type – ceramic aluminium oxide with surface coating, nominal pore size of 0.1 μm
System Design TMPmax = 1.4 bar (MetaWater *TMP max.* = 6 bar (during backwashing))
Flux – 48 L/m^2.h

Removal Mechanisms

Any removal of CoC's by CMF is expected to be by adsorption onto a fouling layer and onto solid particulates that will then be removed by size exclusion. Fragmented organic residues may coagulate and form particulates that are then removed by size exclusion.

Reported LRV for CMF

The data of Figure 1 would lead one to believe that the role of the CMF in the removal of CoC's is significant, with an almost 40% removal relative to the feed to the AWTP. The effect on the removal of sterols is particularly strong and a possible clue to the mechanism, namely removal of particulates with high K_{ow} molecules (i.e. sterols) adsorbed thereon. This in itself is possibly a consequence of the fact that the feed to the AWTP is substantially higher in particulates (seen as turbidity) than will be the case at Davis Station where an MBR will precede the AWTP. The low removal of total DOC and lack of literature data to indicate that this barrier can remove significant quantities of CoC's through molecular size exclusion means that it is difficult to make a robust claim for CoC removal short of CoC fragments from ozone treatment that have become more hydrophobic than the parent compound and precipitated from solution. It is important none the less that this barrier is working effectively to reduce the fouling organic load in the BAC and RO barriers.

Biologically Activated Carbon (BAC)

BAC design and specifications

EBCT – 20 minutes
Volume = 400L
Backwash - air scour and backwash; activated by filtrate volume or excessive pressure drop or turbidity in the filtrate
Carbon - Acticarb BAC GA1000N 8x30 Mesh
Performance measurements – On-line turbidity measurements (usually 0.15 - 0.28 NTU)

No LRV is claimed over the BAC although adsorption and assimilation of BDOC is expected. The majority of these compounds are molecular fragments from ozone treatment and a quantitative assessment of a differential removal by molecular class is not able to be made. As with the MF barrier, operation of this barrier is critical to reduce fouling in the RO and reduce AOC influent to the environment. The effluent of the BAC is fed to the RO and the RO concentrate is sent to waste.

Reverse Osmosis (RO)

RO Design and Specifications

Membranes- Dow BW30
Module design – 5 x single elements in series
Mode of operation – operated at 70% recovery with recirculation to achieve this, semi-continuous with near continuous operation in the summer and operation for 4 hours every second day during winter, membranes are flushed with permeate whenever they shut down. An osmotic backwash has been observed when shut down.
Average Flux – 23 L/m^2.h
Monitoring permeate - conductivity, flowrate
On-line integrity sensors – conductivity across each element and across the feed and permeate.

Removal Mechanisms

- The expected method of removal is through size exclusion (MW cut-off) and ionic rejection from the polymer network of the RO membrane. An extra mechanism of removal is entrapment in the filtration fouling layer.
    - .

Reported LRV for RO

There have been a range of literature studies looking at the rejection of both organic and inorganic species by RO. Figure 1 shows that the AWTP showed good rejection of organic CoC's across the RO barrier. Figures 2 and 3 shows the barrier was also very good in the rejection of DOC, TN and NDMA. The AWTP uses conductivity across the process for on-line verification. Typical operational LRV data for ionic species (predominately inorganic salts) is shown in Figure 4. A claimed LRV=1.5 is made for inorganic ionic species across this barrier when operated to the same conditions as for pathogen removal at SPWWTP.

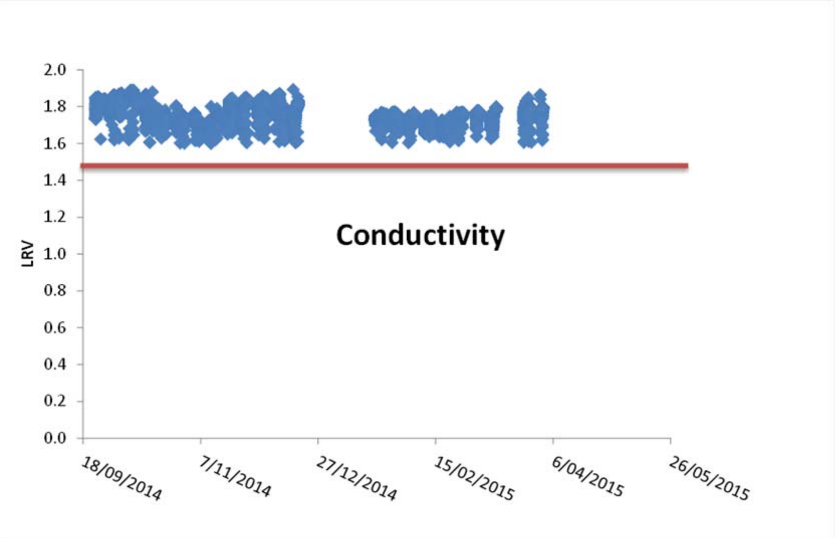

Figure 4: Typical LRVs calculated from conductivity measurements of the feed and permeate at SPWWTP.

Rejection of organic CoC is expected to be on the basis of MW and charge. A standard additions study using combined MBR and then RO by Alturki et al. [22] and review of the associated literature therein shows that rejection of hydrophobic molecules by RO is not as effective as ionic and hydrophilic species, but a combination of 40 trace organics ranging in partition coefficient (1.21 to 6.19@pH8) and size (151 to 454 MW) were removed to below detection limits from an initial dose of 2 μg/L. This is a LRV>2 for a LOD of 0.005 μg/L.

The data for operation of the AWTP at SPWWTP shows that the DOC in the feed to RO is 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 LRV for the organic compounds reflects both size and charge exclusion and the observation that low MW (<200) neutral hydrophilic molecules are likely rejected based on size exclusion but that higher MW, neutral hydrophobic compounds (200<MW<400) adsorb and then diffuse (faster than an ionic species) through the membrane [22]. Table 9 lists all of the species and the average concentrations of all of the compounds detected in the product water. An LRV analysis on an individual molecular basis is not viable as the concentration in the RO feed of most of the chemicals is close to the LOD. There were 15 molecules detected overall. All were at very low concentrations, close to the LOD, except for 2,4,6-Tribromophenol and benzyl alcohol, and all are uncharged at pH 8.

Table 9: Summary of chemicals detected in AWTP product water samples

Name	n	FOD (%)	Average (µg/L)	K_{ow}	MW
(9Z)-9-Tetradecenoic acid, methyl ester	3	50	0.04	4.57	240.385
1-Nonanol	3	50	0.01	3.77	144.255
Ethanol, 2-phenoxy-	3	50	0.03	1.17	138.164
4-Nonylphenol	2	33	0.04	5.76	220.000
Octanol	2	33	0.03	3.00	130.228
4-Methyl-2,6-di-t-butylphenol (BHT)	1	17	0.06	5.10	220.350
Bisphenol A	1	17	0.03	3.40	228.000
2,4,6-Tribromophenol	1	17	0.27	3.89	330.800
Methyl myristate	1	17	0.03	7.43	242.000
Benzyl alcohol	1	17	0.85	1.10	108.140
alpha-Terpineol	1	17	0.02	2.69	154.249
Cholesterol	1	17	0.05	7.11	386.650
Coprostanone	1	17	0.01	9.64	386.645
L-Menthol	1	17	0.01	3.30	156.265
Diethyltoluamide	1	17	0.01	2.02	191.270

n, number of detections; FOD, frequency of detection

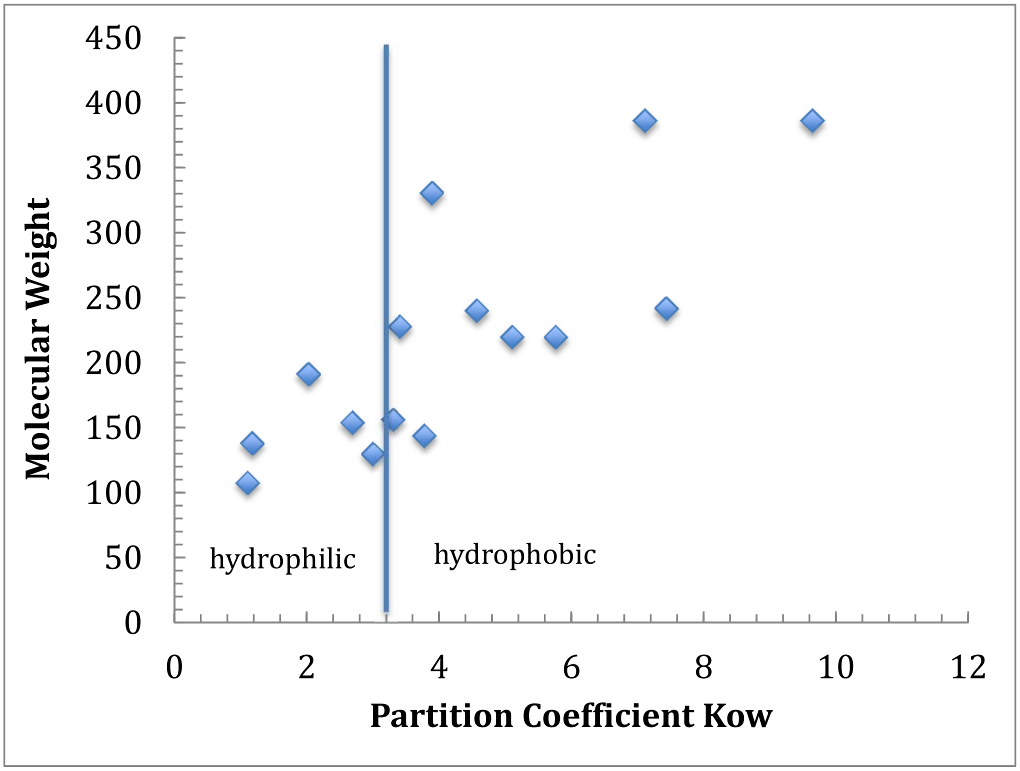

Figure 5: Partition coefficient plotted against MW for organic molecules detected in the product water of the AWTP.

Figure 5 shows the relationship between K_{ow} and MW of compounds present in the product water. It is consistent with the literature, albeit not shown in this way before, wherein molecules of MW>200 only show increased diffusion through the membrane (relative to a charged ion) if they are hydrophobic but there is still a hard MW cut off for MW>400. This is assumed due to the fact that adsorption causes a higher concentration of species close to the membrane. Neutral hydrophilic molecules are able to show an increased diffusion relative to a charged species if they have a MW<200. The K_{ow} =3.2 line, indicated in Figure 5, indicates that no hydrophilic molecule of MW >200 was detected in the RO product water. The definition of hydrophobicity, as put forward by Tadkaew et al. [11], is therefore consistent across both the MBR and RO barriers. The balance between diffusion through the membrane and rejection shows that, removal to >70% for all compounds with a consistent concentration in the feed, including NDMA (as shown in Figure 3) and NDEA [10].

In addition to the analytical assay of compounds, in vitro bioassays were used to measure the effectiveness of the RO barrier. Only feed, RO permeate and RO concentrate were tested. The bioassay determined the ability of chemical compounds (not specified) to bind to a range of receptor sites in genetically modified yeast. These receptor sites looked to determine the presence of:

1. Estrogenic compounds or mimics based on a human and medaka (fish) receptor. Agonists of this gene are molecules with electron rich aromatic rings and are typified by 17β-Estradiol,Estrone, Estriol, Bisphenol A, nonyl phenol and Diethylhexyl phthalate.
2. Aryl hydrocarbons based on a human receptor. Agonists of this gene are molecules with electron rich aromatic rings and aromatic rings with strong electron withdrawing groups including Cl. Molecules of interest include dioxins, PCB's, Benzo[a]pyrene, 4-Methyl-2,6-di-t-butylphenol (BHT) and 3-Methylcholanthrene.
3. A constitutive androstane receptor for compounds that show any xenobiotic activity, including those that bind to the estrogenic and aryl hydrocarbon receptor. Agonists of this gene are molecules with electron rich aromatic rings but also include a range of and are typified by p-*tert*-Octylphenol, Isofenphos, Diethylhexyl phthalate and a wide range of pharmaceuticals.

In addition, a general toxicity test was conducted using a modified photobaterium. The data shows that the product water caused either no response or a minimal response on all tests [10]. The role of RO was observed to be an important but ancillary barrier, since very little activity was observed in the RO concentrate, implying that the ozone barrier and subsequent MF and BAC were doing the bulk of the CoC removal. This is consistent with the expectation that the ozone barrier targets electron rich aromatic and non-aromatic alkene compounds effectively. The modified photo-bacterium test data showed slight activity in the RO concentrate but none in the RO permeate, indicating that the RO barrier was effective on the electron withdrawing aromatic compounds, linear aliphatic and cyclic aliphatic molecules. The data is highly suggestive that the bioassay (CAR) or photo bacterium approach may be very useful as an indicator of barrier performance or as a precursor to determine the need to do multi-residue analysis. After all, only three of the organic molecules found in the product water are listed in the ADWG or AGWR and all concentrations were below guideline values after the ozone barrier. So although the water would by any multi-residue analysis be classified as potable and safe, the photo-bacterium and CAR receptor assays indicate that some CoC's is still detectable and active.

A LRV of 1.0 is therefore claimed for all charged organic molecules, all neutral hydrophilic molecules with a MW >200 and all neutral hydrophobic molecules with a MW>400. The definition of hydrophobic is a K_{ow} > 3.2@pH 8. A LRV of 0.5 is claimed for all other organic molecules. This assumes an operational CCP consistent with that defined to reject pathogens.

Required Operating Parameters

Conductivity measurement is a direct indicator of membrane integrity since it indicates the propensity of a charged molecule to diffuse through the RO membrane. Given that charged CoC's (both organic and inorganic) are removed by the same size exclusion and charge rejection mechanism, then it serves as a CCP for these species. For uncharged (nominally organic molecules), conductivity reduction is indicated to be an over-estimate of performance. Small (<200 MW) neutral molecules are rejected through size exclusion that limits diffusion but in the absence of an additional charge rejection mechanism, the RO membrane will not be as effective on these molecules. Membrane integrity is critical none the less and conductivity measurement is an appropriate surrogate for RO performance. Larger (>200 MW) neutral hydrophobic molecules adsorb and then diffuse through the RO membrane. Rejection is through size exclusion and retarded diffusion but the act of adsorption causes a concentration gradient at the membrane surface that enhances the apparent concentration of the molecule. Once again, membrane integrity is a powerful indicator of RO performance and conductivity measurement is a good surrogate.

Specific flow-rate >1.09 $L.min^{-1}.bar^{-1}$

Overall RO system recovery >60%

An LRV>1.5 from on-line conductivity testing

LRV summary and examples

The analysis herein indicates that the classifications of molecules as listed in the AGWR are not useful in the determination of the likelihood that a particular molecule will be removed by a barrier, since there is often a range of molecular attributes within a particular class. This is not a new conclusion as it has been made by Khan and co-workers in a number of publications [11, 22]. The literature data analysis and data from the AWTP over more than 9 months of operation is consistent and suggests a new classification in terms of the propensity of a particular compound to be removed by a particular barrier and as an indicator of the LRV designation for that barrier. This classification, including subclasses and notes are summarised in Table 10.

Table 10: Classification of molecules for CCP and LRV analysis.

Class	Sub-class	Sub-class 2
Aromatic	Compounds with electron withdrawing groups (EWG) including nitrosamine, halogenated, ethynyl, carboxyl, ester, amide	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
	Compounds with electron donating groups (EDG) and electron rich rings including acyl amino, amino, hydroxyl, alkoxy and akyl groups	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
	Compounds with combinations of EDG and EWG (other)	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
Aliphatic	Compounds with double bonds and EDG	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
	Compounds with EWG	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
	Compounds with combinations of EDG and EWG (other)	Hydrophobic (MW<400) Hydrophilic (MW<200) Charged or Neutral
Inorganic	Metals including Pb, Cd, Fe and Hg	
	Inorganic N containing compounds	
	Radiological	

An assessment of the barrier performance based on this classification is shown in Table 11, including the claimed LRV's. The assessment is extended to consider not just the LRV through the AWTP and MBR, but also includes dilution into the plant (5000:1, LRV = 3.7). This gives an overall LRV that can then be used to determine the maximum amount of a particular chemical that should be allowed to enter the waste collection system based on the maximum guideline value for that chemical in potable water. An overview is presented in Table 10 for the various molecular classifications. Numbers vary from a few grams to 100's of kg, depending on the maximum guideline value, the latter being well beyond the likely carrying size of any water miscible chemical in the AAD chemical manifest.

There is potential to exemplify the outlined process with a number of chemicals of concern. These are shown below and the structures of all compounds detected in the feed to the AWTP are shown in Appendix 1.

> **Triclosan** (a disinfectant with a very low AGWR guideline value and longevity in the environment)
>
> Classification: Aromatic (EWG), pKa=7.9 (charged at pH 8), MW 289.542, K_{ow}=4.76 (hydrophobic)
>
> AGWR max value: 0.35 μg/L
>
> LRV from Table 11 = 5.5, maximum input = 0.11 g/5000L of wastewater. Based on expected flowrates, in summer, this would represent approximately a 6 hour period and in winter, a one day period.

Triclosan is supplied as an additive in disinfectants, soaps, toothpastes and mouthwashes at a concentration of 0.1-1%, typically 0.5%. 'Colgate Total', a popular toothpaste uses 0.3% Triclosan. A

2 ml disinfectant use will supply around 0.01 g of Triclosan to the wastewater system. A spill of 20 ml of Triclosan disinfectant solution has the potential to cause an issue. As an alternative, a typical teeth brushing event would use approximately 0.5 g of toothpaste and deliver 0.0015g of Triclosan to the wastewater collection system. Repeated approximately 100 times in summer, twice a day, has the propensity to deliver 0.15g of Triclosan to the wastewater system in any one six hour period. This would exceed the recommended acceptable level for treatment and source control is indicated. This could be as simple as excluding non-clinical products containing Triclosan or choosing a range of such products such that the number with Triclosan is a moderate percentage of the total number. The case study also highlights issues associated with non-spill events such as showering or teeth brushing that are regular and temporally confined (i.e. they always occur within 2 hours of breakfast). On the upside, this is a very conservative estimate and assumes no role of ozone in the destruction of Triclosan. The studies in the trial period showed an LRV of 1.24 for the ozone barrier. This is not claimed in Table 10 because of the variable role of ozone in the destruction of aromatic molecules with strong EWG's but represents an order of magnitude safety margin in the quoted figures for this compound. The observation of the role of Triclosan destruction by ozone is consistent with the data of Wert et al. [19] who showed that molecules with a second order reaction rate concentration with O_3 $>10^5$ M^{-1} s^{-1} and OH $>10^9$ M^{-1} s^{-1} were removed to >95% or LRV > 1.3.

Ibuprofen (a commonly used painkiller)

Classification: Aromatic (EDG), pKa=5.2 (charged at pH 8), MW 206.281, K_{ow}=2.23 (hydrophilic)

AGWR max value: 400 μg/L

LRV from Table 11 = 5.7, maximum input = 200 g/5000L of wastewater

Ibuprofen is supplied as tablets of 200 mg. Even allowing for the fact that no removal of this compound is claimed through the MBR, it would take over 1000 tablets solubilised into the waste collection system to cause an issue. For a summer community of 120 persons, this is an unlikely event for any six hour period.

Table 11: LRV assessment of barriers in the AWTP including indications of maximum instantaneous inputs based on ADWG and AGWR guideline values for CoC's. The LRV associated with dilution is 3.7, representative of a dilution of 1:5000. The maximum spill value in kg is calculated for a range of maximum guideline values.

CLASS	SUB-CLASS	MBR Max 1.0	Ozone Max 1.0	RO Max 1.5		LRV 3.0	TOTAL LRV incl dilution	SPILL MAX (kg) for AGWR max value 1 μg/L	10 μg/L	100 μg/L	1 mg/L	10 mg/L	100 mg/L
AROMATIC	EDG	hydrophobic	all	charged		2.8	6.5	0.00316	0.0316	0.316	3.16	31.6	316.2
				neutral	other	2.8	6.5	0.00316	0.0316	0.316	3.16	31.6	316.2
					MW<400	2.5	6.2	0.00158	0.0158	0.158	1.58	15.8	158.5
		hydrophilic	all	charged		2.0	5.7	0.00050	0.0050	0.050	0.50	5.0	50.1
				neutral	other	2.0	5.7	0.00050	0.0050	0.050	0.50	5.0	50.1
					MW<200	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
	EWG	hydrophobic	all	charged		1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
				neutral	other	1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
					MW<400	0.8	4.5	0.00003	0.0003	0.003	0.03	0.3	3.2
		hydrophilic	all	charged		1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
				neutral	other	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
					MW<200	0.5	4.2	0.00002	0.0002	0.002	0.02	0.2	1.6
				charged		1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6

LRV claim
1.5
1
0.8
0.5

CLASS	**SUB-CLASS**	**MBR**	**Ozone**	**RO**		**LRV**	**TOTAL LRV**	**SPILL MAX (kg) for AGWR max value**					
		Max 1.0	**Max 1.0**	**Max 1.5**		**3.0**	incl dilution	1 µg/L	10 µg/L	100 µg/L	1 mg/L	10 mg/L	100 mg/L
	other	hydrophobic	all	neutral	other	1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
					MW<400	1.3	5.0	0.00010	0.0010	0.010	0.10	1.0	10.0
		hydrophilic	all	charged		1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
				neutral	other	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
					MW<200	0.5	4.2	0.00002	0.0002	0.002	0.02	0.2	1.6
ALIPHATIC	EDG	hydrophobic	all	charged		2.8	6.5	0.00316	0.0316	0.316	3.16	31.6	316.2
				neutral	other	2.8	6.5	0.00316	0.0316	0.316	3.16	31.6	316.2
					200<MW<400	2.5	6.2	0.00158	0.0158	0.158	1.58	15.8	158.5
		hydrophilic	all	charged		2.0	5.7	0.00050	0.0050	0.050	0.50	5.0	50.1
				neutral	other	2.0	5.7	0.00050	0.0050	0.050	0.50	5.0	50.1
					MW<200	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
	EWG	hydrophobic	all	charged		1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
				neutral	other	1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
					MW<400	0.8	4.5	0.00003	0.0003	0.003	0.03	0.3	3.2
				charged		1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0

CLASS	SUB-CLASS	MBR	Ozone	RO		LRV	TOTAL LRV	SPILL MAX (kg) for AGWR max value					
		Max 1.0	Max 1.0	Max 1.5		3.0	incl dilution	1 µg/L	10 µg/L	100 µg/L	1 mg/L	10 mg/L	100 mg/L
		hydrophilic	all	neutral	other	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
					MW<200	0.5	4.2	0.00002	0.0002	0.002	0.02	0.2	1.6
	other	hydrophobic	all	charged		1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
				neutral	other	1.8	5.5	0.00032	0.0032	0.032	0.32	3.2	31.6
					MW<400	1.3	5.0	0.00010	0.0010	0.010	0.10	1.0	10.0
		hydrophilic	all	charged		1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
				neutral	other	1.0	4.7	0.00005	0.0005	0.005	0.05	0.5	5.0
					MW<200	0.5	4.2	0.00002	0.0002	0.002	0.02	0.2	1.6
Inorganics	Metals	All	All	All		1.5	5.2	0.00016	0.0016	0.016	0.16	1.6	15.8
	Nutrients	All	All	All		2.0	5.7	0.00050	0.0050	0.050	0.50	5.0	50.1
	Radiolytic	All	All	All		2.5	6.2	0.00158	0.0158	0.158	1.58	15.8	158.5

Conclusions

The operational data from trial of the AWTP at SPWWTP has allowed a detailed study of barrier performance and the establishment of a basis for the regulation of chemicals based on the molecular structure of the compound. Classification of compounds according to their end use or broad molecular description as is outlined in the Australian Guidelines for Water Recycling was found to be useful in determining the maximum guideline concentration in the product water but was not useful in defining whether a molecule would be removed by a particular barrier. To this end, CoC compounds were classified according to three broad classes, namely aromatics, aliphatics and inorganics. A range of sub-classes and subordinate classes were designated in each of the classes. Five of the seven barriers of the AWTP were given no CCP status in the removal of chemicals as no quantitative mechanism of chemical removal or degradation could be attributed to each of the major molecular classes. The MBR was designated as a CCP barrier and the role of dilution of chemicals in the feed to the MBR was shown to be an important contributing factor in the removal of CoC compounds. Overall, three barriers in the entire wastewater treatment train were given CCP designation for the removal of CoC compounds. In the removal of chemicals of concern:

- A LRV of 1.0 is claimed for Total N and a LRV of 0.8 for hydrophobic organic chemicals for the MBR barrier with CCP requirements.
- A LRV of 1.0 is claimed for the ozone barrier for electron rich aromatic compounds and alkenes with CCP requirements.
- A LRV of 1.0 is claimed for the RO barrier for all compounds except neutral hydrophilic molecules with a MW<200 and neutral hydrophobic molecules with a MW<400, with CCP requirements.
- A LRV of 0.5 is claimed for the RO barrier for neutral hydrophilic molecules with a MW<200 and neutral hydrophobic molecules with a MW<400, with CCP requirements.
- The MF and BAC barriers were observed to be important functional barriers for the removal of organic compounds to aid both the quality of the environmental discharge from the AWTP and reduce fouling of the RO barrier. No LRV or CCP requirements are claimed for these barriers.
- The UV, calcite filter and Cl_2 barriers were given no status in the removal of CoC's from the product water.
- Table 11 provides an overview of the maximum concentrations of chemicals that should be introduced into the wastewater collection system such that there is no risk of CCP performance breaches.

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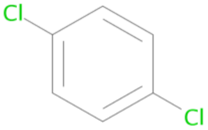
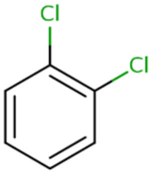
Appendix 1

Chemical structures of typical molecules measured by multi-residue analysis in the feed to the AWTP at Selfs Point.

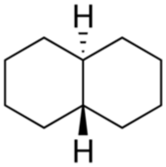
1. 1,4-Dichlorobenzene



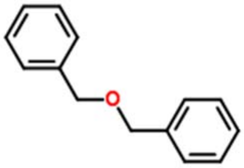
2. 1,2-Dichlorobenzene



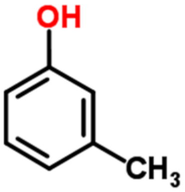
3. *trans*-Decahydronaphthalene



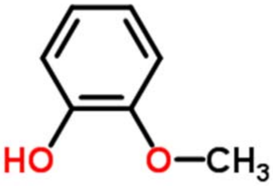
4. Dibenzyl ether



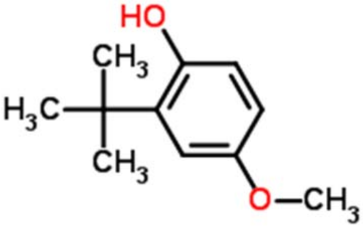
5. 3-methyphenol



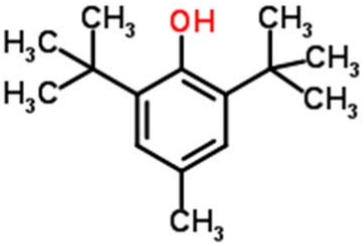
6. 2-Methoxyphenol



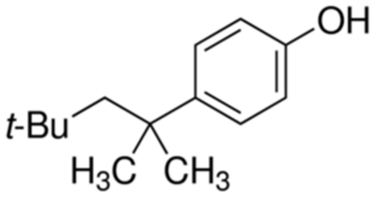
7. 2-tert-Butyl-4-methoxyphenol



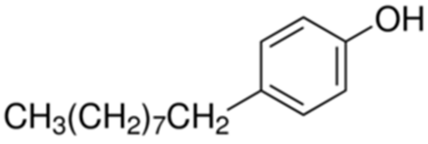
8. 4-Methyl-2,6-di-t-butylphenol (BHT)



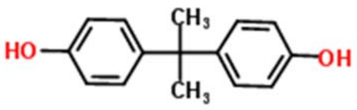
9. 4-tert-Octylphenol



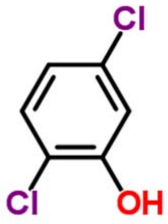
10. 4-Nonylphenol



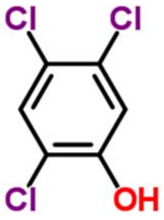
11. Bisphenol A



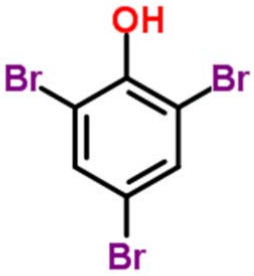
12. 2,5-Dichlorophenol



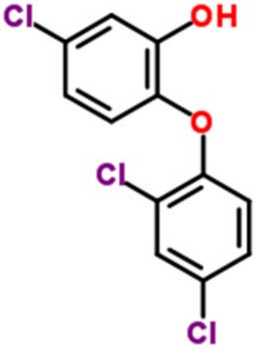
14. 2,4,5-Trichlorophenol



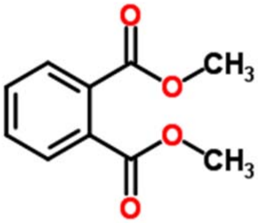
15. 2,4,6-Tribromophenol



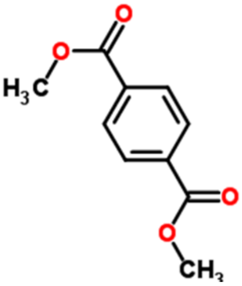
16. Triclosan



17. Dimethyl phthalate

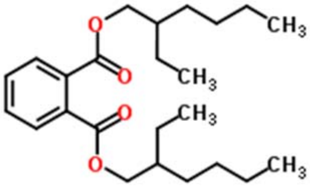


18. Dimethylterephthalate

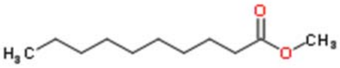


19. (9Z)-9-Tetradecenoic acid, methyl ester

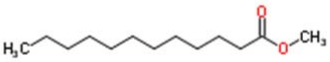
20. Bis(2-ethylhexyl)phthalate (DEHP)



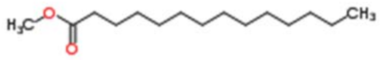
21. Methyl decanoate



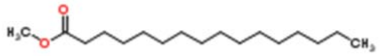
22. Methyl dodecanoate



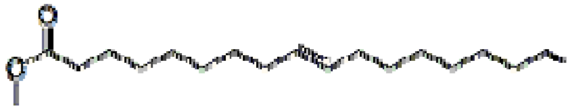
23. Methyl myristate



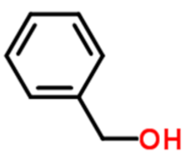
24. Methyl palmitate



25. Elaidic acid methyl ester

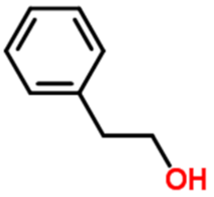


26. Benzyl alcohol

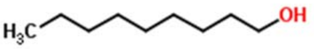


27. Octanol

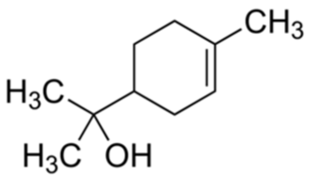
28. Phenylethyl alcohol



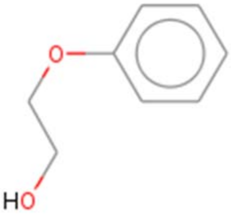
29. 1-Nonanol



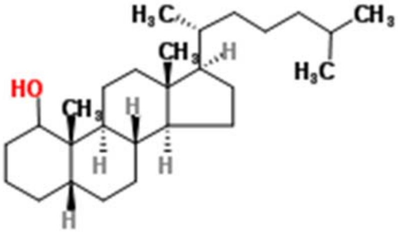
30. alpha-Terpineol



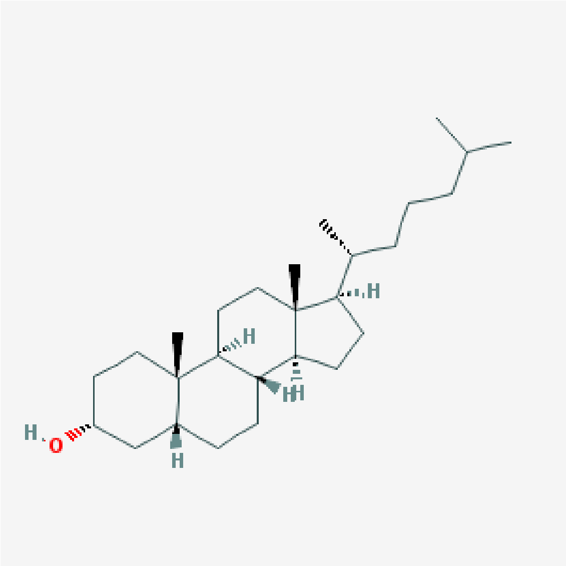
31. Ethanol, 2-phenoxy- (NIST)



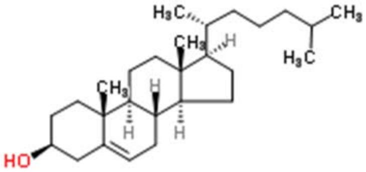
32. Coprostanol (chemspider)



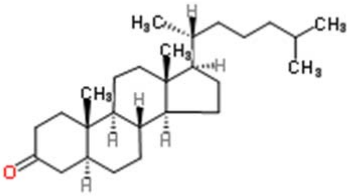
33. Epicoprostanol (pubchem)



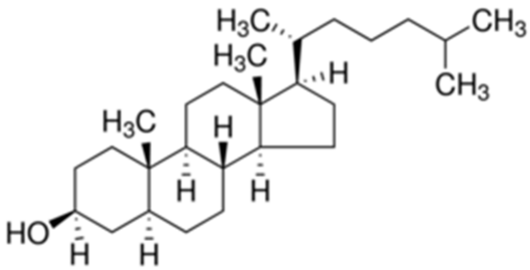
34. Cholesterol (chemspider)



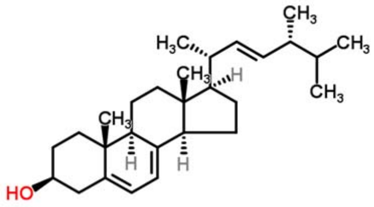
35. Coprostanone (chemspider)



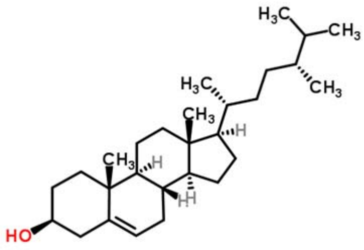
36. Cholestanol (sigma-aldrich)



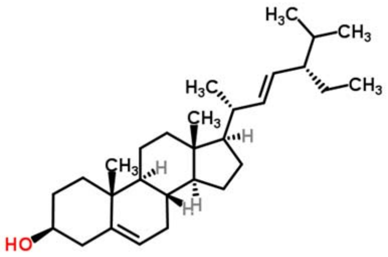
37. Ergosterol (CS)



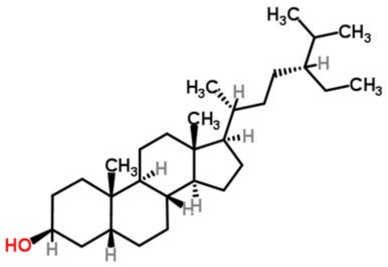
38. Campesterol (CS)



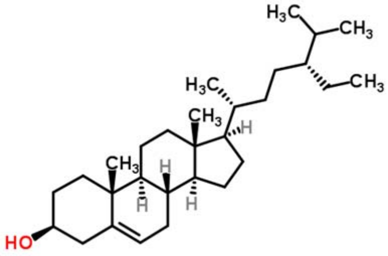
39. Stigmasterol



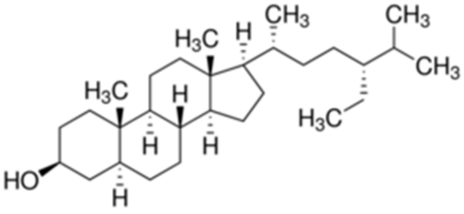
40. 24-Ethyl coprostanol



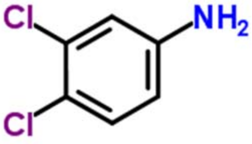
41. beta-Sitosterol



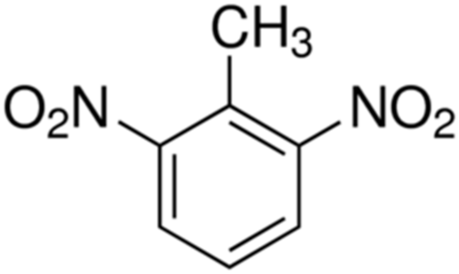
42. Stigmastanol (SA)



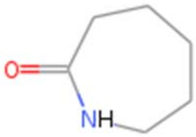
43. 3,4-Dichloroaniline



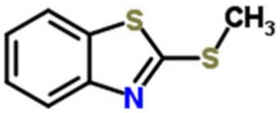
44. 2,6-Dinitrotoluene



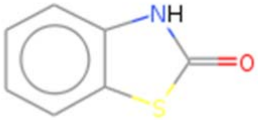
45. e-Caprolactam



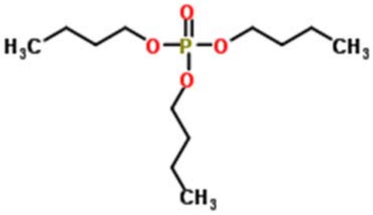
46. 2-(Methylthio)-benzothiazol



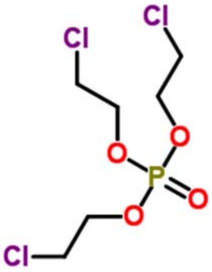
47. 2(3H)-Benzothiazolone



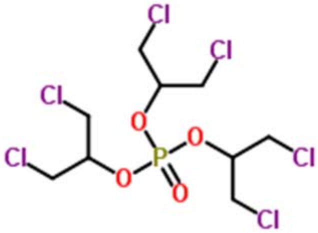
48. Tributyl phosphate



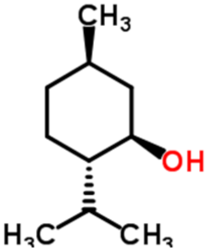
49. Tris(2-chloroethyl) phosphate



50. Tris(1,3-dichloro-2-propyl) phosphate

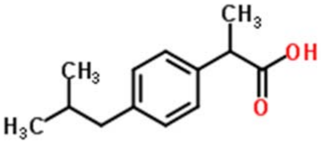


51. L-Menthol

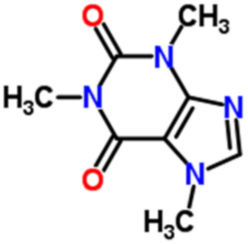


52. Diethyltoluamide

53. Ibuprofen

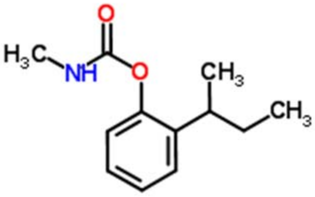


54. Caffeine

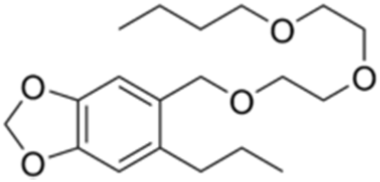


55. Carbamazepine

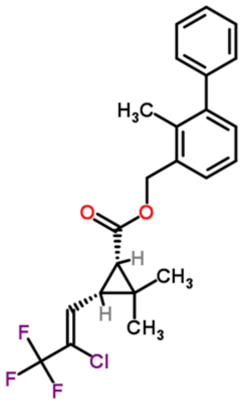
56. Fenobucarb



57. Piperonyl butoxide



58. Bifenthrin



59. Simetryn