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Removal of Pharmaceuticals and Endocrine Disrupting Compounds in a Water Recycling Process using Reverse Osmosis Systems

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Abstract

A detailed investigation was carried out to evaluate the occurrence, persistence and fate of a range of micropollutants at different processing points at a full-scale water recycling plant (WRP) in Queensland, Australia. The WRP, which combines an advanced water treatment plant (AWTP) with a wastewater treatment plant (WWTP), produces high quality recycled water for industrial users. The concentrations of 11 pharmaceuticals from various therapeutic categories and two endocrine disrupting chemicals were examined in full-scale microfiltration and reverse osmosis membrane facilities. Salicylic acid was the most abundant analyte in the WWTP influent, with a concentration range of 11 to 38 µg/L, followed by bisphenol A with concentrations ranging from 6 to 23 µg/L. The concentration of all analytes decreased on average by one order of magnitude following primary and secondary treatment. Gemfibrozil, primidone and carbamazepine were found to have lower removal efficiencies (74-78%) than other compounds during these stages, which could indicate lower biodegradability. The microfiltration and reverse osmosis systems were found to further lower the pollutant concentrations by an order of magnitude. The overall removal efficiencies in the final recycled water were above 97 %, resulting in product water concentrations of lower than 0.1 µg/L for most compounds. An exception to this finding was observed for bisphenol A, which was detected in concentrations up to 0.5 µg/L in the final recycled water.

Keywords: Water Recycling, Reverse Osmosis (RO), Pharmaceuticals, Endocrine Disrupting Compounds, Wastewater.

1. Introduction

In recent years, increasing attention has been paid to the presence of micropollutants such as pharmaceuticals and their residues in wastewater treatment plant (WWTP) effluents and the aquatic environment. The occurrence and fate of both organic and inorganic micropollutants in the environment have long been recognised as issues of public health and environmental concern. A wide range of organic micropollutants have been detected and identified in sewage and effluent-impacted water bodies, including surface waters and groundwater [1-4].

Municipal wastewater systems are a major pathway for the disposal of pharmaceutical compounds, as confirmed by the fact that concentrations measured in WWTP influents reflect the amount consumed as measured by sales of pharmaceuticals [5]. Extensive studies have been conducted on the performance of wastewater treatment plants with regard to the removal of micropollutants. Results show that a number of pharmaceuticals are not removed effectively by conventional activated sludge treatment and considerable amounts of these pharmaceuticals are found in both effluent and sewage sludge [6-8]. Organic micropollutant removal in WWTPs is mainly accomplished by adsorption, biodegradation and volatilisation [9]. The chemical structure and physicochemical properties of pollutants greatly influence the effectiveness of these removal mechanisms.

As concerns over the presence of micropollutants in drinking water continue to grow, the use of membrane processes such as reverse osmosis (RO) and nanofiltration (NF) is becoming increasingly common in water treatment plants. Currently, a number of Australian water recycling facilities employ membrane systems to treat wastewater effluents. Recent studies have examined the removal of emerging micropollutants by ultrafiltration (UF), NF and RO [10-13]. Most of these investigations were performed at bench scale using flat sheet membrane units or dead-end filtration cells, feed waters with high solute concentrations and short membrane operation times. Feed waters spiked with target solutes and virgin membranes were employed, neglecting water matrix effects and membrane fouling, which is commonly observed in full-scale applications.

The removal processes of micropollutants in RO are complex and, despite many investigations, poorly understood. The rejection of micropollutants by RO is reported to be influenced by the dipole moment of compounds [14], the hydrophobicity of compounds (represented by K_{ow}) and the compound molecular size [15]. Under actual conditions, it is difficult to elucidate the core mechanisms for the rejection of micropollutants by RO. This rejection is governed by solute-solute and solute-membrane interactions [16].

The main objective of this study was to investigate, over the period of one year, the occurrence and fate of micropollutants, mainly endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs), in a metropolitan water recycling plant (WRP). The concentrations of micropollutants were examined in full-scale MF and RO membrane facilities treating real wastewater. The WRP used for this study employs a conventional activated sludge process in the WWTP phase and dual membranes (MF followed by RO) in the advanced water treatment plant (AWTP) phase. The effectiveness of micropollutant removal was investigated at both effluents of the WWTP and the AWTP. The target compounds were selected on the basis of previous detection in wastewater combined with anticipated health and environmental effects or bioaccumulation potential.

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2. Materials and Methods

2.1 *Facility Overview*

The combined WWTP and AWTP considered in this study is located in Australia and receives mainly municipal wastewater. The WWTP consists of a grit removal unit and a diffused air activated sludge process, configured in the following sequence; anaerobic, primary anoxic, aerobic and secondary anoxic zones. The solids retention time (SRT) in the activated sludge process is around 13 days and the hydraulic retention time (HRT) is 24 hrs. The AWTP comprises of automatic backwashing 400 µm screens, followed by MF and RO processes as shown in Figure 1.

[Figure 1]

The WWTP received 152 ML/day between May 2005 and July 2006, from which it discharged 143 ML/day of effluent water into the ocean. More than 13 ML/day were recycled through the AWTP, which produced 9 ML/day of very high quality water. The product water was delivered to a local industry, where it was mainly used as cooling tower make-up. The reject flow (MF backwash and RO brine), which amounted to 29 % of the AWTP influent, or approximately 3.8 ML/day, was sent back to the head of the WWTP.

Sample Campaigns

Composite raw wastewater samples and grab samples from the secondary effluent and the recycled water were taken as shown in Figure 1. The composite samples were collected by an automatic device at half hour intervals during 24 hour periods. Sample volumes collected were not proportional to the influent flow. All samples were collected in glass bottles (2.5 L), placed on ice and shipped overnight to the laboratory for testing. Sampling was carried out during the following months: May, September, November and December 2005, as well as February, April and June 2006.

2.2 *Target Analytes*

The one-year project was designed to evaluate the occurrence and fate of thirteen micropollutants in the WRP. These compounds represent two main micropollutant groups: endocrine disrupting chemicals (EDCs) (bisphenol A and nonylphenol) and pharmaceutically active compounds (e.g., salicylic acid, diclofenac and carbamazepine) as shown in Table 1 [17, 18, 19, 20, 21, 22, 23, 24, 25].

[Table 1]

The compounds selected for this study have physicochemical properties that are representative of a wide range of organic compounds potentially present in impaired water sources. The target micropollutants were classified into acidic and neutral compounds. Table 1 shows the molecular weight, partitioning coefficient (log K_{ow}), dissociation constant (pK_a) and solubility of the target micropollutants. These characteristics are used in predicting the behaviour of micropollutants under clinical conditions and in environmental assessments.

2.3 *Analytical Methods*

Physicochemical Water Characterisation

Upon receipt of samples in the laboratory, a small portion of each sample (50 to 100 mL) was poured into a glass bottle and allowed to settle before the physicochemical characteristics of the sample were measured.

Total organic carbon contents (TOC) were determined according to Method 5310B [26] using a Shimadzu TOC-V_{CSH} (Total Organic Carbon Analyzer) equipped with ASI-V autosampler [27]. The TOC was determined by measurement of non-purgeable organic carbon (NPOC – the fraction of TOC not removed by gas stripping). The nitrogen content was determined by measuring total nitrogen (TN) using a chemiluminescence detector with a Shimadzu Total Nitrogen Module (TNM1) coupled with the Shimadzu TOC–V_{CSH} [27].

Ultraviolet absorption (UV) was measured at a wavelength of 254 nm according to Method 5910 [26] using a Shimadzu UV-Visible Spectrophotometer (model UV 1700 Phara Spec). Turbidity (T) measurements were performed according to Method 2130 [26] using a turbidity meter (HACH, model 2100N, HACH, S.A/N.V, USA). The electrical conductivity (EC) of samples was measured with a conductivity meter as a surrogate parameter according to Method 2510 [26]. Measurement of pH was performed according to Method 4500-H^+ [26] with a pH meter.

Micropollutant Analysis

Upon receipt in the laboratory, samples were filtered using three different filters: GF/D (2.7 µm) and GF/F (0.7 µm) Whatman filters and 0.48 µm nylon filter membranes (Alltech, Australia). Filtered samples were kept in amber bottles overnight at 4°C. The following day, samples were allowed to reach room temperature and adjusted to pH 2-3 by addition of 4 M sulphuric acid to enhance trapping of acidic compounds on the solid phase extraction (SPE) sorbent. MilliQ water (1 L) was also spiked with a standard mixture of the investigated compounds to confirm recovery of analytes. Samples were analysed in batches consisting of 5-6 samples, spiked samples and a blank. A detailed description of the method of analysis was published by Al-Rifai *et al.* [28].

For SPE, 60 mg Water Oasis HLB sorbent cartridges (Waters, Australia) were used. The SPE was performed on a 24-fold extraction manifold (Supelco, Visiprep 24). The SPE cartridges were conditioned sequentially with 5 mL methyl tert-butyl ether (MTBE), 5 mL methanol and 5 mL MilliQ water prior to use. Extraction of 1 L samples was carried out under vacuum at a flow rate of approximately 15 mL/min. After sample loading, the cartridges were washed with 3 mL (5% v/v) methanol in water. In order to eliminate the presence of water from the eluant, a column of anhydrous sodium sulphate was prepared and fitted under the SPE column before the elution procedure started. The SPE columns were eluted with 5 mL (10% v/v) methanol in MTBE. The elution volume was then evaporated to dryness at 39°C under a stream of nitrogen.

In order to determine PhAC and EDC concentrations, a derivatization step was necessary. The extract residues were dissolved in 300 µL of acetonitrile and then derivatized by adding 100 µL of BSTFA (N,O-bis (trimethylsilyl) trifluoroacetamide) and TMCS (trimethylchlorosilane) (99:1). The analytes were allowed to react for 1 h at 70°C. Finally, 100 µL of fluazifop standards were added to each sample before injection as an instrument internal standard to confirm the accuracy of the volume of each sample injected onto the GC column.

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Identification and Quantification of Compounds

A Shimadzu-GC 17A gas chromatograph equipped with an auto-injector model AOC-20i, a mass detector model QP5000, a Phenomenex Zebron ZB-5 column and a Split/Splitless injector was used for identification and quantification of compounds. The oven temperature program was 100 ^{o}C; 30 ^{o}C/min.; 150 ^{o}C (4 min); 3 ^{o}C/min; 195 ^{o}C; 1 ^{o}C/min; 205 ^{o}C (5 min); 30 ^{o}C/min; 250 ^{o}C (3 min). The injection port was maintained at 270 ^{o}C and operated in splitless mode. Helium was used as a carrier gas (flow rate 1 mL/min) and the interface temperature was held at 270^{o}C. For identification of each analyte, three compound-specific ions were recorded in single-ion monitoring mode (SIM).

Deuterated internal standards (acetaminophen-d_4, carbamazepine-d_{10}, gemfibrozil-d_6, ibuprofen-d_3, 4-n-nonylphenol d_6, phenytoin-d_{10} and salicylic acid-d_6,) were added to the initial water samples and were followed through the entire analytical procedure to improve its accuracy. Quantification was carried out by calculation of the response factor based on the area of the target analyte and deuterated standard.

Method Validation

Extraction recoveries of target compounds were evaluated by determining the concentration in WWTP influent and effluent samples spiked with known concentrations of standards (50 ng/L). The recoveries vary between 70 and 92% and are shown in Table 2. Blanks (non-spiked samples) for PhACs and EDCs were analysed through the entire procedure with every batch and their concentrations were subtracted from the spiked waters.

[Table 2]

Standard calibration curves generated using linear regression analysis gave generally good fits to the data (i.e. $R^2 > 0.97$) over the established concentration range (5-50 ng/L, excluding where this concentration range fell below the detection limits of a particular compound). A five-point calibration was performed daily, and possible fluctuations in signal intensity were checked by injection of standard solution at two concentrations after each 8–10 injections.

The reproducibility of the method was studied by analysing five replicates of the recovery samples to ensure correct quantification. Reproducibility was calculated as errors with a 95% confidence interval, which was found to range from 3.4–9.5%, as shown in Table 2. Method detection limits (MDL) and method quantification limits (MQL) were determined from spiked water samples as the minimum detectable amount of analyte with a signal to noise ratio of 3 and 10, respectively. Method quantification limits ranged from 1-50 ng/L and are given in Table 2.

3. Results and Discussion

3.1 *Characterisation of Untreated and Recycled Water*

Analysis of the raw wastewater quality was conducted along with the secondary effluent and recycled water analyses in order to study the treatment efficiency of both the WWTP and the AWTP. Physicochemical parameters measured at the three sample locations during the period of May 2005 to June 2006 are shown in Table 3. Large variations in measurements were observed throughout the sampling period (e.g., influent TOC varied from 43 to 77 mg/L), which could be associated with the incidence of high rainfall.

[Table 3]

The WWTP effectively reduced TN and TOC in the wastewater by 91% and 72%, respectively (Table 3). Nitrogen is commonly identified as a limiting nutrient in water bodies and careful control of its release is necessary to prevent the eutrophication of sensitive aquatic environments [29]. TN was further reduced to a mean concentration of 0.3-1.0 mg/L in the product water (see Table 3). Similar reductions in nitrogen (91%) by RO filtration were reported by Khan *et al*. [30]. In comparison, the salinity parameter, expressed as EC, was not reduced by the WWTP, but was reduced by 92% in the AWTP.

A clear improvement in water quality can be observed from the WWTP effluent to the recycled water produced by the AWTP, in particular with respect to TOC and TN concentrations (Table 3). The combination of activated sludge, MF and RO proves to be an effective treatment system for the whole range of physicochemical parameters considered. Microfiltration allows for the removal of colloidal particles, microorganisms and other particulate materials of size larger than the membrane pores (in this case 0.1 μm) [14]. The combination of MF with RO then allows for efficient removal of monovalent and multivalent ions, as well as suspended particles, colloids, turbidity and microorganisms (e.g., algae, bacteria and viruses).

3.2 *Occurrence of PhACs and EDCs in Influents*

Concentrations of the PhACs and EDCS in the influent and effluent of the investigated WWTP are summarised in Figure 2. Gemfibrozil, naproxen, acetaminophen and salicylic acid were found in all influent samples. Clofibric acid, phenytoin and diclofenac were the least frequently detected compounds with the lowest concentrations.

[Figure 2]

Acetylsalicylic acid (aspirin), one of the top ten pharmaceuticals dispensed in Australia [31], is easily degraded to salicylic acid, a more active form of the chemical [32]. Salicylic acid was found in the influent at concentrations significantly higher than other target compounds, ranging from 11.1×10^3 to 38.5×10^3 ng/L. This high occurrence of salicylic acid can be linked to its high solubility (see Table 1). The concentrations measured are consistent with those reported in other studies [5, 33-35]. Variations of one order of magnitude in concentrations of salicylic acid were observed over the survey period. The high concentrations of salicylic acid were most likely indicative of higher rates of consumption of salicylic acid in conjunction with other medicines recorded during September 2005. During this time of the year, the recorded minimum and maximum temperatures were 10.6 ^{o}C and 23.0 ^{o}C, respectively, while rainfall was 14.6 mm. Decreased degradation rates of target compounds could be a result of low temperatures. Also, lower rainfall could diminish the effect of dilution during that time.

Ibuprofen had the second highest concentration among the pharmaceutical analytes in this study. The concentrations measured are consistent with those reported by others [7, 22, 36], but are larger by one order of magnitude than observations by Stumpf [37] and Bendz [38]. Ibuprofen is one of the most commonly detected drug residues in surface waters [6].

Acetaminophen (paracetamol) was ranked third among the top ten most dispensed drugs in Australia, with 4.5 million prescriptions in the year 2003 [31]. Acetaminophen was detected in all of the

wastewater samples, with the highest concentrations measured in September 2005 and the lowest concentrations in May 2005 and April 2006. These concentrations were somewhat lower than those previously reported [33, 35].

Carbamazepine was present in the wastewater at concentrations up to 2.5×10^3 ng/L. Since only 2-3% of carbamazepine doses are excreted by the human body unmetabolised [6], the occurrence of carbamazepine's primary metabolite – carbamazepine 10,11-epoxide – should be assessed in future investigations.

The concentrations of PhACs in the influent may be related to higher consumption during the cold season of the year when more illness occurs. The months of September 2005 and June 2006 had the lowest mean temperatures during the sampling campaign, at 23.0°C and 21.8°C, respectively. Contradicting results were obtained by Coetsier *et al*. [39] and Castiglioni *et al*. [40] regarding the significance of seasonal variations in PhAC concentrations. Coetsier *et al*. [39] observed lower concentrations of carbamazepine in the winter months, but no significant seasonal variation in diclofenac and ibuprofen concentrations. Castiglioni *et al*. [40] reported lower ibuprofen loads to a sewage treatment plant during the summer period.

Among the EDCs, bisphenol A was found in the highest concentration range of 6.3×10^3 to 23.0×10^3 ng/L. Bisphenol A is a "slightly to moderately" toxic industrial chemical that is rapidly biodegraded in wastewaters and surface waters [41], but its estrogenic activity has been studied widely, making it a priority endocrine disrupting compound [42].

The concentration of nonylphenol in samples was determined as up to 1.1×10^3 ng/L. The amount of measured nonylphenol only represents 27% of the nonylphenol ethoxylates (NPnEOs – nonionic surfactants which are used in household and industrial applications), while the remainder is constituted of 61% as NP_1EO (nonylphenol mono-ethoxylate) and 12% as NP_2EO (nonylphenol diethoxylate) in the influent of WWTPs. Under anaerobic conditions, NPnEOs biodegrade to yield the most toxic 4-substituted monoalkylphenol (4-nonylphenol) [43].

3.3 *Removal of PhACs and EDCs by WWTP processes*

Removal efficiencies of the target compounds in the WWTP were calculated as relative amounts to the influent concentrations using equation (1);

$$R=\frac{C_i - C_e}{C_i}\cdot 100\% \qquad (1)$$

where C_i and C_e are the concentrations measured in the influent and effluent of the WWTP, respectively. Results of these removal efficiencies are presented in Figure 3.

[Figure 3]

All the acidic pharmaceuticals were removed efficiently by the WWTP, with average removals ranging from 77 to near 100% and variabilities of 3.5–8%, with the exception of diclofenac which was removed at efficiencies of 57 to near 100% with a variability of 40%. This high variability in diclofenac removal was related to infrequent detection at low concentrations. Furthermore, this compound has the largest molecular weight, the lowest aqueous solubility and is one of the most hydrophobic acidic compounds tested. This may affect its biodegradability. In general, the removal efficiencies found in this study

were consistent with those found in other treatment plants using activated sludge as secondary treatment process [34, 37]. The removal efficiencies for single compounds can vary greatly from one WWTP to another depending on the type of treatment applied (e.g. biological and physicochemical) and the residence time of water in the primary sedimentation tank [44].

Highly variable removal efficiencies have been reported for ketoprofen and naproxen, with respective removals ranging from 40–65% and 40–90% in Spain [44] and from 51– near 100% and 55–98% in Finland [22]. In this study, ketoprofen removal ranged from 83–93% and naproxen removal from 85–98%. This variability can be partly explained by the different hydraulic retention times of WWTPs [44], and by the low hydrophilic nature of naproxen and ketoprofen (log $K_{ow}\approx3$) [36] and their low biodegradability [38].

Salicylic acid had the highest removal efficiencies, which can be attributed to the microbial and chemical degradation processes incurred during the treatment as described by Nakada [36]. Acetaminophen was found to be eliminated efficiently due to its biodegradability. In Germany, acetaminophen was detected in less than 10% of all sewage effluents and was not detected in river water [34].

Carbamazepine was found to have a relatively low removal efficiency compared to the other target compounds. This can be partly explained by its hydrophilic nature (log $K_{ow}<3$) and chemical stability [45]. Clofibric acid and phenytoin were removed to below detection limit by the WWTP. However, due to infrequent detection at low concentrations, no conclusions can be drawn.

Removal efficiencies for bisphenol A were above 90%, which is consistent with findings of other studies [9, 36]. Clara *et al*. [9] concluded that the nearly complete removal of bisphenol A in some WWTPs is mainly due to biodegradation, which is highly dependent on the activated sludge process SRT. No bisphenol A removal was observed in a highly loaded WWTP operating at low SRTs (1–2 days).

Nonylphenol had relatively low removal rates in this study, as was reported by Nakada *et al*. [36] and Clara *et al*. [9] for WWTPs in Austria and Japan. More recently, Clara *et al*. reported that 90% of the nonylphenol and its ethoxylates (NPnEO) were removed in the effluent of Austrian WWTPs, with more than 85% due to biotransformation [46]. Conversely, the removal of nonylphenol in a WWTP which implemented an activated sludge process was ascribed to its accumulation onto sewage sludge as a result of its lipophilic nature [47].

With the introduction of the activated sludge process, the efficiency of modern sewage treatment plants at removing micropollutants from sewage influent has increased significantly. The removal mechanisms for pharmaceuticals in activated sludge processes include biological and chemical degradation, biotransformation, as well as adsorption to and subsequent removal in waste sludge [50]. A comparison of the performance of an activated sludge process and a trickling filter for wastewater treatment suggests that microbial activity plays an important role in PhAC removal [34]. Understanding of the complex biological process is currently not sufficient to tailor removal towards the broad range of micropollutants that are abundant in wastewater effluents.

The results of this study show that micropollutants are not eliminated completely in sewage effluents. Therefore, implementing advanced technologies such as membrane processes is necessary for adequate removal of micropollutant compounds.

3.4 *Removal of PhACs and EDCs by MF/RO Systems*

The concentrations of PhACs and EDCs were reduced as these compounds passed through the treatment plant. Concentrations of target compounds in the recycled water demonstrate that the MF/RO

process is an effective treatment method for the removal of the targeted compounds, except for bisphenol A (Table 4). Bisphenol A was detected in all product water samples in concentrations ranging from 20-464 ng/L. These concentrations are not surprising since bisphenol A had the second highest concentration among the compounds found in the influent. Many researchers have investigated the removal of bisphenol A by NF and RO membranes [11, 51-55]. Despite the fact that these studies were conducted in laboratory or small-scale plants, the bisphenol A removal efficiencies observed were comparable to the results found in the present study.

[Table 4]

Clofibric acid, diclofenac and phenytoin were not detected in any product water samples. Other compounds (nonylphenol, gemfibrozil, ibuprofen, ketoprofen, naproxen, acetaminophen, primidone, salicylic acid and carbamazepine) were detected in most product water samples at a maximum concentration of 120 ng/L (Table 4). Recent studies have shown that the concentrations of micropollutants in the effluent of WWTPs are often higher than the product water concentrations measured in this study by more than one order of magnitude [6, 36, 44, 56]. This shows that the addition of a MF/RO dual membrane system to a conventional treatment plant will significantly increase the removal rate of PhACs detected in the wastewater.

More than half of the analysed recycled water in this study was found to have PhACs at concentrations below 100 ng/L. However, no comprehensive drinking water guidelines currently exist for PhACs and risk assessments conducted to date have not reported that the micropollutants of PhACs detected in drinking water pose a significant health risk to consumers. Likewise, although EDCs are not designed for human consumption, no evidence exists to suggest that their presence in drinking water has adverse health effects. Humans are commonly exposed to PhACs and EDCs in greater doses through medication, food intake or application of personal care products than through drinking water [57]. Using a simple calculation based on our findings, the maximum possible intake of gemfibrozil from drinking water in a lifetime (assuming an intake of 2L per day over 70 years) would be 1.7 mg/ lifespan, while a single therapeutic dose of gemfibrozil is typically 100 mg or more. Much work is yet to be carried out to investigate the long term effects of such micropollutants taking into account the bioaccumulation of contaminants discharged to the environment.

4. Conclusions

Population growth, over consumption, climate change and severe droughts are limiting the availability of fresh water throughout the world, and particularly in Australia. As an attempt to meet increasing water demand, water authorities are increasingly considering and implementing water recycling. The fate of micropollutants in water resources is becoming an issue of concern as the consumption of micropollutants and the intensity of water recycling increases.

The purpose of this research was to investigate the effectiveness of WWTPs and AWTPs at removing EDCs and PhACs. The one-year monitoring study revealed the following:

The activated sludge, MF and RO processes proved to be a reliable combination for the removal of the whole range of physicochemical parameters considered. The low values achieved (i.e. EC, TN, TOC) demonstrate the significantly improved quality of recycled water. This high quality permits the use of recycled water for a number of applications in which the presence of pollutants such as salts, organic matter or nutrients could have undesirable effects.

Thirteen micropollutants (including PhACs and EDCs) were investigated over a whole year in the WRP. Gemfibrozil, naproxen, acetaminophen and salicylic acid were found in all WWTP influent samples tested, with the highest concentrations for salicylic acid. Other PhACs and EDCs were detected less frequently in the influent. Removal efficiencies in the activated sludge process was generally incomplete, with a variation from 77% to not detectable, and varied throughout the year. Furthermore, the MF and RO membrane processes contributed to the removal of micropollutants in the AWTP, such that concentrations below 0.1 µg/L were reached in the recycled water for all pollutants except bisphenol A.

Although concentrations of less than 500 ng/L were measured in the product water for bisphenol A, the presence of this compound is a serious concern and a challenging task for researchers and practicing engineers using RO systems for water recycling.

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Figure Captions

Figure 1. Schematic diagram of the Wastewater Treatment Plant (WWTP) and Advanced Water Treatment Plant (AWTP).

Figure 2. Removal efficiencies of PhACs and EDCs in the WWTP and AWTP. Each box represents one compound and each bar represents one sample. Removal percentages for both the WWTP and AWTP were calculated respective to the compound concentration in the WWTP influent.

Figure 3. Concentrations of PhACs and EDCs (ng/L) in (A) influent and (B) effluent of the WWTP.

Figure 1

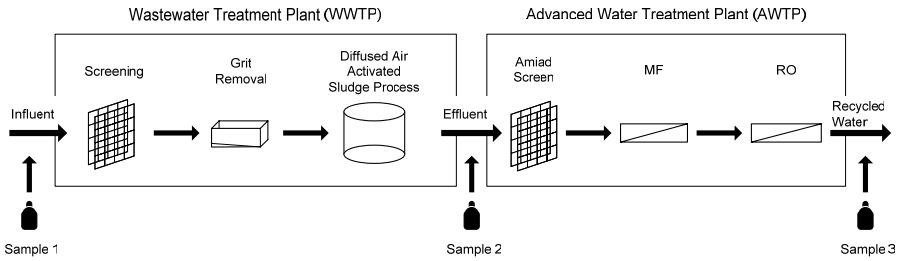

Figure 2

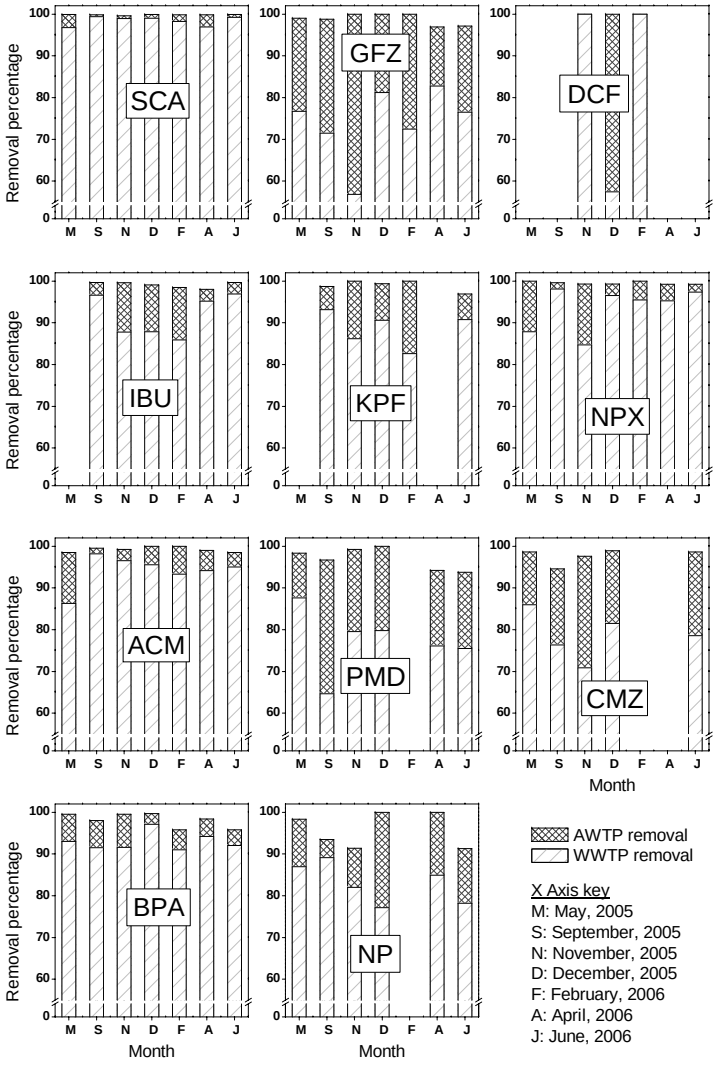

Figure 3

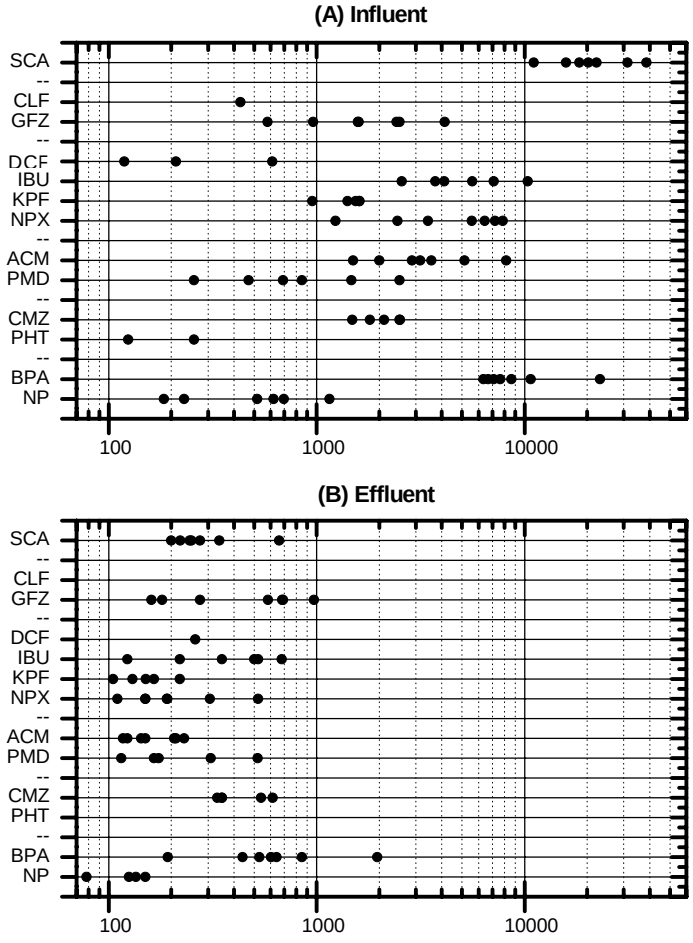

Table 1 General characteristics of target compounds

Compound	Acronym	Classification	Mol Weight (g/mol)	log Kow	pKa	Water Solubility (mg/L)	Solubility index [a]
Acidic							
Salicylic acid	SCA	Analgesics	180.2 138.1 (aq) [b]	2.26[17], 1.19[18]	2.97[17], 3.5[18]	2240[17], 5000[18]	SS
Clofibric acid	CLF	Antihyperlipidemics	214.5	2.57[19]	N/A [c]	583[19]	VSS
Gemfibrozil	GFZ	Antihyperlipidemics	250.2	4.39-4.77[20, 21]	4.42-4.7[20, 21]	19[20, 21]	
Diclofenac	DCF	Non-steroidal, anti-inflammatory	318.1 296.2 (aq) [b]	4.51[20], 0.7[18]	4.0-4.2[18, 20, 22]	2.4[20]	PI
Ibuprofen	IBU	Non-steroidal, anti-inflammatory	206.2	3.14-4.5[17-21, 23]	4.9-5.7[17, 18, 20-22]	21[17, 20, 21], 10[18]	PI
Ketoprofen	KPF	Non-steroidal, anti-inflammatory	254.3	3.12[20, 23]	4.45[20, 22]	51[20]	PI
Naproxen	NPX	Non-steroidal, anti-inflammatory	230.2	3.18[21, 23]	4.15-4.5[21, 22]	16[21], 159[20]	PI
Neutral							
Acetaminophen	ACM	Analgesics	151.2	0.46 -0.89[18, 21]	9.4-9.7[18, 21]	100[18]	VSS
Primidone	PMD	Analgesics	218.3	0.85[20]	12.26[20]	500[18, 20]	VSS
Carbamazepine	CMZ	Anticonvulsant	236.3	2.3-2.93[18, 21, 23]	7[18], 0.37-2[21]	10[18],18[21]	PI
Phenytoin	PHT	Anticonvulsant	252.3	2.47[5]	8.33[5]	10[24]	
Bisphenol A	BPA	Non-steroidal estrogenic	228.3	3.32[17, 23]	10.1[25]	120[17, 25]	PI
Nonylphenol	NP	Non-steroidal estrogenic	220	4.48[23, 25]	10.3[25]	5[25]	PI

[a] Solubility index: ($_{PI}$): practically insoluble <100mg/L; ($_{VSS}$): very slightly soluble 100-1000mg/L: ($_{SS}$): slightly soluble: 1-10g/L

[b] (aq): aqueous

[c] N/A: not applicable

Table 2 Recoveries of the target PhACs and EDCs in the influent

Compound	Recovery (%)			SD [a] (%)	MQL [b] (ng/L)
	Min	Max	Mean		
Salicylic acid	75	85	80	1.7	1
Clofibric acid	81	92	87	2.0	8
Gemfibrozil	80	90	86	1.8	2
Diclofenac	75	92	84	3.0	23
Ibuprofen	85	92	88	1.3	6
Ketoprofen	75	95	87	3.4	9
Naproxen	84	92	89	1.4	4
Acetaminophen	76	84	79	1.4	2
Primidone	71	82	77	1.9	12
Carbamazepine	75	91	82	3.4	5
Phenytoin	76	89	80	2.4	50
Bisphenol A	85	92	89	1.2	2
Nonylphenol	70	85	78	2.7	1

[a] SD: Standard deviation (number of samples: 5)

[b] MQL: Method quantification limit

Table 3 Characteristics of WWTP influent and effluent and WRP product water

Characteristics	Influent [a]			Effluent [a]				Product Water [a]			
	Min	Max	Mean ± SD[c]	Min	Max	Mean ± SD[c]	%Removal	Min	Max	Mean± SD[c]	% Removal
pH	7.0	7.2	7.1 ± 0.1	7.6	7.9	7.8 ± 0.1	–	6.2	8.1	7.3 ± 0.8	–
TOC (mg/L)	43.0	77.4	60.9 ± 14.2	8.7	49.1	19.6 ± 18.0	72.2	0.8	1.8	0.8 ± 0.6	95.1
TN (mg/L)	38.6	52.5	45.1± 6.0	0	6.7	3.7 ± 2.9	90.9	0.3	1.0	0.6 ± 0.3	84.4
EC (mS/cm)	1.7	3.1	2.2 ± 0.6	1.6	2.9	2.1 ± 0.6	9.4	0.1	0.2	0.2 ± 0.1	92.1
Turbidity (NTU)	77.0	245.0	152.0 ± 77.9	4.6	24.6	11.7 ± 7.9	92.5	0.9	6.9	3.8 ± 2.2	66.7
UV (1/cm) [b]	0.88	1.77	1.40 ± 0.3	0.00	2.90	0.92 ± 1.22	45.2	0.00	0.14	0.04 ± 0.06	95.0

[a] Number of samples: 7

[b] UV absorption was measured at 254 nm

[c] SD: Standard deviation

Table 4 Concentrations of PhACs and EDCs (ng/L) in recycled water

Months	Compounds												
	SCA	CLF	GFZ	DCF	IBU	KPF	NPX	ACM	PMD	CMZ	PHT	BPA	NP
May	16	ND [a]	25	ND	ND	ND	ND	23	42	35	ND	44	20
Sep	60	ND	28	ND	30	20	35	40	49	80	ND	464	15
Nov	70	ND	ND	ND	18	ND	24	27	7	50	ND	30	60
Dec	30	ND	ND	ND	50	10	39	ND	ND	20	ND	20	ND
Feb	30	ND	ND	ND	55	ND	ND	ND	ND	ND	ND	300	ND
Apr	20	ND	50	ND	50	ND	50	20	40	ND	ND	121	ND
Jun	20	ND	120	ND	20	44	55	44	29	35	ND	450	54
Mean [b]	35	ND	56	ND	37	25	41	31	33	44	ND	204	37
Standard deviation	21	ND	44	ND	16	17	12	11	16	23	ND	197	23

[a] ND: not detected

[b] Mean of positive detection