Seasonal variations in fate and removal of trace organic chemical contaminants while operating a full-scale membrane bioreactor

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ABSTRACT

Trace organic chemical (TrOC) contaminants are of concern for finished water from water recycling schemes because of their potential adverse environmental and public health effects. Understanding the impacts of seasonal variations on fate and removal of TrOCs is important for proper operation, risk assessment and management of treatment systems for water recycling such as membrane bioreactors (MBRs). Accordingly, this study investigated the fate and removal of a wide range of TrOCs through a full-scale MBR plant during summer and winter seasons. TrOCs included 12 steroidal hormones, 3 xeno-estrogens, 2 pesticides and 23 pharmaceuticals and personal care products. Seasonal differences in the mechanisms responsible for removing some of the TrOCs were evident. In particular the contribution of biotransformation and biomass adsorption to the overall removal of estrone, bisphenol A, 17β-estradiol and triclosan were consistently different between the two seasons. Substantially higher percentage removal via biotransformation was observed during the summer sampling period, which compensated for a reduction in removal attributed to biomass adsorption. The opposite was observed during winter, where the contribution of biotransformation to the overall removal of these TrOCs had decreased, which was offset by an improvement in biomass adsorption. The exact mechanisms responsible for this shift are unknown, however are likely to be temperature related as warmer temperatures can lower sorption efficiency, yet enhance biotransformation of these TrOCs.

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1. Introduction

In the past decades, water recycling has emerged as an important component of water management practices as pressure on water resources has increased. Decentralised wastewater treatment systems (or package plants) are becoming the preferred option for sewage treatment and recycling in regional and rural communities where connection to a centralised sewer networks is not possible or is economically unfeasible. Membrane bioreactors (MBRs) are becoming a favoured technology for decentralised water treatment and recycling due to their small footprint and the ability to produce high quality effluent over conventional activated sludge (CAS) systems (Coleman et al., 2009; Le-Minh et al., 2010; Vuono et al., 2013). MBRs comprise a combination of a CAS process with microfiltration or ultrafiltration membrane separation, which enables these systems to produce effluents of suitable quality for a variety of reuse applications. MBRs can achieve excellent effluent qualities with respect to pathogens, suspended solids, dissolved organic carbon and nitrogen (Yang et al., 2009).

Throughout the last decade, interest in the ability of MBRs to eliminate trace organic chemicals (TrOCs) such as steroidal hormones, xeno-estrogens, pesticides, pharmaceuticals and personal care products (PPCPs) has increased — particularly for decentralised systems in regional water reclamation schemes (e.g. indirect potable reuse) (Coleman et al., 2009; Le-Minh et al., 2010). These trace chemical contaminants are of concern for the finished water from these water recycling schemes because of their potential adverse environmental and public health effects (Farré et al., 2008; Jury et al., 2011). The removal mechanisms for TrOCs through MBRs are complex and include biotransformation, adsorption to biomass, volatilisation, adsorption to the membrane, and physical retention by the membrane

(Stevens-Garmon et al., 2011; de Wever et al., 2007). Given that the molecular weight cut off for microfiltration is much larger than the TrOCs dimensions, the membranes are not expected to retain TrOCs through steric exclusion, unless the chemicals adsorb to larger particles or the membrane itself (de Wever et al., 2007). Adsorption to the membrane is considered as minor important due to limited available sorption sites (de Wever et al., 2007). The low Henry's constant ($H < 10^{-4}$) for the targeted TrOCs in this study suggests that volatilisation is an insignificant removal mechanism for these compounds (Stevens-Garmon et al., 2011; US EPA, 2011; Nguyen et al., 2012). Therefore, biotransformation and adsorption to biomass are expected to be the two most important removal pathways for these TrOCs.

The majority of previous MBR work (Bo et al., 2009; Kantiani et al., 2008; Kimura et al., 2005; Tadkaew et al., 2011; Kim et al., 2007) focused on the analysis of TrOCs in the aqueous phase alone and therefore the removal via adsorption to biomass versus removal via biotransformation was not distinguished. A few recent studies have investigated the contribution of different removal mechanisms to the overall removal of TrOCs though MBR treatment (Kim et al., 2014; Trinh et al., 2016). However, seasonal effects on these removal mechanisms were not addressed. Both biotransformation and adsorption processes are temperature dependent and for most compounds, sorption increases with decreasing temperature (ten Hulscher and Cornelissen, 1996), and biotransformation efficiency reduces at lower temperature (Cirja et al., 2008), thus seasonal variations are expected to affect the removal mechanisms of TrOCs by MBRs. Understanding these effects is important for proper operation, risk assessment and management for MBR systems in water reuse schemes.

Accordingly, this paper presents a study on the fate and removal of 40 TrOCs through a full-scale package MBR plant under normal operating conditions during winter and summer seasons. This research is novel because this investigation was undertaken at a full-scale package MBR plant treating real municipal wastewater, and both the aqueous (influent and effluent) and the biomass samples were analysed during the two seasons. A full mass balance was calculated to estimate the contribution of biotransformation and adsorption to biomass to the overall removal of the trace chemicals by the MBR in these two sampling events. Key monitoring parameters such as pH, dissolved organic carbon (DOC) and total nitrogen (TN) were also investigated to provide information about general treatment process performance.

2. Materials and methods

2.1. Description of the package MBR

Samples were collected from a full-scale package MBR plant (with a capacity of 800 equivalent persons) located in Bega Valley, New South Wales (NSW), Australia. The treatment process was comprised of a fine screen (3 mm), a bioreactor tank, two parallel-submerged microfiltration membrane modules and a medium pressure ultraviolet (UV) disinfection unit. The sludge retention time (SRT) of the bioreactor was 10–15 days, the hydraulic retention time (HRT) was 1 day and the mixed liquor suspended solids (MLSS) concentration was 7.5–8.5 $g \cdot L^{-1}$. The bioreactor tank was intermittently aerated in 10 minute cycles (dissolved oxygen set-point of 1 $mg \cdot L^{-1}$) to achieve simultaneous nitrification and denitrification. The submerged membrane modules were made of hollow fibre membranes (Koch Puron), which have an effective pore size of 0.1–0.2 μm. For cleaning, scour air was applied to the membranes using a positive displacement blower and backwashing occurred every 360 s for a period of 60 s. Chemical backwashing occurred automatically every three weeks, in accordance with the manufacturer's recommendations, to maintain a transmembrane pressure of <20 kPa. The membrane unit was designed to achieve an average flux of 25 $L \cdot m^{-2} \cdot h$. All of the final permeate was used for irrigation. The package MBR plant was described in more details in previous publications (Trinh et al., 2012a; Trinh et al., 2012b).

2.2. Sample collection

Daily time proportional composite aqueous samples of influent (0.5 L), MBR permeate (1 L), and grab samples of mixed liquor (0.5 L) were taken in triplicates over a 5-day-period in winter 2010 and a 5-day-period in summer 2011, giving a total of 30 influent samples, 30 permeate samples and 30 mixed liquor samples. The winter sampling was undertaken when temperature in the bioreactor was in the lowest range (15 ± 1 °C) and the summer sampling was undertaken when temperature in the bioreactor was in the highest range (24 ± 1 °C) of the bioreactor temperature profile during 2010 and 2011.

2.3. Sample preparation and analysis

After collection, the mixed liquor samples were immediately filtered through 0.7 μm Millipore glass fibre prefilters and the solid biomass was stored in 60 mL plastic containers. These samples were then frozen, freeze-dried and extracted following the procedure reported in previous publications (Coleman et al., 2009; Trinh et al., 2011a). The influent samples were also immediately filtered through 0.7 μm Millipore glass fibre prefilters. All aqueous samples including filtered influent and permeate were then spiked with isotopically labelled standards of TrOCs of interest for accurate isotope dilution quantification. These aqueous samples were extracted onsite using solid phase extraction (SPE). The SPE procedure was previously reported (Trinh et al., 2011a).

TrOCs of interest in this study include 7 steroidal estrogens (17α-estradiol, 17β-estradiol, estrone, estriol, 17α-ethynylestradiol, levonorgestrel, mestranol), 5 androgens (testosterone, etiocholanolone, androstenedione, androsterone, dihydrotestosterone), 3 xeno-estrogens (bisphenol A, 4-nonylphenol, propylparaben), 2 pesticides (atrazine, linuron) and 23 PPCPs (atenolol, atorvastatin, *o*-hydroxyatorvastatin, *p*-hydroxyatorvastatin, caffeine, *N,N*-diethyl-*meta*-toluamide (DEET), diclofenac, dilatin, enalapril, hydroxyzine, ibuprofen, ketoprofen, meprobamate, naproxen, paracetamol, risperidone, simvastatin, simvastatin hydroxy acid, sulfamethoxazole, triamterene, triclocarban, triclosan, and trimethoprim). These TrOCs were selected considering the following factors: their potential adverse impacts to human health and the environment (Farré et al., 2008; Jury et al., 2011), their high annual consumption in Australia (Khan and Ongerth, 2004), their diversity in terms of physio-chemical characteristics (e.g., neutral, acidic, ionic, hydrophobic and hydrophilic), and the analytical capability of the laboratory. Concentrations of TrOCs were determined using previously reported liquid chromatography tandem mass spectrometry (LC–MS/MS) (Trinh et al., 2012a; Vanderford and Snyder, 2006) and gas chromatography tandem mass spectrometry (GC–MS/MS) methods (Trinh et al., 2011b). A summary of these analytical methods is presented in the Supplementary Information section. The source/use of TrOCs of concern is also presented in Table S1 of the Supplementary Information section. LOQs for permeate samples were 10 $ng.L^{-1}$ for bisphenol A, 7.5 $ng.L^{-1}$ for dihydrotestosterone and in the range of 0.4 to 5.0 $ng \cdot L^{-1}$ for other chemicals. LOQs for biomass samples (in $ng \cdot g^{-1}$ dried biomass) and influent samples (in $ng \cdot L^{-1}$) were twice as high than LOQs of permeate samples. The detailed LOQs of all chemicals are presented in Table S2 of the Supplementary information section.

2.4. Mass balance calculation

As discussed in the Introduction section, given the physico-chemical properties of the TrOCs and the characteristics of the microfiltration membrane in this study, biotransformation and adsorption to biomass are the two most important removal mechanisms for the chemicals by the MBR, and other removal pathways are considered as negligible. Therefore, the concentrations of TrOCs in influent, MBR permeate and biomass were used together with the aqueous and biomass flow data to establish a mass balance for the fate of each chemical. The equations

for mass balance calculation including equations for the percentage over-all removal and the percentage removal via adsorption to biomass were reported in previous publications (Trinh et al., 2016; Trinh et al., 2011a). The percentage removal via biotransformation was equalled to the per-centage overall removal minus the percentage removal via adsorption to biomass. When the concentrations of the TrOCs in permeate or in bio-mass were under the LOQs, the LOQ values were used to calculate the mass balance and the results were noted as less than values presented.

3. Results and discussion

3.1. Basic water quality parameters

In order to provide information about general treatment process performance, key monitoring parameters such as pH, DOC and TN were also analysed in addition to TrOCs analysis. In general, the pH, DOC and TN data between the summer and the winter samplings were comparable. Permeate pH was around 8. The DOC and TN removal efficiencies were consistently high (≥90%) in both seasons. The results were consistent with a previous study which found that seasonal varia-tions did not affect the COD concentration within the MBR permeate (Arevalo et al., 2014).

3.2. Concentrations of TrOCs in the influent

Concentrations of TrOCs of concern in the influent are presented in Fig. 1. The chemicals were arranged from lower log D_{pH8} (distribution coefficient) to higher log D_{pH8} in the graph. Log D_{pH8} is the log K_{ow} value (partition coefficient) corrected for ionisation at pH 8. Among the analytes, 14 TrOCs including atrazine, dilantin, enalapril, 17α-ethinylestradiol, hydroxyzine, levonorgestrel, linuron, mestranol, mepro-bamate, 4-nonylphenol, simvastatin, simvastatin hydroxy acid, triamterene and risperidone were not detected above their LOQs in the influent, either during winter or summer samplings, so these chemicals were not included in Fig 1. Results from Fig. 1 show that in general the in-fluent concentrations of most of the TrOCs including atenolol, caffeine, paracetamol, naproxen, ibuprofen, diclofenac, estriol, androstenedione, estrone, bisphenol A, etiocholanolone, dihydrotestosterone, androster-one, 17β-estradiol, and triclocarban during the summer were similar to the concentrations observed during winter. 17α-Estradiol was only de-tected in the influent during the summer sampling at a mean

concentration of 5 ng·L^{-1}. The concentrations of propylparaben, DEET and trimethoprim during the summer sampling were half to one log higher than during the winter sampling. Considering the relatively con-stant influent flow rates during the two sampling events, these variations may be due to higher usage of products containing these chemicals in the summer. Previous studies in Switzerland reported that the seasonal loads of antibiotics in wastewater treatment plants (WWTPs) generally corre-late to their distinct seasonal consumption (Göbel et al., 2005; McArdell et al., 2003). The antibiotic sulfamethoxazole was only detected in the in-fluent during the winter sampling at a mean concentration of 596 ng·L^{-1} while trimethoprim was detected in both sampling events. This is per-haps surprising as sulfamethoxazole often administered together with tri-methoprim at a ratio of 5:1 (Göbel et al., 2005). The reason for such a large variation in sulfamethoxazole concentration in the influent is unknown but may be due to transformation between sulfamethoxazole and its ex-creted metabolites in wastewater. The main human metabolite, N^4-acetylsulfamethoxazole, has been found to account for up to 86% of the total load in raw sewage (Göbel et al., 2005; Zhang et al., 2015).

There were no rain events during the sampling periods in this study, thus the impact of dilution by stormwater run-off on concentrations of TrOCs in the influent wastewater was not evaluated. However, the im-pact of dilution by stormwater on concentrations of TrOCs in the influ-ent wastewater could be observed elsewhere. In a previous study in Switzerland, the influent concentrations of ketoprofen, ibuprofen and diclofenac in a winter sampling with long raining period were found to be lower than in previous winter and summer samplings with dry weather. This is possibly due to dilution during wet weather events as the studied WWTPs have combined sewer systems and the flowrate during the raining period was sometimes up to 3 times higher than in the dry period (Tauxe-Wuersch et al., 2005). Another study in the United Kingdom also found that the concentrations of a wide range of PPCPs in the influent wastewater were doubled when the influent flow was reduced by 50% during the dry season (Kasprzyk-Hordern et al., 2009). Similarly, dilution due to precipitation was hypothesised as a cause for lower TrOCs concentration in influent to WWTPs in Turkey and China during wet seasons (Sari et al., 2014; Sun et al., 2014).

In general, the detected concentrations of TrOCs were comparable with previous Australian studies (Le-Minh et al., 2010; Trinh et al., 2016; Leusch et al., 2014; Ying et al., 2008). The day-to-day variability in influent concentrations of TrOCs in this WWTP was generally higher than in a previous study at a larger WWTP in NSW (Trinh et al., 2016).
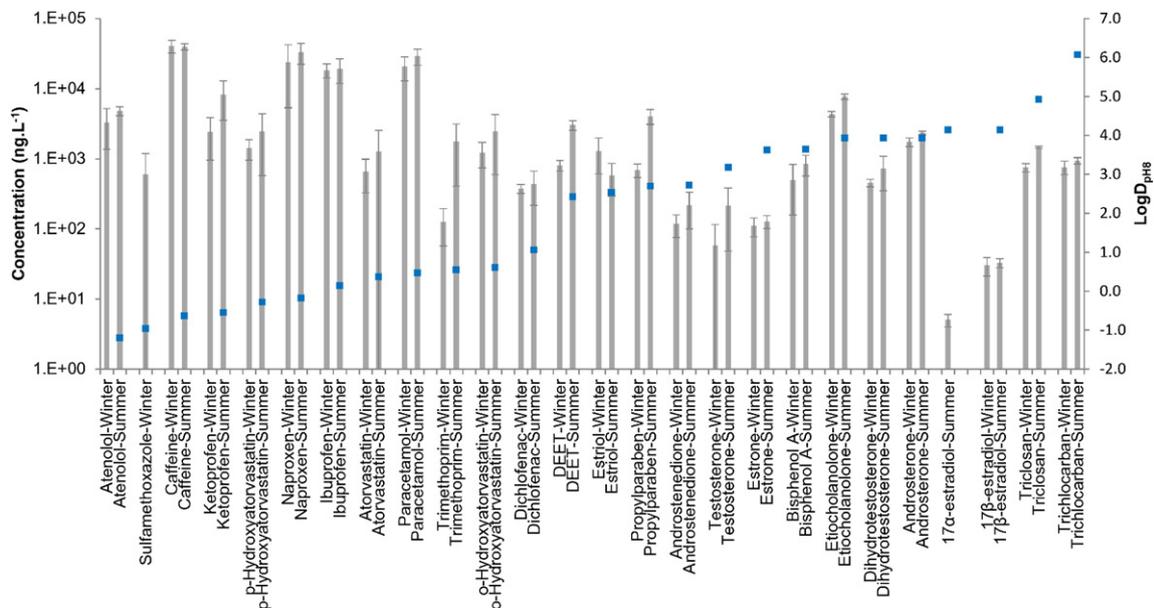

Fig. 1. Concentrations of TrOCs in the influent during different seasons (17α-estradiol and sulfamethoxazole were not detected above its LOQ during the winter sampling).

This result was expected as this WWTP received wastewater from a much smaller catchment (800 equivalent persons) compared to the WWTP in the previous study (500,000 equivalent persons). Previous studies suggest that smaller decentralised sewage catchments exhibit considerably more influent variability in TrOCs concentrations than larger centralised sewage catchments (Teerlink et al., 2012).

3.3. Fate of TrOCs through the MBR

3.3.1. Hydrophilic chemicals

The fate of hydrophilic TrOCs (log $D_{pH8} < 3$) including the percentage remaining in the permeate, the percentage removed via biotransformation and the percentage removed via adsorption to biomass relative to the influent during summer and winter is presented in Fig. 2. Pattern fill with dots denote values calculated from the LOQs when the concentration in biomass and/or permeate was below the LOQs, so the percentage removal by the corresponding mechanism was below the values presented.

Sulfamethoxazole was only detected in the winter sampling with the overall removal efficiency of 62%, and the percentage removed via biotransformation of 59%, indicating that biotransformation was a dominant removal mechanism for this compound. A similar overall removal efficiency of sulfamethoxazole was reported in an MBR operated at the same SRT (15 days), while a higher percentage removal up to nearly 80% was observed when the MBR was operated at SRT ≥ 30 days (Xia et al., 2015). Shorter SRT was reported to lead to a reduction in abundance of bacteria species having the ability to degrade sulphur containing compounds which was hypothesised as a cause for lower removal efficiency of sulfamethoxazole (Xia et al., 2012). Previous MBR studies also concluded that biotransformation is the main removal mechanism for sulfamethoxazole and that adsorption of this chemical to biomass was negligible (Xia et al., 2012; Göbel et al., 2007).

Results from Fig. 2 also revealed that in general, the overall removal efficiencies of most of hydrophilic chemicals including caffeine, ketoprofen, paracetamol, atorvastatin, *o*-hydroxyatorvastatin, *p*-hydroxyatorvastatin, naproxen, ibuprofen, DEET, estriol, propylparaben, androstenedione by the MBR were always above 92% and comparable between the winter and the summer sampling periods. Previous MBR studies also reported similar high overall removal efficiencies (92–100%) for caffeine, ketoprofen, paracetamol, atorvastatin, naproxen, ibuprofen, DEET, estriol and propylparaben (Kim et al., 2014; Trinh et al., 2016; Radjenovic

et al., 2007; Sui et al., 2011; Phan et al., 2015; Komesli et al., 2015). The high removal efficiencies noted here can be attributed to the high SRT and MLSS concentrations in MBRs (Chen et al., 2008; Clara et al., 2005; Fernandez-Fontaina et al., 2013). The percentage removals via adsorption to biomass of the hydrophilic chemicals including caffeine, ketoprofen, paracetamol, atorvastatin, *o*-hydroxyatorvastatin, *p*-hydroxyatorvastatin, naproxen, ibuprofen, DEET, estriol, propylparaben and androstenedione were consistently below 4% in both sampling events. Literature on the contribution of adsorption to biomass to the overall removal of these chemicals by MBRs is very limited. A few recent studies reported that the percentage removals by adsorption to biomass of caffeine, ketoprofen, paracetamol, atorvastatin, naproxen, ibuprofen, estriol and propylparaben by MBR processes varied from 0 to less than 4% (Kim et al., 2014; Trinh et al., 2016). No literature on percentage removal via adsorption to biomass of *o*-hydroxyatorvastatin, *p*-hydroxyatorvastatin, DEET and androstenedione was identified. However, based on the hydrophilicity of these chemicals, insignificant adsorption to biomass was expected for these compounds. The consistently high overall removal efficiencies and high percentage removals via biotransformation of caffeine, ketoprofen, paracetamol, atorvastatin, *o*-hydroxyatorvastatin, *p*-hydroxyatorvastatin, naproxen, ibuprofen, DEET, estriol, propylparaben and androstenedione during the two sampling seasons suggest that these chemicals were transformed by microorganisms that were not subject to temperature changes within the studied range (14–25 °C). These are hydrophilic chemicals so their removals via adsorption to biomass were negligible and not affected by seasonal temperature variations.

Diclofenac was only partially removed by the MBR with the overall removal efficiency during the winter and the summer samplings of 48% and 49%, respectively. The percentage removed via adsorption to biomass of this chemical was 7% in winter sampling and 8% in summer sampling. This partial removal of diclofenac was expected as it has been identified as a rather persistent compound through biological treatment processes (Fernandez-Fontaina et al., 2013). Literature reported a great discrepancy in removal efficiency of diclofenac by MBRs, ranging from 0 to 87%. This variation reported in literature was attributed to different SRTs applied (Radjenovic et al., 2007; Clara et al., 2005; Radjenovic et al., 2009).

In contrast to the other hydrophilic chemicals, the overall removal of trimethoprim in winter (34%) was consistently lower than in summer (91%). The permeate concentration of trimethoprim in both sampling events was similar while the influent concentration during the summer
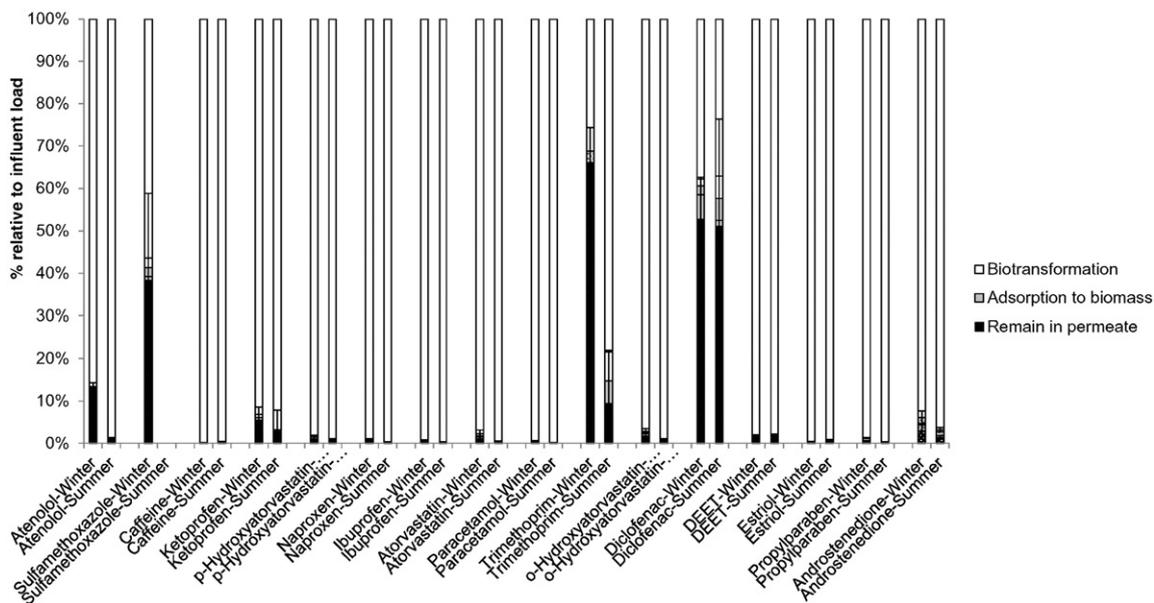

Fig. 2. Fate of hydrophilic TrOCs (log $D_{pH8} < 3$) through MBR treatment (pattern fill with dots denote values calculated from LOQs when the concentrations in biomass and/or permeate were below LOQs, so the percentage removal by the corresponding mechanism was below the values presented; Sulfamethoxazole was not detected above its LOQ in the summer sampling).

sampling was about one log higher than during the winter sampling. This yielded significant higher removal efficiencies for this chemical in the summer. The low percentage removal via adsorption to biomass of trimethoprim (3–5%) in both sampling events was comparable to previous findings (Kim et al., 2014) demonstrating that this removal pathway is insignificant for this chemical.

The temperature difference in the MBR between the winter and the summer samplings in this study was approximately 9 °C (15 ± 1 °C vs. 24 ± 1 °C). In other areas where temperature in winter and summer are more extreme, impacts of temperature changes on removal efficiencies of TrOCs could be larger. A previous study from a WWTP in Finland reported that average removal efficiencies of bezafibrate, ketoprofen, ibuprofen, diclofenac and naproxen increased from 61% to 88% when temperature increased from 7 °C in winter to 21 °C in summer (Vieno et al., 2005). Another study in Turkey reported that the removal of diclofenac through a biological treatment unit for a plant operated at SRT of 10 days was reduced from 66% in summer to 33% in winter when temperature reached 5 °C. For the plant operated at SRT of 20 days, diclofenac removal efficiency decreased from 58% in summer to 50% in winter (Sari et al., 2014).

3.3.2. Hydrophobic chemicals

The fate of hydrophobic TrOCs (log $D_{pH8} > 3$) including the percentage remaining in permeate, the percentage removed via biotransformation and the percentage removed via adsorption to biomass relative to the influent during summer and winter is presented in Fig. 3. Similar to Fig. 2, pattern fill with dots denote values calculated from the LOQs when the concentration in biomass and/or permeate was below the LOQs, so the percentage removal by the corresponding mechanism was below the values presented. 17α-Estradiol was only detected during the summer sampling with the overall removal efficiency of 90%. The percentage removal via biotransformation was 78%, indicating that biotransformation was a dominant removal mechanism for this compound. Results from Fig. 3 show that the mean overall removal efficiencies of the hydrophobic chemicals including testosterone, estrone, bisphenol A, etiocholanolone, dihydrotestosterone, androsterone, 17α-estradiol, 17β-estradiol and triclosan varied from 90% to nearly 100% during the sampling events. These high removal efficiencies were in good agreement with the findings from previous MBR studies, in which similar high overall removal efficiencies (91–100%) for testosterone, estrone, bisphenol A, etiocholanolone, androsterone, 17β-estradiol, triclosan were also reported (Trinh et al., 2016; Cases et al., 2011).

In general, the overall mean removal efficiencies of the hydrophobic chemicals by the MBR in the summer and the winter samplings were comparable. However, the contribution of biotransformation and adsorption to biomass to the overall removal efficiencies of estrone, bisphenol A, 17β-estradiol and triclosan were consistently different between the summer and the winter sampling periods. The percentage removals attributed to biotransformation of these hydrophobic chemicals during summer were considerably (8–62%) higher than in winter. The exact mechanism for this is unknown but may be attributed to an increase in the abundance of specific microorganisms responsible for the biotransformation of these TrOCs, and/or an increase in microbial activity due to warmer temperatures in accordance with Arrhenius law. There are about 300 different species of microorganisms, presents in biological treatment processes treating municipal wastewater (Vieno and Sillanpää, 2014). Literature on the microorganism species that are responsible for degrading specific TrOC in biological wastewater treatment processes is very limited and requires further research. However, as an example, antibiotics have been found to be widely degraded by antibiotic-resistant bacteria such as Firmicutes sp., Aeromonas sp. and Nitrospira sp. (Xia et al., 2015). More specifically, the bacteria Thiothrix sp. and Arenimonas sp. were believed to play an important role in degrading sulphur-based and penicillin antibiotics (Xia et al., 2012).

The observed higher percentage removals via biotransformation of estrone, bisphenol A, 17β-estradiol and triclosan in the summer were in agreement with results from a previous study which reported that the biodegradation of 17β-estradiol in WWTPs increased significantly when the temperature had increased by 15 °C (Layton et al., 2000). In general, microbial activity in biological processes was found to be enhanced with increasing temperature (Cirja et al., 2008). Literature reported that in the mesophilic temperature range (4–39 °C), the rate of the biological reaction in most aerobic waste treatment systems will increase with temperature to a maximum value at 31 °C (Eckenfelder, 2000). Higher temperature in the summer sampling in this study may enhance microbial activity and/or abundancy of microbial groups responsible for the biotransformation of these hydrophobic chemicals, leading to higher percentage removal via biotransformation. In contrast to the removals achieved via biotransformation, the percentage removals attributed to adsorption to biomass of estrone, bisphenol A, 17β-estradiol and triclosan in the summer sampling were consistently (7–62%) lower than that in winter. This observation may be attributed to two reasons. The first is the possible reduction in adsorption efficiency of these hydrophobic chemicals to biomass in the summer sampling
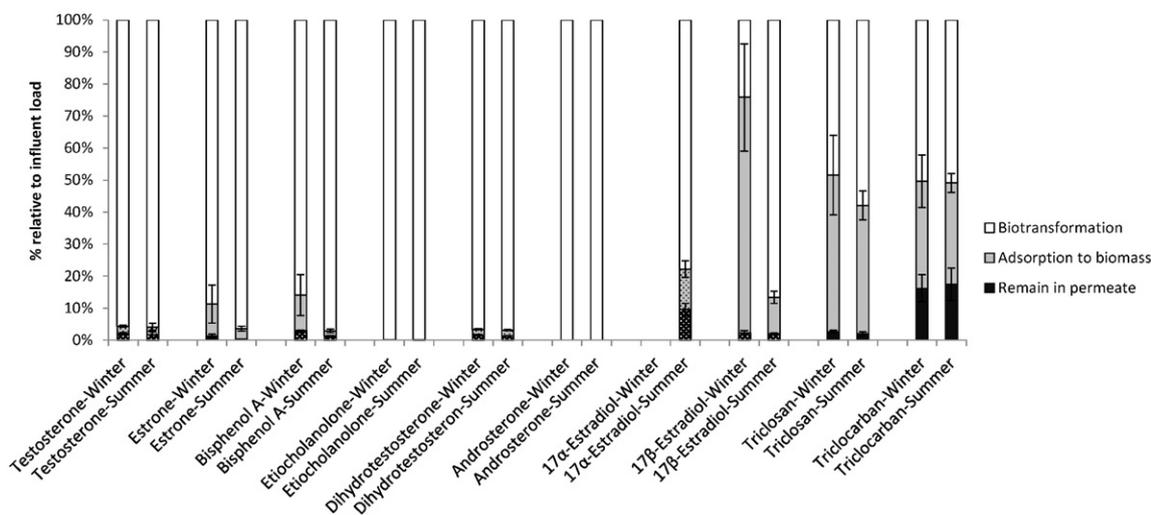

Fig. 3. Fate of hydrophobic TrOCs (log $D_{pH8} > 3$) through MBR treatment (pattern fill with dots denote values calculated from the LOQs when the concentrations in biomass and/or permeate were below the LOQs, so the percentage removal by the corresponding mechanism was below the values presented; 17α-estradiol was not detected above the LOQs in any influent samples during the winter sampling).

as equilibrium sorption of most compounds was reported to decrease with increasing temperature (ten Hulscher and Cornelissen, 1996; Alidina et al., 2014). This was supported by another study which reported that the adsorption of TrOCs to suspended solids in raw sewage was significantly reduced when temperature increased (Cirja et al., 2008; Lindberg et al., 2006; Golet et al., 2003). The second reason is the possible enhancement of biotransformation of these hydrophobic chemicals due to higher temperature in the summer sampling, thus the fraction of hydrophobic chemicals adsorbed to the biomass was transformed quickly and low concentration was remained in the biomass.

For other hydrophobic chemicals including testosterone, etiocholanolone, dihydrotestosterone, androsterone and androstenedione, in both sampling events, the overall removal efficiencies of these chemicals were always higher than 98%, and the percentage removals via adsorption to biomass of these chemicals were consistently below 3%, indicating biotransformation is the dominant removal mechanism for these compounds. Similar observations have been reported in literature (Trinh et al., 2016).

The hydrophobic chemical triclocarban was consistently adsorbed to the biomass during both summer and winter which contributed to 32% and 34% removal, respectively. Similarly, triclosan also adsorbed well to biomass with percentage removal via adsorption to biomass in summer and winter measured to be 40% and 49%, respectively. Previous studies have also shown that sorption to biomass was the main mechanism responsible for the removal of triclosan and triclocarban during wastewater treatment (Coleman et al., 2009; Heidler et al., 2006). Literature data revealed that triclosan was quickly sorbed onto biomass followed by biotransformaton of sorbed triclosan (Stasinakis et al., 2007). In contrast, another MBR study reported that triclocarban and triclosan were not biotransformed but mainly removed via adsorption to biomass. This contradictory result may be due to shorter SRT (6–8 days) applied in the study (Kim et al., 2014).

The MLSS concentration within the bioreactor of the MBR plant was 1 g.L^{-1} higher in summer than in winter. A similar result was reported in a previous MBR study, where the MLSS concentration had decreased from 10 g·L^{-1} at 22 °C to 8 g·L^{-1} at 13 °C, at the same SRT (Zhang et al., 2014). The difference in MLSS concentration may affect the removal mechanisms of the TrOCs as the MLSS concentration determines the loading rate (i.e. the food/mass ratio). Under lower loads, the microbial community may broaden their enzymatic activities, resulting in the biotransformation of a broader range of TrOCs (Cirja et al., 2008; Hai et al., 2014; Ternes et al., 2004).

In this study, the TrOCs in Figs. 2 and 3 were arranged from lower logD$_{pH8}$ to higher logD$_{pH8}$ values to check if there was any noticeable correlation between hydrophilicity/hydrophobicity of the chemicals and the seasonal changes in fate and removal of these chemicals through the MBR. However, no obvious trend was observed. Hydrophilicity/hydrophobicity of the chemicals is an important but not the only dominant factor that affects the fate and removal of TrOCs through the MBR. Biotransformability of the TrOCs is another potential crucial influencing factor. Unfortunately, the biotransformation rate constants (K$_{biol}$) were not available for all the investigated TrOCs, so no comprehensive conclusion about the impact of this factor on seasonal changes in fate and removal of these chemicals through the MBR was able to be elucidated. The available K$_{biol}$ values from previous MBR studies suggest that hydrophilic chemicals having K$_{biol}$ > 1 L·gMLSS^{-1}·d^{-1} such as ibuprofen and paracetamol (Fernandez-Fontaina et al., 2013; Joss et al., 2006; Abegglen et al., 2009) consistently showed high percentage removal by biotransformation through the MBRs in both sampling events. High removal of estrone which is a hydrophobic chemical with K$_{biol}$ > 20 L·gMLSS^{-1}·d^{-1} were also consistently achieved during both sampling events. However, the contribution of biotransformation and adsorption to biomass to the total removal performance of this chemical varied between the two seasons as discussed above. Hydrophilic chemicals which have a K$_{biol}$ ≤ 0.4 L·gMLSS^{-1}·d^{-1} such as sulfamethoxazole, trimethoprim, and diclofenac generally displayed poor

removal by biotransformation as well as poor total removal by the MBR (Fernandez-Fontaina et al., 2013; Joss et al., 2006; Abegglen et al., 2009). Results from a previous CAS study showed that the impacts of temperature variation on overall removal of TrOCs with moderate to low K$_{biol}$ were greater than that of TrOCs with high K$_{biol}$ (Suárez et al., 2012).

The impact of wet weather events on removal of TrOCs by the MBR plant was not assessed in this study as there was no rain event during the sampling periods. However, previous studies have shown that wet weather events not only diluted TrOCs concentrations in influent wastewater but also led to lower removal efficiency of these chemicals by CAS processes (Tauxe-Wuersch et al., 2005; Kasprzyk-Hordern et al., 2009). It was hypothesised that high influent flowrate due to stormwater led to low HRT, resulting in low removal efficiency for these TrOCs (Tauxe-Wuersch et al., 2005). Since the biological process of MBRs is directly analogous to that of CAS systems, similar impact on MBRs is expected. However, the level of impact may be smaller in MBRs as this process can withstand lower HRT compared to CAS systems.

3.4. Concentrations of TrOCs in MBR permeate and Australian guideline values

The maximum concentrations of TrOCs in the MBR permeate were compared with the Australian guideline values for augmentation of drinking water supplies (National Health and Medical Research Council/Environmental Protection and Heritage Council/Natural Resource Management Ministerial Council, 2008) as presented in Table 1. The guidelines have been developed from available health and toxicological information to provide a framework to manage public health risks associated with the implementation of recycled water schemes (National Health and Medical Research Council/Environmental Protection and Heritage Council/Natural Resource Management Ministerial Council, 2008).

Estrone was the only steroidal hormone detected in the MBR permeate at a maximum concentration of 1.8 ng·L^{-1} which was one order of magnitude lower than the Australian guideline value of 30 ng·L^{-1}. Other steroidal hormones and xeno-estrogens including 17α-estradiol, 17β-estradiol, estriol, testosterone, bisphenol A and propylparaben were not detected above the LOQs in the MBR permeate and their LOQs were 1 to 4 orders of magnitudes lower than the Australian guideline values. The guideline values for testosterone metabolites dihydrotestosterone, etiocholanolone, androsterone, androstenedione were not available but are expected to be in a similar range with the guideline value of 7 × 10^3 ng·L^{-1} for testosterone, which was 3 to 4 orders of magnitudes higher than their LOQs.

Triclosan and caffeine were detected at a maximum concentration of 166 ng·L^{-1} and 339 ng·L^{-1}, which were lower than the guideline value of 350 ng·L^{-1} for these chemicals. The guideline value for atenolol is not available but is expected to be in the same range (350 to 40 × 10^3 ng·L^{-1}) with guideline values for other β-blockers which is higher than maximum concentration detected in the MBR permeate in this study. The concentrations of other TrOCs in the MBR permeate were 1 to 5 orders of magnitude lower than Australian guideline values for potable water recycling. The results show that the package MBR plant was consistently removed the TrOCs effectively regardless of seasonal variations, which suggest that MBRs are an effective barrier for the removal of TrOCs.

4. Conclusion

This study investigates the fate and removal of a wide range of TrOCs (steroidal hormones, xeno-estrogens, pesticides and PPCPs) through a full-scale package MBR plant during both summer and winter seasons. The observed trends were justified by systematically comparing with a large number of related references. Substantially higher percentage removal via biotransformation and significantly lower percentage

Table 1
Maximum concentrations of TrOCs in MBR permeate in the current study and Australian guideline values for water recycling ("<" indicates below LOQ).

Chemical	Concentration (ng·L^{-1})	
	MBR permeate	Australian guideline values (National Health and Medical Research Council, 2008)
Steroidal hormones and xenoestrogens		
17α-Estradiol	<0.5	175
17β-Estradiol	<0.7	175
Estrone	1.8	30
Estriol	<1.5	50
Testosterone	<3.0	700×10^1
Dihydrotestosterone	<7.5	Not available, but expected in similar range with testosterone
Etiocholanolone	<3.2	Not available, but expected in similar range with testosterone
Androsterone	<0.7	Not available, but expected in similar range with testosterone
Androstendione	<2.8	Not available, but expected in similar range with testosterone
Bisphenol A	<10	200×10^3
Propylparaben	<5.0	Not available
PPCPs		
Atenolol	337	Not available, but values for other β-blockers are from 350 to 40×10^3
Sulfamethoxazole	140	350×10^2
Caffeine	339	350
Ketoprofen	182	350×10^1
Paracetamol	35	180×10^3
Atorvastatin	9	500×10^1
o-Hydroxyatorvastatin	25	Not available, but expected in similar range with atorvastatin
p-Hydroxyatorvastatin	24	Not available, but expected in similar range with atorvastatin
Naproxen	248	220×10^3
Ibuprofen	115	400×10^3
Trimethoprim	146	700×10^2
Diclofenac	353	180×10^1
DEET	445	250×10^4
Triclocarban	50	Not available
Triclosan	166	350

removal via adsorption to biomass was observed for 17β-estradiol, estrone, bisphenol A and triclosan during summer sampling. The exact mechanisms for this is unknown but may include an increase in abundance of specific microorganisms responsible for biotransformation of these TrOCs, and/or faster chemical transformation following Arrhenius law, and lower sorption efficiency of these chemicals to biomass at higher temperature. Synergistic MBR removal mechanisms resulted in overall TrOC removal resilient to the seasonal variations observed in this study. The study enhances our understanding on the seasonal variations in fate and removals of the TrOCs though MBR processes and could facilitate better risk assessment and management for MBRs in water reuse schemes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.083.

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