Removal and fate of emerging organic micropollutants (EOMs) in municipal wastewater by a pilot-scale membrane bioreactor (MBR) treatment under varying solid retention times

Gurung Khum, Ncibi Mohamed Chaker, Sillanpää Mika

DOI: 10.1016/j.scitotenv.2019.02.308

Accepted Manuscript

Removal and fate of emerging organic micropollutants (EOMs) in municipal wastewater by a pilot-scale membrane bioreactor (MBR) treatment under varying solid retention times

Khum Gurung, Mohamed Chaker Ncibi, Mika Sillanpää

PII: S0048-9697(19)30811-3
DOI: https://doi.org/10.1016/j.scitotenv.2019.02.308
Reference: STOTEN 31054

To appear in: *Science of the Total Environment*

Received date: 29 December 2018
Revised date: 13 February 2019
Accepted date: 19 February 2019

Please cite this article as: K. Gurung, M.C. Ncibi and M. Sillanpää, Removal and fate of emerging organic micropollutants (EOMs) in municipal wastewater by a pilot-scale membrane bioreactor (MBR) treatment under varying solid retention times, Science of the Total Environment, https://doi.org/10.1016/j.scitotenv.2019.02.308

Removal and Fate of Emerging Organic Micropollutants (EOMs) in Municipal Wastewater by a Pilot-scale Membrane Bioreactor (MBR) Treatment Under Varying Solid Retention Times.

Khum Gurung [a*], Mohamed Chaker Ncibi [a], Mika Sillanpää [a]

[a]Department of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130 Mikkeli, Finland.

[*] Corresponding author. Phone: +358 40 932 0496

E-mail: khumgrg@yahoo.com; mika.sillanpaa@lut.fi

Abstract

This study investigates the removal and fate of 23 emerging organic micropollutants (EOMs) including a wide range of pharmaceuticals (antibiotics, β-blockers, analgesics, diuretics, psychostimulants, antiepileptics, immunosuppressives, anticoagulants), and steroid hormones detected in municipal wastewater by a pilot-scale membrane bioreactor (MBR) plant at two different solid retention times (SRTs) of 60 and 21 days. Different removal efficiencies of the selected EOMs were observed and explained based on their physicochemical properties (such as distribution coefficient, log D; dissociation constant, pK_a; solid-water distribution coefficients, and K_d) along with process operating parameters. The dominant removal mechanisms of EOMs were biotransformation and sorption onto the sludge, which were confirmed by the mass balance study. Moreover, changes in the sludge properties, as a consequence of different SRTs, were evaluated based on variations in soluble microbial products (SMP), extracellular polymeric substances (EPS), and capillary suction time (CST). Finally, the quality of the MBR effluent was compared with some established guidelines, which confirmed the fulfilment of water quality requirements for reuse purposes.

Keywords: Municipal wastewater treatment; Membrane bioreactor; Emerging organic micropollutants ; Biotransformation/biodegradation; Solid retention times

1. Introduction

In recent decades, the occurrence of emerging organic micropollutants (EOMs) in the aquatic environment has received a global attention because of its possible environmental intimidations. Globally, a large number of EOMs have been frequently detected at source, and in treated effluent and wasted sludge at wastewater treatment plants (WWTPs) (Clara et al., 2005b; Trinh et al., 2012, 2016). Moreover, the occurrence of EOMs could endanger the reuse of reclaimed wastewater in achieving sustainable water management within the WWTPs (Behera et al., 2011). Most of the EOMs found in wastewater are of anthropogenic origin from various sources such as households, hospitals, veterinary surgeries, farms and pharmaceutical manufacturing facilities, which eventually end up at WWTPs (Clara et al., 2005b). Since conventional WWTPs are not specifically designed to eliminate EOMs, many of these EOMs pass through WWTPs and are thus eventually discharged into the environment (Behera et al., 2011; Jelic et al., 2011; Miège et al., 2009; Sim et al., 2010; Vieno et al., 2005; Yang et al., 2011, 2017; Ying et al., 2009). Some countries such as Australia and Switzerland have adopted discharge guidelines for some EOMs (NHMRC/EPHC/NRMMC, 2008; Oekotoxzentrum Centre Ecotox, 2016). In the EU context, environmental quality standards (EQS) for 45 priority EOMs including first watch list substances like diclofenac, 17-β-estradiol, and 17-α-ethinylestradiol, were stipulated in Directive 2013/39/EU (EU, 2013), but the majority of other EOMs have not yet been addressed. However, recent amendment in directive 2013/39/EU has introduced more watch list substances, in which diclofenac has removed while macrolide antibiotics, methiocarb, neonicotinoids, metaflumizone, amoxicillin and ciprofloxacin have been added (EU, 2018).

To ensure compliance with future discharge requirements, interest in the ability of MBRs in the removal of EOMs from municipal wastewater has increased in recent decades. MBRs are becoming a mature technology in water management practices for wastewater reclamation and reuse due to their ability to produce superior-quality effluent, a relatively small footprint and little sludge (Judd, 2008; Meng et al., 2009). The removal mechanisms of EOMs involved in MBR treatment are complex and include biotransformation/biodegradation, adsorption to sludge, volatilisation, and physical retention by the membrane (Cirja et al., 2008). However, biotransformation and adsorption to biosolids are often reported to be the dominant mechanisms for the removal of EOMs in the MBR process (Clara et al., 2005b; Kim et al., 2014; Radjenović et al., 2009). On that note, physicochemical properties (such as distribution coefficient, log D; dissociation constant, pK_a; solid-water distribution coefficients, and K_d) and functional groups associated with EOMs showed notable effects on their removal (Li et al., 2015; Tadkaew et al., 2011). At the pH above pK_a, phenolic hydroxyl group of some hormones dissociates that leads to the charge repulsion between the negatively charged hormone and negatively charged membrane (Schäfer et al., 2011). Naproxen and diclofenac (pK_a values of 4.2 and 4.15, respectively) deprotonated a at pH 7-8 and rejected by negatively charged membrane surface, whereas carbamazepine (pK_a = 13.9) showed no ionization at same pH level, hence attained a poor removal (Röhricht et al., 2009). At pH 6-7, tetracyclines (pK_a = 4.5) are not charged, hence removed only via adsorption to sludge (Kim et al., 2005). The sorption onto sludge can considered to be insignificant for EOMs with $\log K_d < 2.48$ (Joss et al., 2006). The overall removal efficienices of most of hydrophilic chemicals (log D < 3.2) were above 92% in the MBR (Trinh et al., 2016).

Often previous studies on the removal of EOMs by MBRs focused on the aqueous phase (Bo et al., 2009; Radjenovic et al., 2007; Schröder et al., 2012; Trinh et al., 2012) and their mass load adsorbed in the solid phase was often neglected, which restricts the differentiation between the removal mechanisms via adsorption onto sludge and biotransformation. There is limited literature investigating the fate of EOMs in MBRs when treating real municipal wastewater (Kim et al., 2014; Radjenović et al., 2009; Trinh et al., 2016). Some researchers have estimated the contributions of the adsorption and biotransformation of EOMs based on values of K_d from literature or by direct batch experiments (Clara et al., 2005b; Kimura et al., 2007). Additionally, previous studies on the fate of EOMs in MBR either mainly focused on pharmaceuticals and personal care products (PPCPs) (Radjenović et al., 2009; Suárez et al., 2012; Tambosi et al., 2010; Trinh et al., 2016) or are based on lab-scale batch experiments (Hai et al., 2018; Phan et al., 2014; Tadkaew et al., 2011; Wijekoon et al., 2013). The influence of solid retention times (SRTs) on the removal mechanisms of PPCPs by MBRs has been studied by a few researchers (Clara et al., 2005b; Schröder et al., 2012; Tambosi et al., 2010), but these studies counted either estimated values of K_d or negligible amounts of adsorbed fractions of PPCPs onto sludge, as well as a spiking of PPCPs in the MBR system.

Based on the above identified research gaps, the current study investigates the removal dynamics of 23 frequently detected EOMs in the treatment of real municipal wastewater at an MBR pilot plant operated at two different SRTs. To the best of our knowledge, the removal and fate of EOMs such as iopamidol, hydrocortisone, furosemide, ciprofloxacin, tetracycline, and enalapril have rarely (or not) been studied in the past by MBR processes. A mass balance study was assessed to further confirm the removal mechanisms associated with different EOMs. Besides, the influence of physicochemical properties on the removal of EOMs was

discussed. Additionally, the influence of SRTs on sludge characteristics including dewaterability, major foulants such as soluble microbial products (SMPs), and extracellular polymeric substances (EPS), was discussed. Finally, the quality of MBR-treated effluent in terms of EOMs was compared with some established guidelines.

2. Materials and methods

2.1 MBR system, operational protocol, selected EOMs and sample collection

A pilot-scale MBR system was employed in this study. The schematic diagram indicating major components of the MBR pilot plant is shown in **Fig. 1**. The key features of the MBR pilot plant is described in our previous work (Gurung et al., 2016). Typically, the submerged flat-sheet membrane units (0.4 μm pore size) with membrane surface area of 16 m^2 (KUBOTA Co., Japan) were used for solid-liquid separation. A permeate pump (Thomas, Germany) was used to draw water in an intermittent suction mode. For in-situ cleaning of membranes, the clean-in-place (CIP) tank was also installed and connected with Sodium hypochlorite and Citric acid dosing tanks. Scouring air was supplied to maintain biological activities and to mitigate membrane fouling. The feed to the MBR pilot plant was taken continuously from the outlet of the primary clarifier at the Kenkäveronniemi WWTP, Mikkeli, Finland. This plant treats about 15,000 m^3 of wastewater per day.

Fig. 1 (Here)

In this study, the pilot plant was operated in two different SRTs of 60 days and 21 days in order to investigate MBR performance in treating the pollution load of nutrients, organics, solids and, preferably, the removal of EOMs. **Table 1** summarises the in-depth operational

conditions of the MBR pilot plant for this study. The pilot plant was operated a protocol similar to that reported by other researchers (Van den Broeck et al., 2012). The SRT of 60 days was adapted more than 10 weeks before the actual sampling periods in order to stabilize the activated sludge. However, relatively less adaption period of sludge (about a week) was maintained for SRT of 21 days by wasting required amount of sludge out of the system. Each of the two different SRTs were maintained for stable sludge period of 4 weeks. During the investigation, the permeation flow rate and the transmembrane pressure (TMP) were nearly constant (4-5 kPa), so no in-situ cleaning of membranes was necessary.

A set of 55 EOMs representing a wide range of pharmaceuticals, pesticide and steroid hormones with diverse physicochemical properties were studied. The selection of these EOMs was made based on their increasing annual consumption, potential adverse impacts on health of human and aquatic animals, and stringent future regulations in the EU Water Framework Directive (EU, 2013) on pharmaceuticals and hormones. The physicochemical properties of studied EOMs are summarised in **Table S1** (Supplementary Information). Weekly 24-hour composite aqueous samples of influent (1 L), MBR permeate (1 L) and grab samples of sludge (0.5 L) were collected for 8 weeks (4 samples of each SRT). The sum total of samples included 8 influent, 8 effluent and 8 sludge samples. All the collected samples including liquid and sludge phases were stored in dark and cold conditions (~ -18 ºC) before the analysis.

Table 1 (Here)

2.2 Mass balance calculation

To assess quantitatively the fate of the EOMs, the percentage shares of biotransformation/ degradation, sorption and remaining in effluent were estimated using a mass balance approach (Jelic et al., 2011). The mass flow rates of EOMs in the influent, effluent and sludge were calculated by multiplying measured concentrations in given streams by the corresponding flow data. Then, mass load lost per unit of time (μg d^{-1}) due to all the processes that possibly occur during the MBR process and their relative distributions to the influent mass load were calculated according to the following equations (1) – (4).

$$\text{Overall removal (\%)} = \frac{(C_{Inf} * Q_{Inf} - C_{Eff} * Q_{Eff})}{C_{Inf} * Q_{Inf}} * 100 \quad (1)$$

$$\text{Removal via sorption onto sludge(\%)} = \frac{C_{Sludge} * Q_{Excess\ sludge}}{C_{Inf} * Q_{Inf}} * 100 \quad (2)$$

$$\text{Remain in effluent (\%)} = \frac{C_{Eff} * Q_{Eff}}{C_{Inf} * Q_{Inf}} * 100 \quad (3)$$

$$\text{Removal via biotransformation(\%)} = \text{Overall removal (\%)} - \text{Removal via sorption onto sludge (\%)} \quad (4)$$

where $C_{Inf} * Q_{Inf}$; $C_{Eff} * Q_{Eff}$; *and* $C_{Sludge} * Q_{Excess\ ludge}$ are the mass flow rate (μg/d) of influent, treated effluent and sludge, respectively. $Q_{Excess\ ludge}$ is excess sludge production (kg d^{-1}).

2.3 Analytical Methods

Chemical oxygen demand (COD), total suspended solids (TSS), ammonium nitrogen (NH_4-N), total nitrogen (TN), total phosphorus (TP), mixed liquor suspended solids (MLSS) and

mixed liquor volatile suspended solids (MLVSS) were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, 1999). The CST of sludge was measured using a capillary suction timer (Type 304M, Triton, UK). The concentrations of EPS and SMP of the sludge were determined by previously described methods (Ramesh et al., 2006). At first, 25 mL of sludge sample was centrifuged at 4,000 rpm at 4°C for 30 min. The supernatant was filtered through a 0.45 μm glass filter and measured for SMP. The obtained pallet was resuspended by adding 0.05% NaCl, mixed with vortex mixture and the solution was kept in a water bath (~100 °C) for heat treatment for 60 min. Finally, the supernatant was filtered through a 0.45 μm glass filter and measured for total EPS. Both SMP and EPS were analysed in term of dissolved organic carbon (DOC) using a TOC analyser (TOC-V Series-CPN, Shimadzu, Japan).

The concentrations of EOMs in influent, permeate and sludge samples were analysed using standard solid phase extraction (SPE) followed by UPLC/MS/MS (modified EPA 1694 and modified EPA 539). The measurement uncertainty (MU) was 40%. The MU % was calculated according to the Nordest TR 537 that covered every step in the laboratory analysis.

3. Results and discussion

3.1 Basic performance of MBR

As real municipal wastewater was fed into the MBR, the influent composition varies over time, and does the pollution removal efficiency. **Table 2** summarises the composition of influent wastewater during each period of SRT and the treatment efficiency of the MBR on conventional pollutions such as COD, NH_4-N, TN, and TP. The fluctuations on influent composition were not significant (**Table 2**). The pH of the effluent was around 7. The removal

efficiencies of TSS, COD and NH_4-N were consistently high (>90%,>99.96%, respectively) at both SRTs. For two SRTs, the suspended solids in the effluent samples were below the limit of quantification (LOQ), showing the excellent physical barrier of the MBR system. The pilot MBR plant was not designed to remove TN, but about 15% of removal on both SRTs was achieved due to a simultaneous nitrification-denitrification environment created by intermittent aeration inside the nitrification tank. A relatively consistent removal of TP was also observed (>87%) on both SRTs due to enhanced biological phosphorus removal (EBPR) in the MBR process. Overall, a good effluent quality was observed at both the SRTs with comparable treatment efficiencies.

Table 2 (Here)

3.2 Occurrence of EOMs in the MBR

The median concentrations of the EOMs detected in the influent of the MBR pilot plant are presented in **Fig. 2**. The concentrations of EOMs in WWTPs depend on several factors such as the consumption pattern of pharmaceuticals, the wastewater influent load etc., which might vary within a region or country and from country to country (Radjenović et al., 2009). Of the 55 EOMs, only 23 compounds were analytically detected in the median range from 23 to 145,000 ng L^{-1} (**Fig. 2**) and the remaining 32 compounds were not detected above their LOQs during the testing of both SRTs (**Table S2**). **Fig. 2** indicates that the occurrences of the majority of EOMs including pharmaceuticals and steroid hormones during the SRT of 60 days showed similar tendencies to those observed during the SRT of 21 days, which is

explained by the fact that all the sampling sessions were performed during the spring season. The median concentrations of the EOMs belonging to anti-coagulants, diuretics, psychostimulants and analgesics categories such as iopamidol (2625 ± 2367 ng L^{-1}), furosemide (1864 ± 91 ng L^{-1}), caffeine (140437 ± 6453 ng L^{-1}), hydrochlorothiazide (2035 ± 757 ng L^{-1}), paracetamol (93600 ± 3394 ng L^{-1}), naproxen (3395 ± 276 ng L^{-1}), ibuprofen (14400 ± 565 ng L^{-1}) and diclofenac (1620 ± 394 ng L^{-1}), respectively were observed at the highest levels during the testing periods. More than 50% of the total EOMs in the influent was accounted for these eight compounds. The high concentrations of caffeine, naproxen and ibuprofen are consistent with previous papers that studied the occurrence and treatment of EOMs in real municipal wastewater (Clara et al., 2005b; Kim et al., 2014; Radjenović et al., 2009; Trinh et al., 2016; Vieno et al., 2005). The observed caffeine concentration is in agreement with previous literature (Kim et al., 2014), and is also about four times higher than the values reported in another study (Trinh et al., 2012). Antibiotics such as tetracycline, ciprofloxacin, and trimethoprim were detected at < 1000 ng L^{-1}, which is very common in municipal wastewater (Guerra et al., 2014). The concentrations of EOMs were arranged from lower to higher log D_{pH7} (distribution coefficient) values of compounds (**Fig. 2)**. The log D_{pH7} is the corrected value of log K_{ow} (partition co-efficient) for ionisation at pH 7 (Trinh et al., 2016). The concentrations of steroid hormones including testosterone, progesterone, estrone, and estroil having log D_{pH7} values > 3, were observed at a consistently low level (23 to 510 ng L^{-1}) during both testing periods.

Fig. 2 (Here)

3.3 Removal of EOMs in MBR treatment

The removal efficiencies of selected EOMs observed during the MBR treatment at two different SRTs (60 days and 21 days) are shown in **Fig. 3a-b**. SRT is a very important operational parameter in MBR processes influencing the removal of EOMs (Clara et al., 2005a; Schröder et al., 2012; Taheran et al., 2016; Tambosi et al., 2010). The concentrations of the majority of the EOMs in the treated effluent were observed to be lower (even < LOQs to many EOMs) than in the influent at both SRTs, indicating the efficient attenuation of EOMs by the MBR, regardless of the changing of the SRTs. In general, increasing SRT can improve the biodiversity of slowly growing bacteria, sludge growth and the longer retention of sludge that favours the removal of EOMs (Kimura et al., 2007; Maeng et al., 2013; Taheran et al., 2016; Tambosi et al., 2010). However, some previous researchers confirmed that the removal of ibuprofen, diclofenac, naproxen, ketoprofen and carbamazepine is not significantly affected by changing SRT during MBR treatment (Li et al., 2015).

Of the selected EOMs in this study, 17 EOMs, including steroid hormones, showed consistent removal of more than 90%. Furthermore, three compounds showed moderate removal between 50% and 87% (metoprolol, furosemide, and propranolol), one showed poor removal of 39-46% (diclofenac), and two (carbamazepine and hydrochlorothiazide) were very poorly removed (almost not at all) (-8 to 10%). Psychostimulant (caffeine) was detected at highest concentration among other EOMs at both SRTs, but efficiently attenuated with a removal efficiency of up to 99.7%. These results are in agreement with many previous works (Kim et al., 2014; Trinh et al., 2016, 2012). An effective attenuation of caffeine is achievable even at a relatively short SRT (Maeng et al., 2013).

Moreover, EOMs including anti-coagulant (iopamidol) and immunosupressive (hydrocortisone), whose fate was studied for the first time in the MBR process, were efficiently removed in the range of 90-96%. Regarding β-blockers, atenolol and bisoprolol were attenuated at consistently high removal efficiency (92 -97%) at both SRTs, whereas two other β-blockers (metoprolol and propranolol) were attenuated slightly higher at a longer SRT of 60 days (82-84%) than in shorter SRT days of 21 (50-60%). Very high removal efficiencies of analgesics (paracetamol, ibuprofen, ketoprofen, naproxen) were observed ranging from 96 to >99.9%. The higher removal of paracetamol is due to its structure that allows unrestricted access of bacteria and enzymes to the sterically unprotected molecule that is then subsequently modified (Tambosi et al., 2010). Moreover, the removal of ibuprofen, ketoprofen and naproxen is partially accompanied by the heterotrophic bacteria community, which is highly favourable in extended SRTs, and less so by slow-growing ammonia-oxidising bacteria (Falås et al., 2012). The higher removal results of analgesics are in agreement with those reported by many researchers (Kim et al., 2014; Radjenović et al., 2009; Schröder et al., 2012; Tambosi et al., 2010). On the other hand, diclofenac (analgesic) was attenuated at relatively low efficiency compared to other analgesics with median removal efficiencies of 38% and 45% at SRTs of 60 days and 21 days, respectively. A great discrepancy in the removal efficiency of diclofenac via MBR was reported in some literature (0 to 87%) (Clara et al., 2005a; Trinh et al., 2016). A slow or non-biotransformation rate of diclofenac has been reported by other researchers (biotransformation rate constant, $K_{biol} < 0.1$ g^{-1} ss d^{-1} in MBR) (Trinh et al., 2016; Vieno and Sillanpää, 2014).

The diuretics (furosemide and enalapril), which were rarely studied in MBRs, were highly attenuated at both the SRTs with median removal efficiencies of 87% and 96%, respectively.

These results are consistent with the previous study (Kim et al., 2014). On the other hand, the attenuation of diuretic (hydrochlorothiazide) was very low or hardly removed at all in this study. During SRT of 21 days, the removal efficiency ranged from -52 % to 13% (median -1 %), which was slightly enhanced at SRT of 60 days achieving removal efficiency between -19% and 41% (median 10%). The comparably poor removal of hydrochlorothiazide (~5%) is reported by other researchers when treating municipal wastewater with full-scale MBR (Radjenović et al., 2009). The increased concentrations of hydrochlorothiazide in treated effluent, more than the influent levels (i.e. negative removal efficiency), might be due to the transformation of metabolites such as unmeasured products of the human metabolism and/or metabolites that could be converted back to their parent compounds during the biological treatment process. This phenomenon of ''negative removal'' was also reported in other studies (Jelic et al., 2011).

The attenuation of an anti-epileptic drug (carbamazepine) was very low and frequently not removed, regardless of varying SRTs. At an SRT of 60 days, the median removal efficiency of carbamazepine was close to 2% (not removed in two samples out of four), whereas non-removal was observed (median – 8 %) at an SRT of 21 days. This means that, in most of the events, effluent concentrations of MBR were greater than influent levels. The major metabolite of carbamazepine in humans is 10,11 epoxy-carbamazepine, which is excreted principally as glucuronide and further to glucuronide-conjugates via the hydroxylation of the aromatic ring. These glucuronide-conjugates can presumably be cleaved in a biological process and so increase in the effluents (Ternes, 1998). The recalcitrant behaviour and non-removal of carbamazepine in MBR treatment due to poor degradability have been reported in many other studies (Clara et al., 2005b; Radjenovic et al., 2007; Wijekoon et al., 2013).

Concerning the removal of antibiotics, consistently high removal efficiencies were achieved at 87 to 98%. Tetracycline, ciprofloxacin and trimethoprim were attenuated at a comparable level at both SRTs with removal efficiencies of 98%, 93%, and 94%, respectively. Comparable results in the removal of tetracycline and ciprofloxacin were reported by Kim et al, which was the only research studied to-date in the MBR process (Kim et al., 2014), where the SRT was kept relatively slow at 6-8 days. This indicates that the removals of tetracycline and ciprofloxacin were not significantly affected by changes in SRTs. Nevertheless, a wide range of removal efficiencies were reported in literature from non-removal to nearly 67% (Kim et al., 2014; Radjenović et al., 2009). Although trimethoprim is often presumed to be recalcitrant to activated sludge bacteria, its poor biotransformation was reported to be achievable by slow-growing bacteria (Radjenović et al., 2009).

The median removal efficiency of steroidal hormones (testosterone, progesterone, estriol, estrone) in the MBR process at both SRTs is presented in **Fig. 3**. Results indicated that steroid hormones were attenuated effectively by the MBR, achieving steady removal efficiency of over 98%. These results are in agreement with other studies performed on MBRs (Maeng et al., 2013; Trinh et al., 2016, 2012).

Fig. 3 (Here)

3.4 Behaviour of EOMs in MBR treatment: application of mass balances

The removal mechanisms of EOMs in MBR treatment form a complex process characterised by four major pathways: (i) biotransformation or degradation; (ii) sorption onto the sludge (via excess sludge removal); (iii) volatilisation or stripping by aeration; and (iv) physical retention due to size exclusion by membranes (Cirja et al., 2008; Li et al., 2015). Since the Henry's law constant (K_H) values of the selected are low ($< 10^{-6}$) (Table **S1**), the removal of these compounds by volatilisation is insignificant. Moreover, the typical molecular weight cut-off (MWCO) of MF and UF membranes are well above several thousand daltons (Da) (Taheran et al., 2016), so the retention of EOMs (MWCO between 200 and 800 Da) in the MBR process cannot be expected due to size exclusion. Therefore, the dominant removal mechanisms of EOMs were presumably via biotransformation and sorption onto the sludge, which was confirmed by the mass balance calculations as shown in **Fig. 4**. The daily mass loads of EOMs via biotransformation, sorption onto sludge and remaining in effluent are interpreted as shared proportions relative to the influent load **(eqs. 1- 5)**.

Among the selected EOMs, the highest significant biotransformation rates (83-99.9%, median 99%) were observed for atenolol, caffeine, paracetamol, naproxen, ibuprofen, estriol and progesterone. Similarly, high biotransformation rate was accounted to iopamidol, furosemide and trimethoprim (58-92%, median 86%). Moderate biotransformation was observed for diclofenac (median 33%). Enhanced biotransformations of metroprolol, hydrochlorothiazide, and propranolol were achieved at SRT of 60 days (78%, 27% and 51%) compared to SRT of 21 days (37%, 0% and 0%, respectively). On the other hand, carbamazepine showed high resistance to biotransformation, so was highly detected in the effluent. The biotransformation

proportions observed for naproxen, ibuprofen, trimethoprim, enalapril, atenolol, metroprolol and furosemide are consistent with previous studies (Jelic et al., 2011; Joss et al., 2006; Kim et al., 2014).

On the other hand, some of the EOMs were observed to be removed via sorption to sludge as indicated in **Fig. 4**. EOMs can be sorbed to sludge and subsequently removed while wasting the excess sludge from the bioreactor. The mechanism of sorption occurs via absorption and adsorption (Li et al., 2015). Absorption occurs due to the hydrophobic interactions of the aliphatic and aromatic groups of EOMs with the liphophilic cell membrane of some microorganisms and the fat fractions of sludge, whereas adsorption involves the electrostatic interactions of the positively charged (e.g., amino groups) to negatively charged surface of microorganisms (Cirja et al., 2008). Most of the EOMs were frequently detected in the sludge under LOQ (10 to 500 ng g^{-1}, median 100 ng g^{-1}) (**Fig S1**). Other EOMs were detected in the range of 38-3,750 ng g^{-1} (median 275 ng g^{-1}) at which ciprofloxacin followed by hydrochloro-thiazide were the highest detected in the sludge. This result is in agreement with a previous study, where ciprofloxacin was most frequently detected in MBR sludge, although the concentration level was considerably higher (> 10^3 ng g^{-1}) (Kim et al., 2014). From the results, ciprofloxacin posed a serious challenge due to very strong affinity to the sludge with a sorption fraction of more than 90%. Relatively higher sorption of ciprofloxacin is reported by many researchers (Kim et al., 2014). Biosorption as a dominant mechanism for the removal of ciprofloxacin is reported by many authors (Githinji et al., 2011; Guerra et al., 2014). Similarly, propranolol, carbamazepine and testosterone showed moderate sorption efficiency to the sludge (10-50%, median 32%), whilst weak sorption affinities were observed for rest of the EOMs (0-21%, median 6%).

In order to better understand the fate of EOMs due to sorption to the sludge, sludge-water distribution coefficients or sorption coefficients (log K_d) were experimentally assessed by dividing the concentration of EOMs in sludge (ng kg^{-1}) by their concentrations in effluent water (ng L^{-1}) (Loke et al., 2002; Radjenović et al., 2009). The corresponding log K_d for high sorption fractions of > 90% and moderate fraction (10-50%) were 3.0 to 4.9 (**Fig. 4**), demonstrating their removal by strong sorption to sludge. These results are comparable with the findings of other researchers (Kim et al., 2014). Nevertheless, many compounds which showed a high degree of removal via biotransformation (e.g. tetracycline, bisoprolol, enalapril, ketoprofen, ibuprofen, hydrocortisone, estriol, estrone and progresterone) accounted for the high log K_d values (3.9 to 4.3), indicating that these EOMs are attenuated simultaneously by biodegradation and partitioning onto biosolids (Guerra et al., 2014). On the other hand, the relatively low value of log K_d (2.6 to 3.0) was calculated for diclofenac, carbamazepine and hydrochlorothiazide, indicating their poor removal efficiencies via sorption. In general, the higher biotransformation of EOMs was followed by lower sorption potential, which was not in accordance with the calculated log K_d. These results suggest that log K_d values may vary plant-to-plant depending on operating conditions and the extent of removal efficiencies (Kim et al., 2014). Indeed, the biotransformation of EOMs is enhanced by the sorption process due to the longer retention time of solids in the MBR process (Tadkaew et al., 2011).

Fig. 4 (Here)

3.5 Other factors influencing the removal of EOMs in MBR

Hyrophphobic interaction is also one of the key mechanisms controlling biosorption of EOMs, hence the removal efficiencies in MBR processes (Cirja et al., 2008). Most of the EOMs quantified in the influent load at both testing periods were hydrophilic (log D_{pH7} < 3.2) (Hai et al., 2018; Tadkaew et al., 2011; Wijekoon et al., 2013) ranging from pharmaceuticals to steroid hormones. Of the four hormones, only testosterone, estrone and progresterone are hydrophobic (log D_{pH7} > 3.2) (**Fig. 3**). Hydrophobicity can be defined by log K_{ow} for non-ionic and log D for ionic compounds (Taheran et al., 2016). All three hydrophobic EOMs showed consistently high removal efficiency of 96-99% (median 97%). Similar results have been reported in other studies (Suárez et al., 2012). The higher removal efficiency of hydrophobic compounds might be due to: (i) the dominating mechanism of sorption to the sludge that facilitates enhanced biological degradation, and (ii) possessing only e-donating groups (EDGs) that enhance better oxidation (Tadkaew et al., 2011). High log D is characteristic of hydrophobic EOMs, poor hydrosolubility and high sorption tendency on organic constituents of sludge matrix (Cirja et al., 2008). Moreover, the calculated log K_d values of these EOMs were above 4, indicating substantially high sorption affinity to the sludge.

On the other hand, the removal of hydrophilic EOMs (log D_{pH7} <3.2) varied from 'limited removal' (carbamazepine and hydrochlorothiazide) to almost complete removal (paracetamol, caffeine and ibuprofen). It is very obvious that the removal of hydrophilic EOMs varies significantly since they have diverse molecular structures and functional groups (**Table S1**). Varying removal efficiencies accounted for in hydrophilic EOMs can be explained based on the qualitative framework by Tadkaew et al (Tadkaew et al., 2011) as: (i) compounds

possessing only EDGs (slightly hydrophobic such as estriol) could achieve high removal (~99%); (ii) compounds possessing both EDGs and e-withdrawing (EWGs) such as amide and chloride in their molecular structure (Tadkaew et al., 2011; Wijekoon et al., 2013) including paracetamol, ibuprofen, diclofenac, hydrocortisone, naproxen, propranolol, trimethoprim, ciprofloxacin, bisoprolol, caffeine, furosemide, metroprolol, tetracycline, atenolol and iopamidol with varying removal efficiencies ranging from 37-99.9%; (iii) compounds possessing only strong EWGs such as hydrochlorothiazide and carbamazepine (0-10%). Therefore, the dominating removal mechanism of hydrophobic compounds is strongly influenced by their intrinsic biodegradability as sorption to sludge is less significant (Tadkaew et al., 2011).

Another aspect may be the degree of ionisation (pK_a) of the selected EOMs, which controls their ionisation state as a consequence of pH variation in the solution. For EOMs including ibuprofen, diclofenac, naproxen, ketoprofen, enalapril, caffeine, furosemide, tetracycline and ciprofloxacin possessing a pK_a of between 0.52 and 6.43 (Table **S1**), removal efficiencies varied from 38-99%. The results are partially consistent with the previous work, where acidic EOMs showed low removal efficiency in neutral pH condition. This might be related to the fact that these EOMs are negatively charged at neutral pH due to the presence of carboxyl functional group in their structures (Urase et al., 2005). Likewise, EOMs with pK_a values of 7 to 15 (**Table S1**) showed varied removal efficiencies ranging from 'non-removal' to more than 97%, with the lowest being carbamazepine and hydrochlorothiazide and the highest being paracetamol. Carbamazepine and hydrochlorothiazide both have a basic amine functional group, which may be protonated to gain a positive charge under neutral pH (Nghiem and Khan, 2007; Urase et al., 2005). This phenomenon may have increased their

hydrophilicity which was confirmed by their noticeably higher concentrations in the MBR effluents (**Fig S1**).

The molecular weights (MWs) of the selected EOMs varied from 151 g moL^{-1} (paracetamol) to 777 g moL^{-1} (iopamidol) in this study (**Table S1**). However, the removal tendencies of EOMs in relation to MWs were not clear. For example, paracetamol and caffeine were almost completely removed although their MWs were the lowest on the list (151 and 194 g moL^{-1}), whereas the removal efficiencies of other EOMs with MWs ranging from 206-777 g moL^{-1} varied from non-removal to more than 99.6%. EOMs with higher MW may provide more branches that allow microbes to selectively cleave certain target sites and subsequently initiate degradation (Tadkaew et al., 2011).

Furthermore, the average MLSS concentrations inside the reactor were 8.5 ± 0.8 g L^{-1} and 3.7± 1.1 g L^{-1} at SRTs of 60 days and 21 days, respectively. Results showed that the removal of metroprolol, hydrochlorothiazide, propranolol and carbamazepine was enhanced while operating the MBR at high SRT (i.e. high MLSS concentration) (**Fig. 3**). At increasing SRTs, the amount of sludge wasted from the bioreactor decreases, which allows longer retention and subsequent degradation of less polar EOMs in the system. The higher specific area provided by increasing MLSS concentration enables more enzymatic activities (Cirja et al., 2008).

3.6 Influence of SRTs on sludge characteristics

Fig. 5 shows the variations in SMP and EPS during the MBR treatment at two different SRTs. Although the TMP profile of the MBR system was quite stable during the testing periods of both the SRTs, noticeable changes in the concentrations of SMP and EPS were observed. SMP concentration increased from 5.6 to 15.5 mg $gMLVSS^{-1}$ (about 3 times) while SRT was

lowered from 60 days to 21 days. Similarly, more EPS were released at an SRT of 21 days (103 mg $gMLVSS^{-1}$) than the longer SRT of 60 days (51 mg $gMLVSS^{-1}$). A comparable trend of EPS variation was reported by other researchers (Massé et al., 2006). As SRT increased, concentrations of SMP and EPS decreased as most of the substrates were consumed for the metabolism of microorganisms (Park et al., 2015). Nevertheless, extremely high SRTs can accumulate high soluble and particulate matters due to the increase in MLSS concentration, leading to an increase in viscosity that demands high scouring air for membranes (Krzeminski et al., 2012). However, since effluent flow was relatively stable, which substantiates the robustness of the MBR process, no clear correlation of SMP and EPS to membrane fouling was observed in this study. The consistent rate of fouling might have been adequately mitigated by continuous physical membrane-cleaning processes such as intermittent membrane relaxation and the use of scouring air involved in the pilot operation. Many researchers reported that the release of SMP and EPS concentration decreases as the sludge stays longer in the bioreactor, and increases when lowering the SRT (Grelier et al., 2006; Meng et al., 2009). The presence of EOMs in MBR may affect microbial activities and the structure community of microorganisms in activated sludge, which increases the endogenous respiration rates and subsequently releases EPS (Avella et al., 2010). However, studying the extent of EOM influence on releasing SMP and EPS was out of the scope of this study.

Furthermore, the dewaterability of MBR sludge was also assessed at both SRTs in terms of their corresponding CST values (**Fig. 5)**. The average CST of the sludge operated at an SRT of 60 days (31 s) was about twice as high as at an SRT of 21 days (15 s). An increasing trend of sludge CST with increasing SRT is reported by other researchers, which indicates that the sludge with high CST is difficult to dewater due to the high content of bound water (Ng et al.,

2006). Also, increasing SMP and EPS concentrations indicated the decreasing CST of sludge due to increased fractions of fine and colloidal particles, and vice versa (Grelier et al., 2006).

Fig. 5 (Here)

3.7 MBR effluent quality in compliance with Australian and Swiss guidelines

To evaluate the quality of MBR-treated effluent in terms of EOMs concentrations, the observed concentrations of EOMs were studied in compliance with the Australian (NHMRC/EPHC/NRMMC, 2008) and Swiss guideline values (Oekotoxzentrum Centre Ecotox, 2016) (**Table 3**). Nevertheless, no guidelines or standards have yet been proposed for EOMs selected by the EU. A wider range of pharmaceuticals and steroid hormones was established in the Australian guidelines than in the Swiss guidelines. Most of the studied EOMs were observed well below the guideline values of both the standards (**Table 3**). No steroid hormones were detected above their LOQs, which were lower than both the guidelines. Among diuretics, enalapril was detected below the LOQ (10 ng L^{-1}), whereas hydrochlorothiazide and furosemide were frequently detected in the range of 185-1700 ng L^{-1}. Similarly, immunosuppressive (hydrocortisone) was not detected above its LOQ, but no guidelines for diuretics and immunosuppressives are available or have been proposed so far. Caffeine was detected at a concentration of 60-328 ng L^{-1}, which was lower than the guideline value of 350 ng L^{-1}, but it showed excellent removal efficiency of more than 99% in MBR treatment since the influent concentration was very high (140437 ± 6453 ng L^{-1}). Regarding poorly removed carbamazepine, the observed concentration of 480-665 ng L^{-1} was lower than

both guidelines. Overall, the results indicated that the quality of effluent by MBR treatment fulfilled the water quality requirements for reuse purposes, regardless of varying SRTs.

Table 3 (Here)

4. Conclusion

The removal and fate of selected EOMs by the MBR pilot plant at varying SRTs were studied. Only 23 EOMs were detected in the influent wastewater during the testing periods above their LOQs. Diverse removal dynamics for selected EOMs were observed. The application of mass balance assessment proved that biotransformation and sorption onto sludge were the dominant mechanisms associated with the removal of EOMs. Even though the EOMs removal efficiencies were not that significant at SRTs of 21 and 60 days, enhanced removal of the majority of EOMs were observed at longer SRT. Therefore, SRT of 60 days would be preferred to be implemented, which would additionally help in releasing less concentrations of SMP and EPS. This study has expanded the understanding of the removal and fate of the EOMs (some of which were never or rarely studied before in MBR) via MBR treatments under different operating conditions (i.e. SRTs), which certainly helps in achieving more sustainable water management.

5. Acknowledgements

The authors would like to thanks Business Finland Oy (Innovaatiorahoituskeskus) (formerly Tekes- the Finnish Funding Agency for Technology and Innovation) for funding this work as

part of the **Smart Effluents Project**. Special thanks to Reijo Turkki, Risto Repo, Anne Bergman and Päivi Luukkonen for their continuous support in operating and maintaining the MBR pilot plant during the sampling periods. We also thanks Eurofins Environment Testing Finland Oy for its laboratory analysis support.

6. References

APHA, 1999. Standard Methods for the Examination of Water and Wastewater. Stand. Methods 541–541.

Avella, A.C., Delgado, L.F., Görner, T., Albasi, C., Galmiche, M., de Donato, P., 2010. Effect of cytostatic drug presence on extracellular polymeric substances formation in municipal wastewater treated by membrane bioreactor. Bioresour. Technol. 101, 518–526. https://doi.org/10.1016/j.biortech.2009.08.057

Behera, S.K., Kim, H.W., Oh, J.-E., Park, H.-S., 2011. Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci. Total Environ. 409, 4351–4360. https://doi.org/10.1016/j.scitotenv.2011.07.015

Bo, L., Urase, T., Wang, X., 2009. Biodegradation of trace pharmaceutical substances in wastewater by a membrane bioreactor. Front. Environ. Sci. Eng. China 3, 236–240. https://doi.org/10.1007/s11783-009-0004-9

Cirja, M., Ivashechkin, P., Schäffer, A., Corvini, P.F.X., 2008. Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). Rev. Environ. Sci. Biotechnol. 7, 61–78. https://doi.org/10.1007/s11157-007-9121-8

Clara, M., Kreuzinger, N., Strenn, B., Gans, O., Kroiss, H., 2005a. The solids retention time—a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. Water Res. 39, 97–106. https://doi.org/10.1016/j.watres.2004.08.036

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H., 2005b. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Res. 39, 4797–4807. https://doi.org/10.1016/j.watres.2005.09.015

EU, 2018. Commission Implementing Decision (EU) 2018/840 [WWW Document]. URL http://data.europa.eu/eli/dec_impl/2018/840/oj/eng (accessed 1.22.19).

EU, 2013. EU. Directive 2013/39/EU of the European Parliament and of the Council [WWW Document].

Falås, P., Andersen, H.R., Ledin, A., la Cour Jansen, J., 2012. Impact of solid retention time and nitrification capacity on the ability of activated sludge to remove pharmaceuticals. Environ. Technol. 33, 865–872. https://doi.org/10.1080/09593330.2011.601764

Garcia-Becerra, F.Y., Ortiz, I., 2018. Biodegradation of Emerging Organic Micropollutants in Nonconventional Biological Wastewater Treatment: A Critical Review. Environ. Eng. Sci. 35, 1012–1036. https://doi.org/10.1089/ees.2017.0287

Githinji, L.J.M., Musey, M.K., Ankumah, R.O., 2011. Evaluation of the Fate of Ciprofloxacin and Amoxicillin in Domestic Wastewater. Water. Air. Soil Pollut. 219, 191–201. https://doi.org/10.1007/s11270-010-0697-1

Grelier, P., Rosenberger, S., Tazi-Pain, A., 2006. Influence of sludge retention time on membrane bioreactor hydraulic performance. Desalination, International Congress on Membranes and Membrane Processes 192, 10–17. https://doi.org/10.1016/j.desal.2005.04.131

Guerra, P., Kim, M., Shah, A., Alaee, M., Smyth, S.A., 2014. Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes. Sci. Total Environ. 473–474, 235–243. https://doi.org/10.1016/j.scitotenv.2013.12.008

Gurung, K., Ncibi, M.C., Fontmorin, J., Särkkä, H., Sillanpää, M., 2016. Incorporating Submerged MBR in Conventional Activated Sludge Process for Municipal Wastewater Treatment : A Feasibility and Performance Assessment. J. Membr. Sci. Technol. 6. https://doi.org/10.4172/2155-9589.1000158

Hai, F.I., Yang, S., Asif, M.B., Sencadas, V., Shawkat, S., Sanderson-Smith, M., Gorman, J., Xu, Z.-Q., Yamamoto, K., 2018. Carbamazepine as a Possible Anthropogenic Marker in Water: Occurrences, Toxicological Effects, Regulations and Removal by Wastewater Treatment Technologies. Water 10, 107. https://doi.org/10.3390/w10020107

Jelic, A., Gros, M., Ginebreda, A., Cespedes-Sánchez, R., Ventura, F., Petrovic, M., Barcelo, D., 2011. Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment. Water Res. 45, 1165–1176. https://doi.org/10.1016/j.watres.2010.11.010

Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A., Siegrist, H., 2006. Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Res. 40, 1686–1696. https://doi.org/10.1016/j.watres.2006.02.014

Judd, S., 2008. The status of membrane bioreactor technology. Trends Biotechnol. 26, 109–116. https://doi.org/10.1016/j.tibtech.2007.11.005

Kim, M., Guerra, P., Shah, A., Parsa, M., Alaee, M., Smyth, S.A., 2014. Removal of pharmaceuticals and personal care products in a membrane bioreactor wastewater treatment plant. Water Sci. Technol. 69, 2221–2229. https://doi.org/10.2166/wst.2014.145

Kim, S., Eichhorn, P., Jensen, J.N., Weber, A.S., Aga, D.S., 2005. Removal of Antibiotics in Wastewater: Effect of Hydraulic and Solid Retention Times on the Fate of Tetracycline in the Activated Sludge Process. Environ. Sci. Technol. 39, 5816–5823. https://doi.org/10.1021/es050006u

Kimura, K., Hara, H., Watanabe, Y., 2007. Elimination of Selected Acidic Pharmaceuticals from Municipal Wastewater by an Activated Sludge System and Membrane Bioreactors. Environ. Sci. Technol. 41, 3708–3714. https://doi.org/10.1021/es061684z

Krzeminski, P., Iglesias-Obelleiro, A., Madebo, G., Garrido, J.M., van der Graaf, J.H.J.M., van Lier, J.B., 2012. Impact of temperature on raw wastewater composition and activated sludge filterability in full-scale MBR systems for municipal sewage treatment. J. Membr. Sci. 423–424, 348–361. https://doi.org/10.1016/j.memsci.2012.08.032

Li, C., Cabassud, C., Guigui, C., 2015. Evaluation of membrane bioreactor on removal of pharmaceutical micropollutants: a review. Desalination Water Treat. 55, 845–858. https://doi.org/10.1080/19443994.2014.926839

Loke, M.-L., Tjørnelund, J., Halling-Sørensen, B., 2002. Determination of the distribution coefficient (logKd) of oxytetracycline, tylosin A, olaquindox and metronidazole in manure. Chemosphere 48, 351–361. https://doi.org/10.1016/S0045-6535(02)00078-4

Maeng, S.K., Choi, B.G., Lee, K.T., Song, K.G., 2013. Influences of solid retention time, nitrification and microbial activity on the attenuation of pharmaceuticals and estrogens in membrane bioreactors. Water Res. 47, 3151–3162. https://doi.org/10.1016/j.watres.2013.03.014

Massé, A., Spérandio, M., Cabassud, C., 2006. Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high

solids retention time. Water Res. 40, 2405–2415. https://doi.org/10.1016/j.watres.2006.04.015

Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S., Yang, F., 2009. Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. Water Res. 43, 1489–1512. https://doi.org/10.1016/j.watres.2008.12.044

Miège, C., Choubert, J.M., Ribeiro, L., Eusèbe, M., Coquery, M., 2009. Fate of pharmaceuticals and personal care products in wastewater treatment plants – Conception of a database and first results. Environ. Pollut., Special Issue Section: Ozone and Mediterranean Ecology: Plants, People, Problems 157, 1721–1726. https://doi.org/10.1016/j.envpol.2008.11.045

Ng, H.Y., Tan, T.W., Ong, S.L., 2006. Membrane Fouling of Submerged Membrane Bioreactors: Impact of Mean Cell Residence Time and the Contributing Factors. Environ. Sci. Technol. 40, 2706–2713. https://doi.org/10.1021/es0516155

Nghiem, L., Khan, S., 2007. Effects of operating conditions on the removal of trace organic contaminants by a loose nanofiltration membrane. Fac. Eng. - Pap. Arch. 1–12.

NHMRC/EPHC/NRMMC, 2008. National Water Quality Management Strategy [WWW Document]. URL https://nhmrc.gov.au/health-advice/water-quality-and-health (accessed 10.29.18).

Oekotoxzentrum Centre Ecotox, 2016. Swiss Proposals for Acute and Chronic Quality Standards [WWW Document]. Oekotoxzentrum Cent. Ecotox. URL http://www.ecotoxcentre.ch/ (accessed 10.26.18).

Park, H.-D., Chang, I.-S., Lee, K.-J., 2015. Principles of Membrane Bioreactors for Wastewater Treatment [WWW Document]. URL https://www.crcpress.com/Principles-of-Membrane-Bioreactors-for-Wastewater-Treatment/Park-Chang-Lee/9781466590373 (accessed 10.1.18).

Phan, H.V., Hai, F.I., Kang, J., Dam, H.K., Zhang, R., Price, W.E., Broeckmann, A., Nghiem, L.D., 2014. Simultaneous nitrification/denitrification and trace organic contaminant (TrOC) removal by an anoxic–aerobic membrane bioreactor (MBR). Bioresour. Technol., Special Issue: CESE 2013 & Special Issue: ICABB 2013 165, 96–104. https://doi.org/10.1016/j.biortech.2014.03.094

Radjenović, J., Petrović, M., Barceló, D., 2009. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Res. 43, 831–841. https://doi.org/10.1016/j.watres.2008.11.043

Radjenovic, J., Petrovic, M., Barceló, D., 2007. Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Anal. Bioanal. Chem. 387, 1365–1377. https://doi.org/10.1007/s00216-006-0883-6

Ramesh, A., Lee, D.-J., Hong, S.G., 2006. Soluble microbial products (SMP) and soluble extracellular polymeric substances (EPS) from wastewater sludge. Appl. Microbiol. Biotechnol. 73, 219–225. https://doi.org/10.1007/s00253-006-0446-y

Röhricht, M., Krisam, J., Weise, U., Kraus, U.R., Düring, R.-A., 2009. Elimination of Carbamazepine, Diclofenac and Naproxen from Treated Wastewater by Nanofiltration. CLEAN – Soil Air Water 37, 638–641. https://doi.org/10.1002/clen.200900040

Schäfer, A.I., Akanyeti, I., Semião, A.J.C., 2011. Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens. Adv. Colloid Interface Sci., Membrane Separation and Colloid Science 164, 100–117. https://doi.org/10.1016/j.cis.2010.09.006

Schröder, H.F., Tambosi, J.L., Sena, R.F., Moreira, R.F.P.M., José, H.J., Pinnekamp, J., 2012. The removal and degradation of pharmaceutical compounds during membrane bioreactor treatment. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 65, 833–839. https://doi.org/10.2166/wst.2012.828

Sim, W.-J., Lee, J.-W., Oh, J.-E., 2010. Occurrence and fate of pharmaceuticals in wastewater treatment plants and rivers in Korea. Environ. Pollut. 158, 1938–1947. https://doi.org/10.1016/j.envpol.2009.10.036

Suárez, S., Reif, R., Lema, J.M., Omil, F., 2012. Mass balance of pharmaceutical and personal care products in a pilot-scale single-sludge system: Influence of T, SRT and recirculation ratio. Chemosphere 89, 164–171. https://doi.org/10.1016/j.chemosphere.2012.05.094

Tadkaew, N., Hai, F.I., McDonald, J.A., Khan, S.J., Nghiem, L.D., 2011. Removal of trace organics by MBR treatment: The role of molecular properties. Water Res. 45, 2439–2451. https://doi.org/10.1016/j.watres.2011.01.023

Taheran, M., Brar, S.K., Verma, M., Surampalli, R.Y., Zhang, T.C., Valero, J.R., 2016. Membrane processes for removal of pharmaceutically active compounds (PhACs) from water and wastewaters. Sci. Total Environ. 547, 60–77. https://doi.org/10.1016/j.scitotenv.2015.12.139

Tambosi, J.L., de Sena, R.F., Favier, M., Gebhardt, W., José, H.J., Schröder, H.F., Moreira, R. de F.P.M., 2010. Removal of pharmaceutical compounds in membrane bioreactors (MBR) applying submerged membranes. Desalination 261, 148–156. https://doi.org/10.1016/j.desal.2010.05.014

Ternes, T.A., 1998. Occurrence of drugs in German sewage treatment plants and rivers1Dedicated to Professor Dr. Klaus Haberer on the occasion of his 70th birthday.1. Water Res. 32, 3245–3260. https://doi.org/10.1016/S0043-1354(98)00099-2

Trinh, T., van den Akker, B., Coleman, H.M., Stuetz, R.M., Drewes, J.E., Le-Clech, P., Khan, S.J., 2016. Seasonal variations in fate and removal of trace organic chemical contaminants while operating a full-scale membrane bioreactor. Sci. Total Environ. 550, 176–183. https://doi.org/10.1016/j.scitotenv.2015.12.083

Trinh, T., van den Akker, B., Stuetz, R.M., Coleman, H.M., Le-Clech, P., Khan, S.J., 2012. Removal of trace organic chemical contaminants by a membrane bioreactor. Water Sci. Technol. 66, 1856–1863. https://doi.org/10.2166/wst.2012.374

Urase, T., Kagawa, C., Kikuta, T., 2005. Factors affecting removal of pharmaceutical substances and estrogens in membrane separation bioreactors. Desalination, Membranes in Drinking and Industrial Water Production 178, 107–113. https://doi.org/10.1016/j.desal.2004.11.031

Van den Broeck, R., Van Dierdonck, J., Nijskens, P., Dotremont, C., Krzeminski, P., van der Graaf, J.H.J.M., van Lier, J.B., Van Impe, J.F.M., Smets, I.Y., 2012. The influence of solids retention time on activated sludge bioflocculation and membrane fouling in a membrane bioreactor (MBR). J. Membr. Sci. 401–402, 48–55. https://doi.org/10.1016/j.memsci.2012.01.028

Vieno, N., Sillanpää, M., 2014. Fate of diclofenac in municipal wastewater treatment plant — A review. Environ. Int. 69, 28–39. https://doi.org/10.1016/j.envint.2014.03.021

Vieno, N.M., Tuhkanen, T., Kronberg, L., 2005. Seasonal Variation in the Occurrence of Pharmaceuticals in Effluents from a Sewage Treatment Plant and in the Recipient Water. Environ. Sci. Technol. 39, 8220–8226. https://doi.org/10.1021/es051124k

Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Nghiem, L.D., 2013. The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment. Bioresour. Technol. 144, 247–254. https://doi.org/10.1016/j.biortech.2013.06.097

Yang, X., Flowers, R.C., Weinberg, H.S., Singer, P.C., 2011. Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. Water Res. 45, 5218–5228. https://doi.org/10.1016/j.watres.2011.07.026

Yang, Y., Ok, Y.S., Kim, K.-H., Kwon, E.E., Tsang, Y.F., 2017. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. Sci. Total Environ. 596–597, 303–320. https://doi.org/10.1016/j.scitotenv.2017.04.102

Ying, G.-G., S. Kookana, R., W. Kolpin, D., 2009. Occurrence and removal of pharmaceutically active compounds in sewage treatment plants with different technologies. J. Environ. Monit. 11, 1498–1505. https://doi.org/10.1039/B904548A

Figure captions:

Fig. 1. Schematic diagram of the pilot MBR unit with indicated sampling points.

Fig. 2. Occurrences of EOMs in MBR process at two different SRTs (60 days and 21 days) arranged according to their Log D $_{(at\ pH\ 7)}$ values. EOMs with concentration lower than LOQ are not included.

Fig. 3. Median removal efficiencies of EOMs in MBR process at different SRTs. The EOMs with their detection in influent < LOQ are not presented. The LOQ values of EOMs in the effluent are used to calculate % removal whenever measured concentrations are below LOQ. Error bars represents the standard deviation calculated from the duplicate samples taken once in a week.

Fig. 4. Fate of the selected EOMs during MBR process at two different SRTs. The log K_d values to the right showed the distribution of calculated sludge-water distribution coefficients/sorption coefficients of EOMs.

Fig. 5. Variation of SMP, EPS fractions, and CST as a function of varying SRTs.

Table legends:

Table 1. Operational conditions of the MBR pilot plant.

Table 2. Basic performance of MBR system (mean ± standard deviation) at two different SRTs.

Table 3. Comparison of median concentrations of EOMs in MBR effluent with Australian and Swiss guidelines.

Table 1
Operational conditions of the MBR pilot plant.

Parameter	Units	Values min – max (avg.)	
		SRT: 60 days	SRT: 21 days
Hydraulic retention time (HRT)	Hours	40.1 – 45.5 (42.13)	
Flux (Continuous)	L m^{-2} h^{-1}	5.4 - 6.13 (5.84)	
MLSS concentration	mg L^{-1}	7808 - 9688 (8550)	2271 - 4865 (3748)
MLSS/MLVSS	_	0.57 – 0.83 (0.67)	0.3 – 0.68 (0.56)
F/M ratio	kg COD. (kg MLVSS. d)$^{-1}$	0.022 - 0.034 (0.027)	0.06 - 0.11 (0.09)
Specific aeration demand (SAD_m)	m h^{-1}	0.15-0.23 (0.20)	
Dissolved oxygen (DO)	mg O_2 L^{-1}	1.2 - 4.6 (2.9)	
Reactor temperature	°C	14 - 22 (19)	
pH	Unitless	6.0 - 7.4 (6.6)	
Intermittent filtration	Minutes	9-ON/1-OFF	

Table 2

Basic performance of MBR system (mean ± standard deviation) at two different SRTs.

Parameter	SRT:60 days			SRT: 21 days		
	Influent (mg L^{-1})	Effluent (mg L^{-1})	Removal efficiency (%)	Influent (mg L^{-1})	Effluent (mg L^{-1})	Ren effi (%)
TSS	128.0 ± 37.9	< 1	100	133.33 ± 14.1	< 1	100
COD	299.3 ± 55.2	22.7 ± 5.2	92.43	330.0 ± 19.6	23.0 ± 5.3	93.0
NH_4-N	29.7 ± 6.3	< 0.01	> 99.96	38.85 ± 3.2	< 0.01	> 9
TP	3.94 ± 0.7	0.47 ± 0.2	88.12	3.86 ± 1.4	0.49 ± 0.1	87.4
TN	45.0 ± 7.5	38.33 ± 7.1	14.81	50.0 ± 0.74	42.5 ± 4.4	15.0

Table 3
Comparison of median concentrations of EOMs in MBR effluent with Australian and Swiss guidelines.
n.a. values not available; n.p. not proposed; '<' denotes below LOQ.

Compound	Concentration (ng L^{-1})		
	MBR Effluent - SRT 60 (SRT 21)	Australian guideline values (NHMRC/EPHC/NRMMC, 2008)	Swiss guideline values (Oekotoxzentrum Centre Ecotox, 2016)
Iopamidol	200 (350)	400 x 10^3	n.p.
Atenolol	4 (25)	n.a.	330 x 10^3
Tetracycline	<10 (<10)	105 x 10^3	n.p.
Metoprolol	100 (350)	25 x 10^3	750 x 10^3
Furosemide	185 (230)	n.a.	n.p.
Caffeine	328 (60.5)	350	n.p.
Bisoprolol	11 (19.5)	630 x 10^3	n.p.
Ciprofloxacin	50 (51.5)	250 x 10^3	360
Enalapril	<10 (<10)	n.a.	n.p.
Hydrochlorothiazide	1700 (1350)	n.a.	n.p.
Ketoprofen	5 (5)	3.5 x 10^3	n.p.
Trimethoprim	28.5 (42)	70 x 10^3	210 x 10^3
Propranolol	33 (51.5)	40 x 10^3	12 x 10^3
Paracetamol	325 (50)	175 x 10^3	n.p.
Naproxen	19.5 (84)	220 x 10^3	860 x 10^3
Ibuprofen	59 (50)	400 x 10^3	1700 x 10^3
Hydrocortisone	<10 (<10)	n.a.	n.p.
Diclofenac	760 (1050)	180 x 10^1	n.p.
Carbamazepine	480 (665)	100 x 10^3	2000 x 10^3
Estriol	<5 (<5)	50	n.p.
Testosterone	<1 (<1)	7 x 10^3	n.p.
Estrone	<5 (<5)	30	n.p.
Progesterone	<1 (<1)	105 x 10^3	n.p.

Highlights

- Fate of 23 EOMs in pilot MBR treatment at varying SRT was studied.
- At long SRT, EOMs removal majorly enhanced while SMP and EPS concentration lessened.
- Hormones and antibiotics were highly removed than diuretics and anti-epileptics.
- Iopamidol and hydrocortisone (>90% removal) were studied for the first time in MBR.
- MBR Effluent fulfilled the water quality requirements for reuse

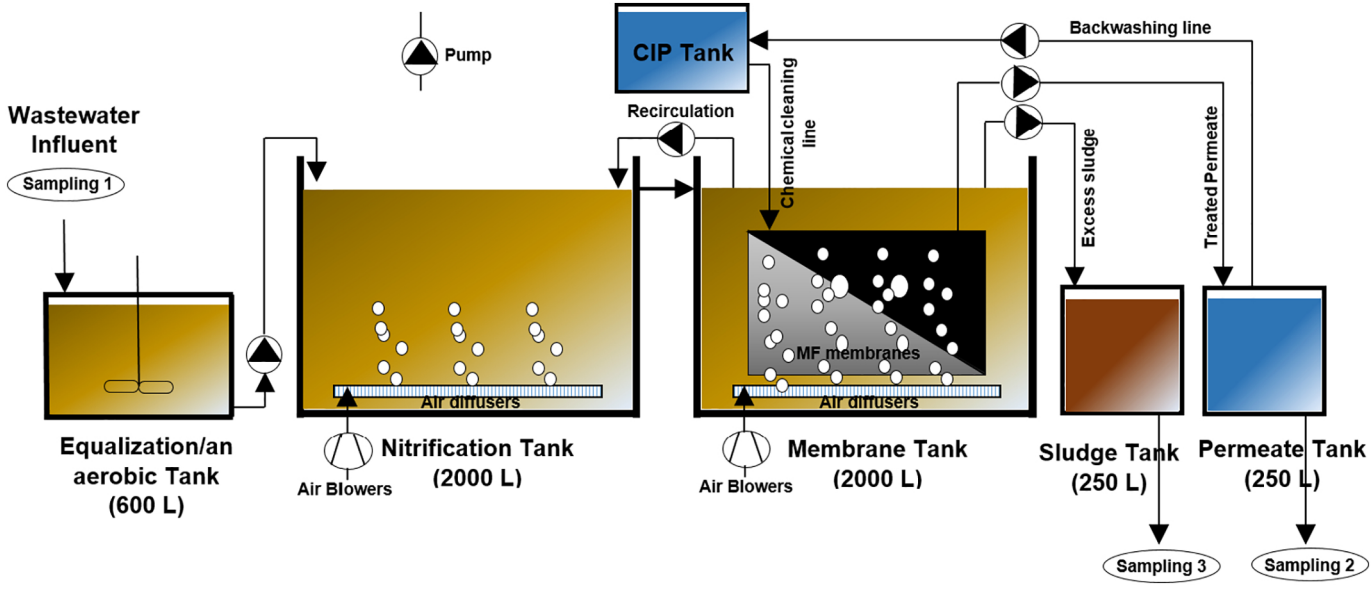
Pump
CIP Tank
Backwashing line
Wastewater Influent
Sampling 1
Recirculation
Chemical cleaning line
Excess sludge
Treated Permeate
MF membranes
Air diffusers
Air diffusers
Equalization/an aerobic Tank (600 L)
Air Blowers
Nitrification Tank (2000 L)
Air Blowers
Membrane Tank (2000 L)
Sludge Tank (250 L)
Permeate Tank (250 L)
Sampling 3
Sampling 2

Figure 1

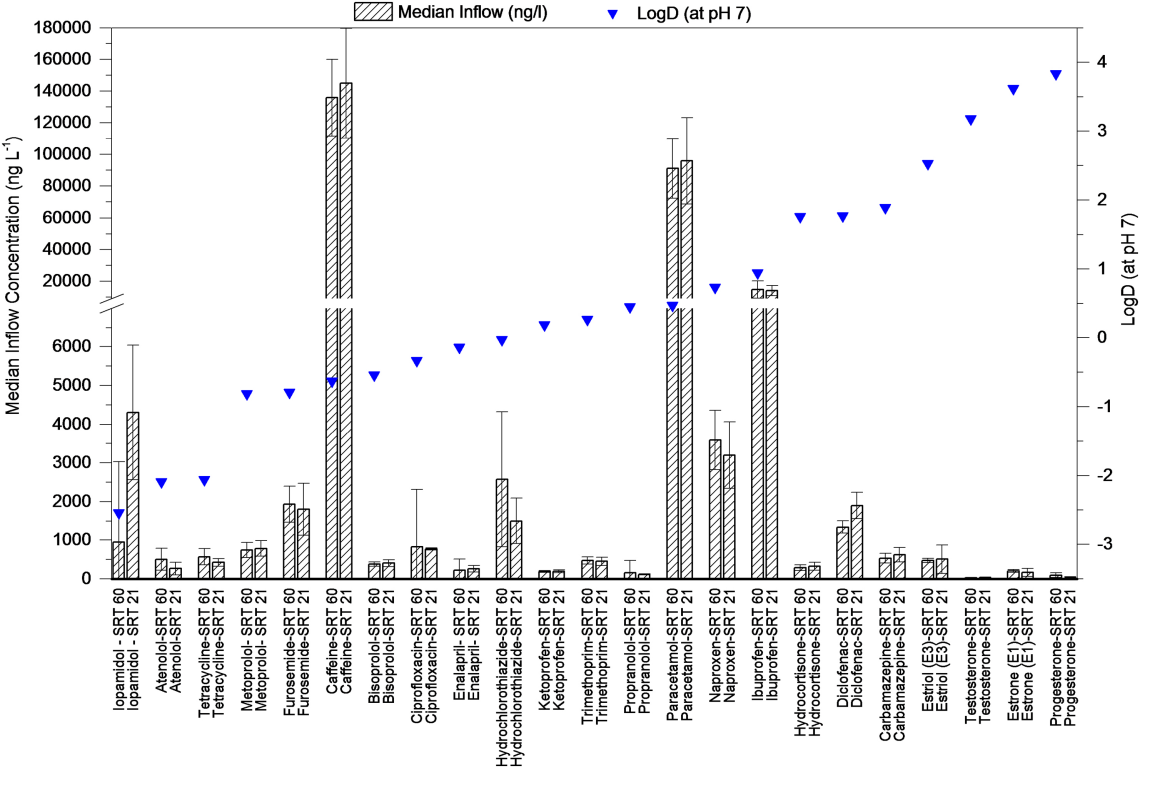
Median Inflow (ng/l)
LogD (at pH 7)
Median Inflow Concentration (ng L-1)
LogD (at pH 7)
180000
160000
140000
120000
100000
80000
60000
40000
20000
6000
5000
4000
3000
2000
1000
0
4
3
2
1
0
-1
-2
-3
Iopamidol - SRT 60
Iopamidol - SRT 21
Atenolol-SRT 60
Atenolol-SRT 21
Tetracycline-SRT 60
Tetracycline-SRT 21
Metoprolol- SRT 60
Metoprolol- SRT 21
Furosemide-SRT 60
Furosemide-SRT 21
Caffeine-SRT 60
Caffeine-SRT 21
Bisoprolol-SRT 60
Bisoprolol-SRT 21
Ciprofloxacin-SRT 60
Ciprofloxacin-SRT 21
Enalapril- SRT 60
Enalapril- SRT 21
Hydrochlorothiazide-SRT 60
Hydrochlorothiazide-SRT 21
Ketoprofen-SRT 60
Ketoprofen-SRT 21
Trimethoprim-SRT 60
Trimethoprim-SRT 21
Propranolol-SRT 60
Propranolol-SRT 21
Paracetamol-SRT 60
Paracetamol-SRT 21
Naproxen-SRT 60
Naproxen-SRT 21
Ibuprofen-SRT 60
Ibuprofen-SRT 21
Hydrocortisone-SRT 60
Hydrocortisone-SRT 21
Diclofenac-SRT 60
Diclofenac-SRT 21
Carbamazepine-SRT 60
Carbamazepine-SRT 21
Estriol (E3)-SRT 60
Estriol (E3)-SRT 21
Testosterone-SRT 60
Testosterone-SRT 21
Estrone (E1)-SRT 60
Estrone (E1)-SRT 21
Progesterone-SRT 60
Progesterone-SRT 21

Figure 2

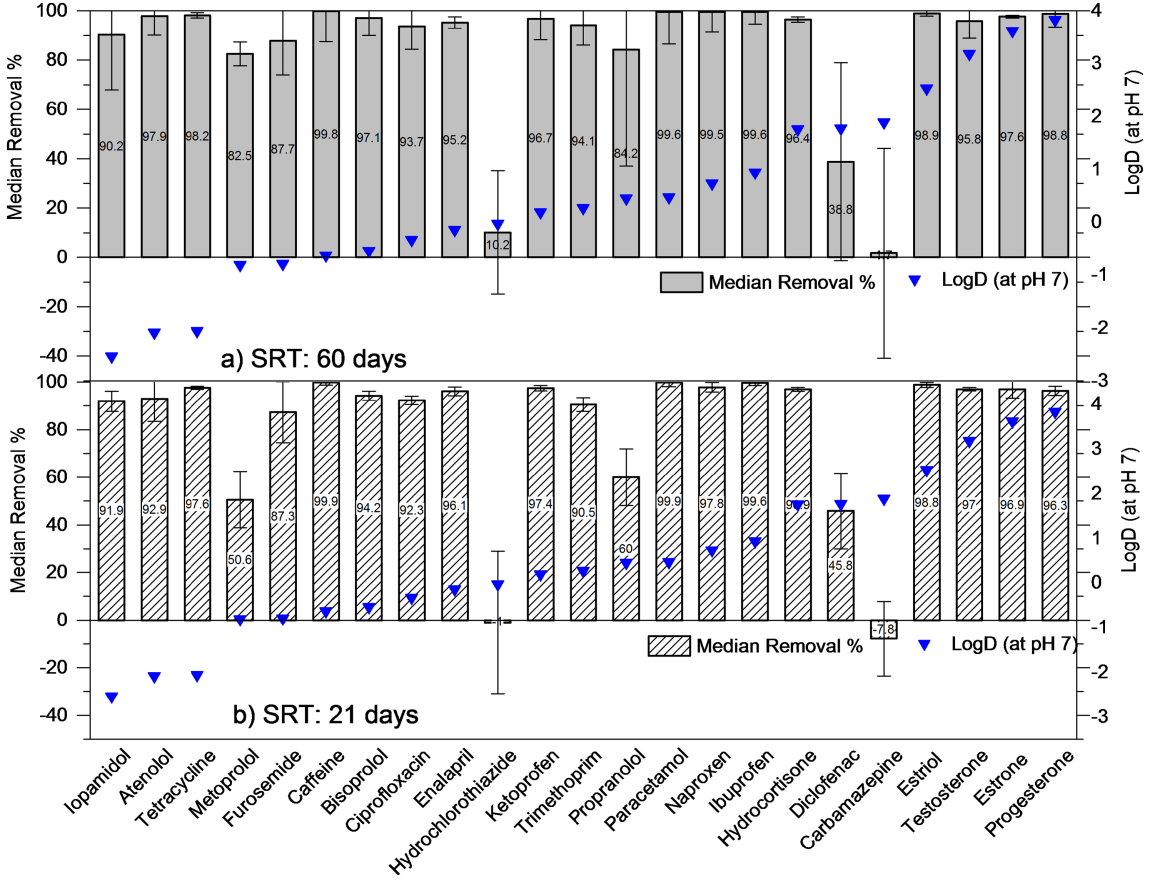
Median Removal %
LogD (at pH 7)
a) SRT: 60 days
b) SRT: 21 days
Median Removal %
LogD (at pH 7)
90.2
97.9
98.2
82.5
87.7
99.8
97.1
93.7
95.2
10.2
96.7
94.1
84.2
99.6
99.5
99.6
96.4
36.8
98.9
95.8
97.6
98.8
91.9
92.9
97.6
50.6
87.3
99.9
94.2
92.3
96.1
97.4
90.5
60
99.9
97.8
99.6
45.8
-7.8
98.8
97
96.9
96.3
Iopamidol
Atenolol
Tetracycline
Metoprolol
Furosemide
Caffeine
Bisoprolol
Ciprofloxacin
Enalapril
Hydrochlorothiazide
Ketoprofen
Trimethoprim
Propranolol
Paracetamol
Naproxen
Ibuprofen
Hydrocortisone
Diclofenac
Carbamazepine
Estriol
Testosterone
Estrone
Progesterone

Figure 3

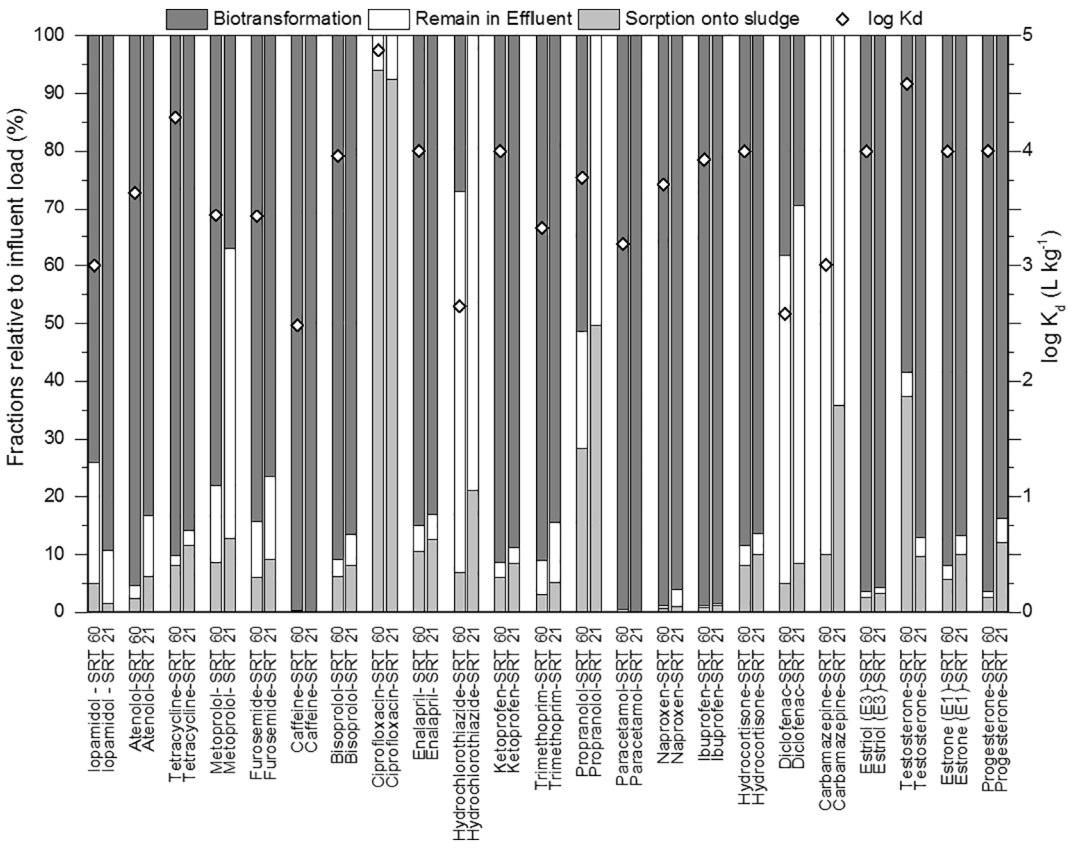
Biotransformation
Remain in Effluent
Sorption onto sludge
log Kd
Fractions relative to influent load (%)
log K_d (L kg^{-1})
Iopamidol - SRT 60
Iopamidol - SRT 21
Atenolol-SRT 60
Atenolol-SRT 21
Tetracycline-SRT 60
Tetracycline-SRT 21
Metoprolol- SRT 60
Metoprolol- SRT 21
Furosemide-SRT 60
Furosemide-SRT 21
Caffeine-SRT 60
Caffeine-SRT 21
Bisoprolol-SRT 60
Bisoprolol-SRT 21
Ciprofloxacin-SRT 60
Ciprofloxacin-SRT 21
Enalapril- SRT 60
Enalapril- SRT 21
Hydrochlorothiazide-SRT 60
Hydrochlorothiazide-SRT 21
Ketoprofen-SRT 60
Ketoprofen-SRT 21
Trimethoprim-SRT 60
Trimethoprim-SRT 21
Propranolol-SRT 60
Propranolol-SRT 21
Paracetamol-SRT 60
Paracetamol-SRT 21
Naproxen-SRT 60
Naproxen-SRT 21
Ibuprofen-SRT 60
Ibuprofen-SRT 21
Hydrocortisone-SRT 60
Hydrocortisone-SRT 21
Diclofenac-SRT 60
Diclofenac-SRT 21
Carbamazepine-SRT 60
Carbamazepine-SRT 21
Estriol (E3)-SRT 60
Estriol (E3)-SRT 21
Testosterone-SRT 60
Testosterone-SRT 21
Estrone (E1)-SRT 60
Estrone (E1)-SRT 21
Progesterone-SRT 60
Progesterone-SRT 21

Figure 4

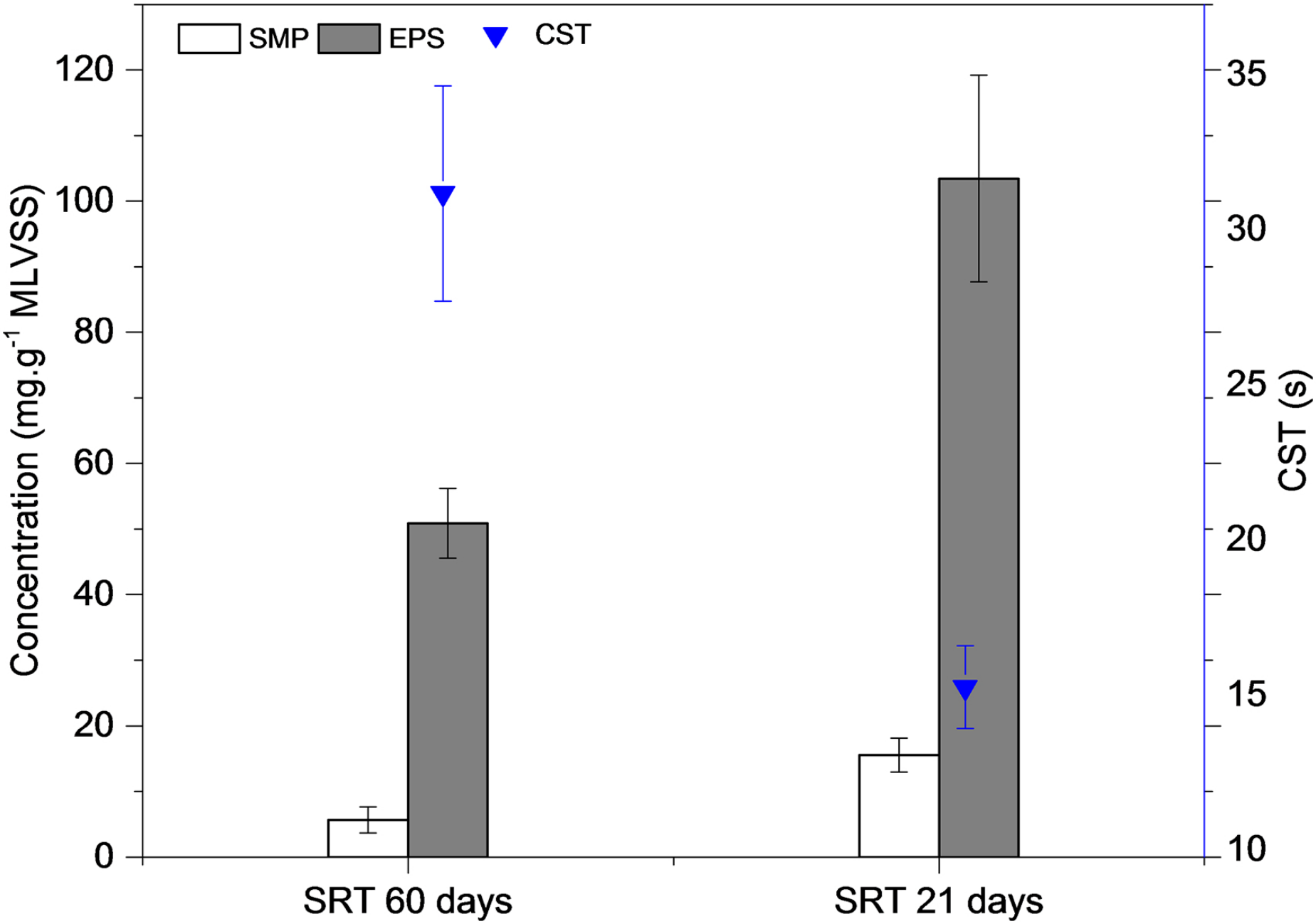
SMP
EPS
CST
Concentration (mg.g-1 MLVSS)
CST (s)
0
20
40
60
80
100
120
10
15
20
25
30
35
SRT 60 days
SRT 21 days

Figure 5