Comparison of the behaviour of selected micropollutants in a membrane bioreactor and a conventional wastewater treatment plant

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Abstract Micropollutants as pharmaceutical active compounds (PhACs), residuals of personal care products or endocrine disrupting chemicals are of increasing interest in water pollution control. In this context the removal efficiencies of sewage treatment plants (STPs) are of importance, as their effluents are important point sources for the release of those substances into the aquatic environment. Activated sludge based wastewater treatment is the worldwide prevalently used treatment technique. In conventional plants the separation of treated wastewater and sludge occurs via sedimentation. A new development is the application of membrane technology for this separation step. The studies focus on the influence of the solids retention time (SRT) on the removal efficiency, as the SRT is the most important parameter in the design of STPs. A conventional activated sludge plant (CASP) and a membrane bioreactor (MBR) were operated at different SRTs. The substances selected are the antiepileptic carbamazepine, the analgesics diclofenac and ibuprofen, the lipid regulator bezafibrate, the polycyclic musks tonalide and galaxolide and the contraceptive 17α-ethinylestradiol. No significant differences in the removal efficiency were detected. Due to the absence of suspended solids in the MBR effluent, substances with high adsorption potential could be retained to slightly higher amounts.

Keywords Conventional sewage treatment; membrane bioreactor; pharmaceuticals; polycyclic musks; solids retention time; wastewater treatment

Introduction Several micropollutants were detected in surface waters in different European countries and the presence of those substances is well documented in the literature (Stan and Heberer, 1997; Heberer et al., 1998; Ternes, 1998; Jørgensen and Halling-Sørensen, 2000). Pharmaceutical as well as personal care products residues are suspected to enter rivers, streams and surface water through the effluent of sewage treatment plants (STPs). Some persistent pharmaceuticals were tracked from municipal sewage to drinking water (Heberer, 2002). Therefore the elimination of these substances within the STP is of elementary interest and must be taken into consideration already during the design process. One of the most important parameters for the design of STPs is the solids/sludge retention time (SRT) or sludge age. The SRT describes the mean residence time of the biomass within the system. It is related to the growth rate of microorganisms, as only such organisms can be detained and enriched within the system that are able to reproduce themselves during this time. According to this definition, STPs with high SRTs allow the enrichment of slowly growing bacteria and consequently the establishment of a more diverse biocoenosis with broader physiological capabilities (e.g. nitrification or the capability for certain elimination pathways) than in STPs operating at low SRTs. In conventional activated sludge plants (CASP) the aeration tank and the final clarifier form one process unit. The separation of treated sewage and sludge occurs in the clarifier via sedimentation, wherefore the ability to sediment is an important selection criterion. The operating biomass concentration in
the mixed liquor is limited by the capacity of the clarifier. In membrane bioreactors this parameter is of negligible influence, as the separation is achieved via membrane filtration. So the plant can be operated at higher biomass concentrations resulting in smaller plant sizes. The most important advantage of MBRs is the complete retention of suspended solids, thus reducing the emissions to the dissolved fraction. At the other hand higher costs and higher requirements in operation and maintenance compared to conventional systems are the dominating disadvantages. In wastewater technology in general micro- and ultrafiltration membranes are used.

During the last few years the number of realized STPs equipped with membrane technology increased notably. Especially in regions with no suitable receiving waters or where treated wastewater is used for groundwater infiltration, MBRs are suitable alternatives to conventional systems.

This study compares the removal capacities regarding selected micropollutants of a full scale conventional activated sludge plant with a pilot plant equipped with an ultrafiltration membrane. The substances selected for this study are the antiepileptic carbamazepine, the analgesics diclofenac and ibuprofen, the lipid regulator bezafibrate, the polycyclic musks tonalide and galaxolide and the contraceptive 17α-ethinylestradiole. According to Sattelberger (1999) the consumed quantities for these compounds in Austria in 1997 amounted to 6,334 kg/year for carbamazepine, 6,143 kg/year for diclofenac, 6,696 kg/year for ibuprofen, 4,474 kg/year for bezafibrate and 4 kg/year for ethinylestradiole in Austria in 1997. No data on the consumption of tonalide and galaxolide were available. Hohenblum et al. (2003) document measured concentrations of these two musk fragrances in different products such as air fresheners, ironing aids or fabric softeners.

Materials and methods

Analytical method

Two different detection methods were used for the analysis of the above mentioned compounds. Ibuprofen, diclofenac, bezafibrate, galaxolide and tonalide were separated and analysed by GC-MS detection after derivatisation with diazomethane and a clean up step by silica gel chromatography. LC-MS/MS was employed for the analysis of carbamazepine. Ionisation of the analytes was done by electro spray ionisation in positive mode. Prior to the sample extraction a surrogate standard (dihydrocarbamazepine or meclofenamic acid) was added to the samples. Two different solid phase extraction phases (cyclohexane (CH)− and ENV+ − phase) were employed for LC-MS/MS sample preparation. The samples were acidified in the case of the C-18 and CH − solid phase extraction cartridges, whereas the addition of a neutral EDTA buffer solution was necessary for the ENV+ phase. The water samples were extracted and enriched by C-18 solid phase cartridges prior to the analysis with GC-MS. To overcome problems due to ion suppression in the LC-MS method, recoveries of the surrogate standard and measurements of multiple dilutions of the extracts were performed. The limit of quantification (LOQ) was set at 20 ng l−1 and the detection limit (LOD) at 10 ng l−1.

The sample preparation for the determination of the hormones included liquid-liquid extraction with ether, followed by SPE with ENV+ cartridges eluted by methanol. After evaporation to dryness a derivatization with dansyl chloride occurred. Prior to extraction surrogate standards were added. The analysis was performed using LC-MS/MS using an injection volume of 20 µl. Ionisation of the analytes was done by electrospray ionisation in positive mode. The limit of detection LOD was 1 ng.l−1 (ARCEM, 2002).

Conventional activated sludge plant (CASP)

The investigated sewage treatment plant (STP) serves a rural community in the South-East
of Austria. The STP is designed for 7,000 population equivalents (pe) (based on 100 g COD pe⁻¹ day⁻¹), of which about 3,000 pe are connected to the sewer system actually. The treatment plant is charged with domestic sewage from a separated sewer system without industrial influents and with strong seasonal fluctuations due to local viniculture. These strong fluctuations are illustrated by means of the COD in the influent (Kroiss, 2002). While the mean COD concentration in the influent amounts to 1,080 mg l⁻¹, the maximum two weeks mean is 1,900 mg l⁻¹ and peak values of more than 6,000 mg l⁻¹ COD were measured in daily composite influent samples. This plant is a typical exponent for a wide range of STPs realized in Austrian rural areas.

The sewage plant is operated with simultaneous sludge stabilization and simultaneous phosphorus precipitation with ferric chloride (FeCl₃) and intermittent and simultaneous nitrification and denitrification. The STP consists of screen and grit chamber, two aeration tanks \( V = 2 \times 1,546 \text{ m}^3 \) and two secondary clarifiers \( V = 2 \times 949 \text{ m}^3 \text{ and } A = 2 \times 304 \text{ m}^2 \) for final sedimentation. The excess sludge is removed very infrequently resulting in a very high sludge retention time (SRT).

Membrane bioreactor (MBR)
The membrane bioreactor was a pilot scale plant situated at the premises of the CASP and charged with the same wastewater. The wastewater is pumped from the grit chamber to a feed tank, from which the denitrification vessel is charged. In addition to the mechanical treatment of the full scale plant a 1 mm punched sieve is installed at the extraction point, reducing the amount of particles and fibres entering the plant. The nitrification as well as the nitrification tank had a reactor volume of 2.5 m³ each. From the nitrification the sludge is pumped to the external situated cross flow membrane module (ultrafiltration). The sludge is recycled to the nitrification vessel and the permeate is stored in a permeate tank. The membrane module was regularly backwashed with treated wastewater from the permeate tank. An internal sludge recycle connected nitrification and denitrification to avoid biomass accumulation in the nitrification and to obtain further nitrogen removal. The excess sludge abstraction occurred from this internal sludge recycle. A flow scheme of the MBR pilot plant is shown in Figure 1.

Sampling
In the MBR three different SRTs of 10 days, 30 days and about 100 days were installed. After a lead time, necessary for the development of an equilibrated system and the establishment of an adapted biocoenosis, the sampling of the two plants was performed. The lead time amounted to 2 to 3 times the SRT. The samples taken were daily composite samples of influent and effluent. The samples of both plants were filtered and the influence of the filters was investigated with spiked standards. No effect of the used filters on the dissolved concentrations was detected.

![Figure 1 Flow scheme of the MBR pilot plant](https://iwaponline.com/wst/article-pdf/50/5/29/420102/29.pdf)
In addition to these analyses conventional wastewater parameters such as chemical oxygen demand (COD), total phosphorus (TP), phosphate (PO$_4$-P), total nitrogen (TN), ammonia (NH$_4$-N), nitrite (NO$_2$-N), nitrate (NO$_3$-N) and suspended solids (SS) were measured.

**Mass balances**

The plausibility of the measured values was controlled via mass balances of phosphorus, nitrogen and COD (Nowak *et al*., 1999; Nowak, 2000). Beside data control, the mass balances also serve to characterize and to illustrate the stability of the systems. Especially the phosphorus balance is a qualified control instrument because the phosphorus load of the influent must be recovered in effluent and excess sludge in prorated distribution. The results of the phosphorus mass balance concerning influent and effluent as well as the specific excess sludge production showed a good correlation and confirmed the process stability of the investigated STPs. To compare the results of the different sampling campaigns the sludge retention time related to 20°C (SRT 20°C) is calculated for both plants. This calculation is based on the COD mass balance, the temperature in the bioreactor and a correction coefficient ($f_T = 1.072$) for the temperature. The calculated solids retention times related to 20°C are summarized in Table 1.

In the full scale plant no possibility to manipulate the SRT existed. Therefore the results of the MBR are compared to results of lab scale plants operated at different solids retention times, too. The results of these laboratory experiments are described in Clara *et al*. (2003).

Based on these flow streams, mass balances for the investigated micropollutants were calculated. The mass balances were based on solved concentration measurements. The adsorbed mass fractions, eliminated via the excess sludge were calculated using specific equilibrium adsorption coefficients $K_D$. The used $K_D$ values are results from the POSEIDON project (POSEIDON, 2002). Those for galaxolide and tonalide are taken from Artola-Garicano *et al*. (2003). As for adsorption processes the organic fraction (volatile suspended solids VSS) of the sludge is relevant (Schwarzenbach *et al*., 1993), this sorption coefficients were normalized to the organic content. This normalization to the organic matter of the sludge takes into account the higher sorption potential of the sludge of the MBR, as the organic matter content is higher in respect to the sludge of the CASP. The calculation with these adsorption equilibrium coefficients is suitable as the hydraulic retention time was higher than the time necessary to reach the adsorption equilibrium.

As the degradation pathways and therefore possible degradation intermediates for most of the investigated micropollutants are not known and have not been measured, degradation is used as a synonym for removal.

**Results and discussion**

The lipid regulator bezafibrate and the analgesic ibuprofen were completely eliminated in both systems. The removal rates reached more than 95% in the conventional system as well as in the membrane bioreactor (Figure 2). Ibuprofen is metabolised to hydroxyl-ibuprofen and carboxy-ibuprofen. These metabolized forms and the unchanged ibuprofen were observed to be completely degraded in STPs (Buser *et al*., 1999), confirming the results obtained in the present study.

**Table 1**  Solids retention time (SRT), temperature (T) and SRT related to 20°C (SRT 20°C) of the two plants

<table>
<thead>
<tr>
<th>Sampling campaign</th>
<th>Conventional activated sludge plant</th>
<th>Membrane bioreactor</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SRT (d)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>May 2002</td>
<td>114</td>
<td>16.8</td>
</tr>
<tr>
<td>July 2002</td>
<td>237</td>
<td>22.1</td>
</tr>
<tr>
<td>December 2002</td>
<td>52</td>
<td>6.8</td>
</tr>
</tbody>
</table>
For bezafibrate a reduction in the removal is observed during the last sampling campaign in December 2002. In both plants the effluent concentrations are higher than during the prior samplings. This fact resulted in lower removal rates, which amounted to about 76% in the MBR and to about 90% in the CASP. As the SRT and the SRT20°C are equal in both systems this behaviour cannot be explained by different operational settings. During the lab scale experiments at SRT 20°C of more than 5 days removal rates of more than 90% were observed, wherefore the sludge age should not be responsible for the lower elimination rate. It seems that for the removal of bezafibrate the temperature is of elementary importance. At low temperatures the degradation rates decrease.

The measured carbamazepine concentrations (mean values and standard deviation) and the calculated removal rates for bezafibrate and ibuprofen for the different sampling campaigns are illustrated in Figure 2.

The antiepileptic drug carbamazepine is not removed in any of the investigated treatment systems. Carbamazepine does not adsorb to the sludge (POSEIDON, 2002) and the effluent concentrations vary within the same range as the influent concentrations. As this antiepileptic drug is not degraded biologically and the pore size of the membrane allows no additional retention, the efficiency of the two systems is equal (see Figure 2). Heberer (2002) summarizes in his review that carbamazepine is not significantly removed (less than 10%) in STPs. Also during soil passage no significant removal was observed (Zessner et al., 2003; Preuss et al., 2001).

A more differentiated behaviour was detected for diclofenac (Figure 3). In the conventional STP removal rates between 40% and 60% were calculated for the different sampling campaigns. Interpreting these results, the very high SRT has to be pointed out. During the first sampling campaign in the MBR, during which the plant was operated with a SRT of
about ten days, no removal was detected. That result corresponds to the results of the lab scale experiments (Clara et al., 2003). In the lab scale facilities even at higher SRTs no removal of diclofenac occurred, whereas the removal in the MBR increased with higher SRT. The higher SRT operated is only one possible explanation, as in both systems running at similar SRT 20°C (during the December sampling campaign) comparable removal rates were obtained. But also in the literature the data concerning the removal of diclofenac vary strongly. Whereas Ternes (1998) reports removal rates up to 69% in different STPs, Zwiener et al. (2001) observed only 1–5% removal in pilot plants.

For the two polycyclic musks, tonalide and galaxolide, similar results were obtained during the three sampling campaigns. About 80% of the influent load is removed (Figure 4), whereby the effluent concentrations in the MBR were slightly lower than the effluent concentrations of the CASP. But as these two substances are very hydrophobic (Artola-Garicano et al., 2003) and tend to adsorb to the sludge, for an estimation of the mass flux abstracted from the system via the wasted sludge based on measurements of dissolved concentrations, the applied specific adsorption coefficients \( K_D \) are essential. For the calculation in this study \( \log K_D \) values of 2.6 for tonalide and of 2.7 for galaxolide were used (Artola-Garicano et al., 2003). These two substances were not investigated in the laboratory experiments. As only poor literature data is available, no comparison of these results with measurements at other STPs could be performed.

The oral contraceptive \( 17\alpha \)-ethinylestradiole (EE2) was eliminated in the two investigated systems in comparable amounts. The results of the different sampling campaigns vary notable. During the first two samplings in May and July 2002 removal rates of 60% to 70% were obtained in the conventional system as well as in the membrane bioreactor. The December sampling resulted in a 60% removal of EE2 in the CASP, whereas no removal was observed in the MBR. One reason for this can be a possible outlier in chemical analysis.

**Figure 3** Relative tonalide and galaxolide loads in influent, effluent and excess sludge of the MBR and the CASP

**Figure 4** Relative loads of \( 17\alpha \)-ethinylestradiole in influent, effluent and excess sludge of the MBR and the CASP
In one effluent sample of the MBR a concentration significantly higher than the influent concentrations was measured. Ignoring this value, a removal of about 65% is calculated, which would correspond to the results of the prior samplings and the result calculated for the CASP. The mean effluent concentrations of both plants varied between 1 and 3 ng l\(^{-1}\) during all samplings. This result corresponds to different monitoring studies on EE2 concentrations in STP effluents, summarized in Heberer (2002). Baronti et al. (2000) reported removal rates of EE2 of about 85% in an activated sludge treatment plant.

**Conclusions**

All investigated substances reported comparable results within the two investigated sewage treatment systems. For some of the investigated substances (e.g. diclofenac) a SRT dependency of the achieved removal was observed. This corresponds to the results of lab scale experiments. No significant differences between the removal rates in the conventional activated sludge plant and the membrane bioreactor were observed. Those results confirm the assumption that the ultrafiltration membrane does not lead to any further retention of the observed compounds. This conclusion seems plausible since no additional retention concerning filtration effects could be expected due to the molecular size of the investigated compounds. The biological degradation is dependent on the SRT. This statement is also valid for the case that the studied substances are degraded only in a co-metabolism as a co-substrate, because in this case the SRT necessary for the degradation of the primary substrate is the relevant parameter.

The conventional plant, which was compared with the MBR had nearly no suspended matter in the effluent (mean value 4.5 mg l\(^{-1}\) SS). Therefore no differences could be detected for any of the selected substances in this plant. In dependency on the suspended solids concentration in the effluent and the specific adsorption coefficient the importance of the sorbed fraction increases. Therefore, especially for substances which strongly tend to adsorb to the sludge, slightly better effluent qualities have to be expected for membrane bioreactors, due to the absence of suspended solids in the effluent of the treatment plant.

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