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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.

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

Abbreviations: MBRs, membrane bioreactors; CAS, conventional activated sludge; TrOCs, trace organic chemicals; PPCPs, pharmaceuticals and personal care products; DOC, dissolved organic carbon; TN, total nitrogen; NSW, New South Wales; UV, ultraviolet; SRT, solid retention time; HRT, hydraulic retention time; MLSS, mixed liquor suspended solid; SPE, solid phase extraction; DEET, *N,N*-diethyl-*meta*-toluamide; LC–MS/MS, liquid chromatography–tandem mass spectrometry; GC-MS/MS, gas chromatography - tandem mass spectrometry; LOQs, limit of quantifications; WWTP, wastewater treatment plant; Kbiol, biotransformation rate constant.

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(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 xenoestrogens (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