Ozonation of nursing home wastewater pretreated in a membrane bioreactor

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ABSTRACT

Nursing home (NH) wastewater was pretreated in an ultrafiltration membrane bioreactor (MBR) and subsequently ozonated in a pilot plant in order to evaluate the elimination of pharmaceutically active compounds (PhACs). Dosing of the pre-treated wastewater with 5 mg ozone (O₃) L⁻¹ led to the elimination of >50% for nearly all investigated PhACs in the ozonation plant, whereas dosing 10 mg O₃ L⁻¹ increased elimination to >80%. A total hydraulic retention time of 12.8 min proved sufficient for PhAC elimination. Specific ozone consumption and influent dissolved organic carbon (DOC) (8.2–9.5 mg L⁻¹) were in similar ranges for all three performed trials. Combining the MBR with subsequent ozonation at a dosage of 5 mg O₃ L⁻¹ achieved elimination of >90% and effluent concentrations below 250 ng L⁻¹ for nearly all the investigated PhACs. Influent concentrations of the MBR were comparable to those found in municipal wastewater. Thus, the recommended dosage for PhAC elimination of 5 mg O₃ L⁻¹ (i.e. a specific consumption of 0.6 g O₃*(g DOC)⁻¹) is in the same range as for municipal wastewater. However, due to a smaller plant size, the specific costs for treating NH wastewater would significantly exceed those of treating municipal wastewater.

Key words | organic micropollutants, oxidation, pharmaceutically active compounds, residential care home wastewater

ABBREVIATIONS

5-MBT Methylbenzotriazole
AA 4-Aminoantipyrine
AAA 4-Acetylaminoantipyrine
ALL Allopurinol
ATL Atenolol
Br⁻ Bromide
BrO₃⁻ Bromate
BTA 1H-Benzotriazole
BUP Bupropion
CBZ Carbamazepine
DCF Diclofenac
DOC Dissolved organic carbon
FAA 4-Formylaminoantipyrine
HRT Hydraulic retention time
HPLC High performance liquid chromatography
Hy-BUP Hydroxybupropion
IBC Intermediate bulk container
IBU Ibuprofen
MS Mass spectrometry
MBR Membrane bioreactor
MET Metoprolol
MTF Metformin
N-Ac-SMX N-Acetyl-sulfamethoxazole
ND Not determined
NH Nursing home
NH₄-N Ammonium nitrogen
NO₂-N Nitrite nitrogen
NO₃-N Nitrate nitrogen
O₃ Ozone
OMP Organic micropollutant
PAN Pantoprazole
PhAC Pharmaceutically active compound
SAC₂₅₄ Spectral absorption coefficient at 254 nm
SMX Sulfamethoxazole
SRT Sludge retention time
TMD Tramadol

INTRODUCTION

The removal of pharmaceutically active compounds (PhACs) and other organic micropollutants (OMPs) from wastewater has been the object of several studies (Luo et al. 2014; Bui et al. 2016). Due to their incomplete elimination in state-of-the-art wastewater treatment, OMPs are released into water bodies and might pose a risk to the aquatic environment (Bui et al. 2016). The application of different advanced wastewater treatment processes has already been investigated. Membrane processes are currently not suitable for large-scale OMP elimination: ultrafiltration and microfiltration processes and their applications in membrane bioreactors generally do not achieve high OMP elimination whilst nanofiltration and reverse osmosis processes show good OMP elimination but induce high costs and energy demand (Siegrist & Joss 2012; Luo et al. 2014). Advanced oxidation processes involving the in-situ generation of hydroxyl radicals as strong oxidants have also been the object of multiple studies (Miklos et al. 2018). However, their relatively high energy demand compared to ozonation alone and other processes restrict these from large-scale applications in wastewater treatment for the time being. Based on the present findings, the most suitable treatment technologies for removing PhACs and OMPs from both municipal and hospital wastewater have proven to be oxidation via ozonation and adsorption to granular or powdered activated carbon (Luo et al. 2014; Verlicchi et al. 2015; Bui et al. 2016; Gomes et al. 2017). In the process of ozonation, ozone (O₃), due to its instability, is generated on site at the wastewater treatment plant (WWTP), generally from liquid oxygen. The ozone/oxygen gas mixture produced is subsequently brought into contact with the wastewater by the means of diffusers or injectors. OMPs are oxidized via two different pathways. The direct pathway involves a fast, direct and selective reaction of ozone with a multitude of compounds. Here, electron-rich parts of the compounds such as deprotonated amines, double bonds or activated aromatic systems are attacked by ozone. In the indirect pathway, a rapid and unselective radical chain reaction takes place, induced by the decomposition of the unstable ozone molecule into hydroxyl (-OH) radicals (Gottschalk 2010). During ozonation reactions, the compounds are generally not completely mineralized but only partially oxidized and turned into transformation products. A very important transformation product of ozonation is bromate, which results from bromide present in wastewater due to chemical and waste industries, for example (Soltermann et al. 2016). Due to its carcinogenic effects, bromate has a limit value of 10 μg L⁻¹ in the German drinking water ordinance. The occurrence of bromates increases in proportion to the amount of bromide and the amount of surplus ozone in the ozonation inflow (Beier 2010). To remove transformation products, a biologically active post-treatment (e.g. polishing pond or sand filter with biological activity, cf. Zhang et al. 2017) is usually considered necessary to minimize potential environmental risks (Abegglen & Siegrist 2012). Apart from the elimination of OMPs, ozonation also contributes to wastewater disinfection (Abegglen & Siegrist 2012). Typically applied specific ozone dosages for OMP elimination in municipal wastewater, normalized to the influent dissolved organic carbon (DOC) content of the ozonation plant, range from 0.25 to 1.5 g O₃*(g DOC)⁻¹ (cf. Antoniou et al. 2015; Lee et al. 2015).

Regarding the removal of PhACs from hospital wastewater in a bench-scale ozonation plant, Lee et al. (2014) found that 38 out of the 56 investigated OMPs were eliminated by more than 90% at a specific ozone dosage of 0.5 g O₃*(g DOC)⁻¹. Hansen et al. (2016) stated that 21 of 33 PhACs investigated were eliminated to more than 90% in batch experiments at dosages below 1 g O₃*(g DOC)⁻¹. Transferred ozone dosages between 0.45 and 2 g O₃*(g DOC)⁻¹ were applied in the PILLS (Pharmaceutical Input and Elimination from Local Sources) project, which investigated the effectiveness of ozonation on hospital wastewater that had been pre-treated in a membrane bioreactor (MBR). The project partners used a pilot-scale ozonation plant and a dosage of 1.08 g O₃*(g DOC)⁻¹ was selected to further assess the cost-benefit of treating hospital wastewater (McArdell et al. 2011; Nafo et al. 2012; Kovalova et al. 2013). Concerning contact times, values between 12 and 23 min in the ozonation plant were investigated. Based on his results from treating hospital wastewater with ozone, 7.5 to 15 min of contact time are recommended by Beier (2010).

Up to now, several studies have focused on ozonation kinetics and found that the elimination of OMPs depend on the substance-specific kinetic constants, both for the direct and indirect reaction pathways (Huber et al. 2003; von Sonntag & von Gunten 2012; Lee et al. 2013; Gomes et al. 2017; Mathon et al. 2017). Other factors influencing the effectiveness of ozonation processes include nitrite
concentrations, the organic load of the wastewater (Abegglen & Siegrist 2012) and pH (for some compounds, cf. Bourgin et al. 2017). Therefore an adequate biological pre-treatment of the wastewater is required, in order to minimize competing reactions. Apart from conventional activated sludge treatment, the use of an MBR can be considered a suitable pre-treatment. Its application has already been thoroughly investigated in several studies focusing on hospital wastewater treatment (Beier 2010; Beier et al. 2011; Kovalova et al. 2012; Verlicchi et al. 2015). In addition to an adequate biological pre-treatment, the elimination of selected PhACs as well as some wastewater disinfection was observed (Luo et al. 2014; Verlicchi et al. 2015).

These studies have so far shown the suitability of ozonation for the removal of PhACs and other OMPs from both municipal wastewater and wastewater from hospitals. Everding et al. (2015) showed that nursing homes can, similarly to hospitals, be potential point sources for emissions of PhACs into wastewater. Due to demographic changes, an increase in the impact of such institutions is to be expected in the future and the emissions of PhACs from such institutions should therefore not be neglected. To our knowledge, no previous studies on the occurrence of PhACs in nursing home wastewater and techniques for their removal have been performed so far. Therefore, the aim of this study was to assess the concentrations of PhACs contained in nursing home wastewater and to investigate the effectiveness of ozonating wastewater from this type of institution. This study could therefore improve the knowledge both of ozonation performance and decentralized treatment of wastewater from healthcare facilities for PhAC elimination. In order to ensure adequate biological pre-treatment, an MBR was used to treat the wastewater prior to transfer to the ozonation plant. In the MBR process, biological treatment and membrane filtration (ultrafiltration or microfiltration) are combined (Luo et al. 2014). Compared to conventional activated sludge processes, the operation takes place at higher sludge retention times (SRTs) and a higher effluent quality is achieved, especially regarding suspended solids and microbiological parameters (Siegrist & Joss 2012). Therefore, the effectiveness of both ozonation alone and the combination of ozonation with the MBR were investigated in this study.

MATERIALS AND METHODS

Nursing home

The nursing home (NH) investigated had an average of 271 residents in 2010, 2011 and 2012. The specialism of the NH was psychiatric diseases. Approximately three out of four residents were aged 60 and above. Residents younger than 60 mostly suffered from psychiatric diseases or alcoholism. The sewer collecting the NH’s wastewater, which was mostly collected in a separate sewer system, started in a village with 800 inhabitants and served a 33,500 population equivalent WWTP (cf. Herrmann et al. 2015). A separation of the NH sewage from the municipal wastewater of the village upstream was not feasible, so slight dilution effects by the municipal wastewater were to be expected.

Sampling

A simplified flow diagram of the sampling and treatment process is shown in Figure 1. 4,000 L of wastewater were collected from the mixed sewer system on three separate sampling days (2 × Wednesday (NH2, NH3), 1 × Thursday (NH1)) from approximately 7.00 am to 7.00 pm to cover a whole day. During the nighttime, no sampling was performed as water consumption was very low and hence no high loads of PhACs were expected.

At the beginning of each sampling, the sewer receiving the NH wastewater was slightly dammed with sandbags to achieve a sufficient water level in the sewer. A submerged centrifugal pump was placed into the sewer. A screen basket was attached to the pump in order to keep away coarse solids. The water was collected in four intermediate bulk containers (IBCs) with a filling capacity of 1,000 L.
each. IBCs were filled at a continuous pumping rate for 3 hours each. Transport to the trial plant took place overnight.

Pre-treatment in the MBR

After homogenization at the trial plant, the wastewater was stored in three cooled containers (storage at 4 °C) and one non-cooled IBC that served as feed for the MBR. A composite sample of the raw wastewater was made up from the four containers and served as the sample for the influent concentration. (For NH2 an additional sample of each of the four delivered IBCs was taken. Results were consistent with the results of the composite sample.) Biological pre-treatment took place in an MBR with flat sheet ultrafiltration membranes (pore size: 0.04 μm, 10 m² area). The focus of the research project for this study was on wastewater treatment from health care facilities (Pinnekamp et al. 2015). In order to keep the bioocoenosis of the MBR alive in between the trials, the MBR was continuously supplied with wastewater from the effluent originating from the primary clarifier of the local WWTP. The MBR treatment procedure was the following: filling of the MBR took place until a predefined level was reached. Then a denitrification phase of 20 min began. After 5 min of pre-aeration, a cycle of 8 min filtration (with aeration) and 2 min of relaxation was initiated and repeated until a pre-defined level was reached and filling of the MBR restarted. Usually, five cycles of filtration and relaxation were needed. The MBR was operated at a flow rate of 50 L h⁻¹, corresponding to a net flux of 5 L m⁻² h⁻¹. Hence, the hydraulic retention time (HRT) of the wastewater was around 12 hours. To keep the dry matter content at approximately 12 g L⁻¹, part of the activated sludge was removed from the reactor periodically. Consequently, the sludge retention time in the MBR could not be precisely determined, but values exceeding 100 days were assumed.

To maintain the dry matter content at approximately 12 g L⁻¹ for treating the NH wastewater and to simultaneously minimize dilution, a previously calculated amount of activated sludge was discharged from the MBR. Then, the MBR was filled up with raw sewage from the IBC and brought back into operation. The first 1,000 L of NH wastewater were filtered at a lower flow rate (32 L h⁻¹) than the remaining 3,000 L (50 L h⁻¹), so that microorganisms could adapt to the new wastewater by being exposed to a slowly and gradually increasing charge of the NH wastewater for more than 1 day. As Hashimoto et al. (2016) have shown, the microbial communities in MBRs seem to be flexible regarding their metabolic activity. The first 1,000 L of permeate were discharged as they could still contain a high amount of residual wastewater from the local WWTP (cf. Figure 1). Within 3 days after delivery, the water was pumped twice a day from the cooled IBCs to the receiving IBC outside the trial plant, to reach the ambient temperature before entering the MBR. The obtained permeate was regularly transferred to a cooled IBC. In total, 2,400 L of permeate were obtained for further investigations. The obtained permeate was cooled at 4 °C in the dark to inhibit OMP elimination (Vanderford et al. 2011) and ozonated in the pilot plant as soon as possible (cf. Figure 1).

Ozonation plant

The ozonation pilot plant consisted of two 10 L bubble column reactors of 10 cm diameter and 150 cm height each. Ozone was generated from pure oxygen with an Anseros COM-AD 01 generator (Anseros, Germany). In the first reactor, ozone was supplied via a diffusor (pore size of 160 μm). Counter-current and concurrent operation modes were possible. The second reactor served as a post-reactor without further ozone supply. The applied ozone dosages were 2.5, 5, 10 and 15 mg O₃ L⁻¹ and were adjusted via gas flow and ozone concentration in the gas (BMT 964, BMT, Germany). The total HRT for both columns were 12.8 and 25.0 min (cf. Table 1); these were adjusted through the inlet pump and a magnetic inductive flowmeter. Samples were taken from the influent and the effluents of reactors 1 and 2 (ozone concentration measurement with LASA100 tube tests; Dr. Lange, Germany). To ensure safe working conditions, an ozone

<table>
<thead>
<tr>
<th>Ozone dosage</th>
<th>2.5 mg O₃ L⁻¹</th>
<th>5 mg O₃ L⁻¹</th>
<th>10 mg O₃ L⁻¹</th>
<th>15 mg O₃ L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total HRT</td>
<td>12.8 min</td>
<td>25.0 min</td>
<td>12.8 min</td>
<td>25.0 min</td>
</tr>
<tr>
<td>NH 1</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>NH 2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>NH 3</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 1 | Investigated settings
destroyer for the off-gas and a sensor monitoring the ambient air were installed and the container housing the plant was constantly ventilated with fresh air.

To determine the optimal trial duration, pre-testings were performed with permeate from the MBR that was supplied with local wastewater. The pilot plant was operated at a flow rate of 100 L h\(^{-1}\) and an ozone dosage of 5 mg O\(_3\) L\(^{-1}\). Samples were taken at the outflow of the second reactor every 10 min for a total testing time of 120 min. The spectral absorption coefficient at 254 nm (SAC\(_{254}\)) was determined. The SAC\(_{254}\) values dropped as a consequence of ozonation to a level that was significantly lower than the initial one and remained constant after a period of approximately two and a half HRTs. Therefore, in the trials described below, sampling started after 2.5 HRTs for each trial setting. Moreover, preliminary tests for the concurrent and counter-current operation modes were performed. Since a better ozone transfer was determined – by measuring the ozone concentration in the off-gas – in the counter-current operation mode, the subsequent trials were conducted in this mode.

**Analytics**

The scope of investigations included selected PhACs and benzotriazoles as well as various wastewater standard parameters shown in Table 2. Sample preparation for OMP analysis was performed by means of solid phase extraction (Autotrace SPE workstation, Thermo Scientific, USA). Analytical determination of the OMPs was carried out via high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS). Chromatographic separation was performed on a Hypersil Gold aQ (150 × 2.1 mm) column (Thermo Scientific, USA) and a LTQ Orbitrap system (Thermo Scientific, USA) was used for mass spectrometric detection. Xcalibur software (Thermo Scientific, USA) was used for the control of the HPLC-MS system as well as for data analysis. The investigated OMPs had a limit of quantification of 10 ng L\(^{-1}\).

DOC (Dimatoc 2000, Dimatec, Germany) and SAC\(_{254}\) (Lambda 25, Perkin-Elmer, USA) were measured to quantify the organics in the wastewater. The investigated nitrogen and bromine anions were measured according to DIN EN 10304-1 (Deutsches Institut für Normung 2009). Nitrite (NO\(_2\)-N) reacts rapidly with ozone resulting in the formation of nitrate (NO\(_3\)-N). For the chemical oxidation of nitrite 3.43 g O\(_3\)\(^{\ast}\)g N\(^{-1}\) are needed (Abegglen & Siegrist 2002). Due to possible counter oxidations of nitrite, the nitrogen parameters were therefore added to the scope of investigation.

**RESULTS AND DISCUSSION**

**Influent concentrations of PhACs and elimination in the MBR**

Regarding the influent concentrations of the PhACs into the MBR, most of the values were between 1,000 and
10,000 ng L\(^{-1}\) as shown in Figure 2, where on the left axis the mean MBR influent and effluent concentrations for selected PhACs that were detected in all the performed trials are shown. The minimum and maximum influent concentrations into the MBR are indicated with the error bars. The highest values were measured for AAA, a compound with divergent values, and for VAL, a PhAC with very homogeneous values in the trials. The lowest influent concentration was measured for bupropion with 84 ng L\(^{-1}\). Moreover, Figure 2 shows the mean influent concentrations (and mean effluent concentrations) of the subsequent ozonation plant.

The mean eliminations in the MBR are shown in Table 3. In the MBR, 7 of the 13 PhACs shown were eliminated by more than 50% on average: AA, BUP, Hy-BUP, IBU, MTF, MET and VAL with AA, IBU and MTF even achieving an average elimination >90%. The remaining PhACs showed a low average elimination, with even slightly negative values for PAN (−21%) and TMD (−11%). These negative eliminations are due to effluent concentrations that were higher than the influent concentrations for trials NH2 and NH3.

The behavior of the PhACs in the MBR is generally in compliance with other studies investigating the pre-treatment of hospital wastewater with an MBR. In their review study, Verlicchi et al. (2015) similarly report low to moderate elimination for DCF, TMD, MET and CBZ and similarly high degrees of elimination for IBU and VAL, respectively. Kim et al. (2014) observed elimination of up to 100% for IBU and around 99% for MTF for an MBR treating municipal wastewater. Regarding the metamizole metabolites, AAA, AA and FAA, Verlicchi et al. (2015) reported higher values than those observed in the present project; a potential explanation may be found in the discontinuous feeding of the MBR with wastewater from the NH. Elimination processes in the MBR comprise biodegradation, sorption to the suspended solids and stripping by aeration (Siegrist & Joss

<table>
<thead>
<tr>
<th>Mean elimination in %</th>
<th>AAA</th>
<th>AA</th>
<th>FAA</th>
<th>CBZ</th>
<th>DCF</th>
<th>BUP</th>
<th>Hy-BUP</th>
<th>IBU</th>
<th>MTF</th>
<th>MET</th>
<th>PAN</th>
<th>TMD</th>
<th>VAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR</td>
<td>32.4</td>
<td>93.0</td>
<td>37.9</td>
<td>25.4</td>
<td>32.8</td>
<td>79.2</td>
<td>73.9</td>
<td>90.3</td>
<td>95.6</td>
<td>58.0</td>
<td>−20.6</td>
<td>−10.8</td>
<td>85.2</td>
</tr>
<tr>
<td>Ozonation</td>
<td>99.9</td>
<td>92.3</td>
<td>99.8</td>
<td>99.3</td>
<td>99.4</td>
<td>82.9</td>
<td>71.4</td>
<td>71.6</td>
<td>26.8</td>
<td>79.4</td>
<td>76.3</td>
<td>98.6</td>
<td>66.5</td>
</tr>
</tbody>
</table>
As most PhACs are of rather low volatility and high hydrophility, stripping processes are of minor importance and the main pathways for OMP elimination seem to be biodegradation and sorption to activated sludge (Siegrist & Joss 2012). Biodegradation processes seem to be the main trigger for VAL and MET elimination in the MBR – two PhACs with relatively high elimination in this treatment step. Regarding DCF elimination, biodegradation and sorption appear to have only a minor impact and are considered of even lower importance for elimination of CBZ and TMD (Kovalova et al. 2012). All in all, PhAC elimination in the MBR ranges from modest to high depending on the specific characteristics of the substances towards sorption or biodegradation. The increased SRT compared to conventional activated sludge treatment can also lead to higher biodegradation for some PhACs (Luo et al. 2014). Further information on PhAC behavior in the MBR can be found in Pinnekamp et al. (2015). Among the possible reasons for the negative elimination found in the present study for TMD and PAN could be transformation processes and/or even sampling variation (cf. Verlicchi et al. 2012). The influent concentrations of PhACs in the NH wastewater fed into the MBR did not significantly differ from those of municipal wastewater, which was also described by Herrmann et al. (2015).

Due to the fact that the wastewater was stored in a cooling container before the ozonation, there are differences between the concentrations of the MBR effluent and the ozonation influent, as is shown in Figure 2. The reasons for this can be found in the differences in the samples analyzed; yet transformation processes in the cooling container cannot be fully excluded. However, for most of the PhACs, the difference between the two concentrations is relatively small; the biggest differences are observed for AAA and BUP, two PhACs that also have significant differences in their influent concentrations.

### Ozonation plant

**Elimination of wastewater parameters**

SAC$_{254}$ of the ozonation plant influent was approximately 0.200 m$^{-1}$ for all trials. Elimination of SAC$_{254}$ increased with a higher ozone dosage and was approximately 40% for all three trials at a dosage of 5 mg L$^{-1}$ ozone and 12.8 min total HRT. For DOC, elimination of usually less than a few percent was observed, with the exception of approx. 30% elimination for a dosage of 15 mg L$^{-1}$ in trial NH2 at an HRT of 12.8 min. Influent DOC values for all trials were around 9 mg L$^{-1}$. For both parameters, no increase in elimination was achieved at a higher HRT. The low elimination of DOC underlines the assumption that the substances are not completely mineralized but turned into transformation products (Bourgin et al. 2018).

Values for Br$^-$ and BrO$_3^-$ were below the limit of quantification of 0.1 mg L$^{-1}$ for all trials, both in the influent and the effluent. In comparison, bromide levels found in municipal WWTP are also typically below 0.1 mg L$^{-1}$, unless a major bromide source is present in the catchment area (Soltermann et al. 2016). Table 4 contains the mean influent and effluent values of the nitrogen parameters, conductivity and pH for the trials at a HRT of 12.8 min. Effluent values refer to the second reactor of the ozonation plant. NO$_2^-$N influent values were low in all trials. No competing reactions that would have a strong effect on OMP elimination were expected. The relatively high NO$_3^-$N values in the influent of the ozonation plant show that nitrification in the MBR performed well (especially regarding the low NH$_4^+$N ozonation influent values), but denitrification showed potential for some optimization. The influent pH values of the ozonation plant show that the wastewater was almost neutral and no significant change took place during ozonation trials. All in all, the values for all wastewater parameters were in similar ranges for all three trials.

| Table 4 | Mean influent and effluent values for NH ozonation trials (n: number of values) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mean value      | NH1 influent (n = 1) | NH1 effluent (n = 1) | NH2 influent (n = 3) | NH2 effluent (n = 3) | NH3 influent (n = 3) | NH3 effluent (n = 3) |
| pH              | [-] | 6.80 | 6.89 | 7.05 | 6.99 | 7.05 | 7.08 |
| Conductivity    | [μS cm$^{-1}$] | 561 | 540 | 643 | 642 | 668 | 666 |
| NH$_4^+$N       | [mg L$^{-1}$] | 0.2 | 0.26 | 0.2 | 0.2 | 0.82 | 0.83 |
| NO$_2^-$N       | [mg L$^{-1}$] | <0.09 | <0.05 | 0.12 | <0.05 | 0.42 | <0.07 |
| NO$_3^-$N       | [mg L$^{-1}$] | 27.4 | 27.5 | 31.7 | 32 | 38 | 38 |
Elimination of PhACs

The relative elimination of PhACs at ozone dosages of 5 mg O₃ L⁻¹ and 10 mg O₃ L⁻¹ (12.8 min HRT) for effluent samples of the first and the second reactor respectively is shown in Figure 3 (left axis) for trial NH2. The ozonation plant influent concentration of each PhAC is shown on the right axis. The highest influent concentrations were measured for AAA. AA and BUP had very low influent concentrations with 96 and 41 ng L⁻¹, respectively. All other concentrations were between 150 and 4,050 ng L⁻¹.

For some PhACs (AAA, AA, FAA, CBZ, DCF and TMD) elimination via ozonation was already higher than 80% at a dosage of 5 mg O₃ L⁻¹ and did not rise in the second reactor nor with a higher dosage as the limit of quantification (10 ng L⁻¹) had already been reached. Other PhACs, such as IBU, MET and PAN underwent a significant increase in elimination both with a higher ozone dosage and with the additional reaction volume of the second reactor. These results show that even without further ozone, reactions occurred in the second reactor.

Figure 4 shows a comparison of the elimination of PhACs in trial NH2 at a dosage of 5 mg O₃ L⁻¹ at HRTs of 12.8 and 25 min respectively. Doubling the HRT neither led to any increases (e.g. AA, AAA, BUP, CBZ, DCF) nor to a considerable increase in PhAC elimination (e.g. MTF, MET, IBU, VAL). Thus, doubling the retention time would not be beneficial for PhAC elimination. The trends obtained in the figures shown for NH2 were confirmed in trials NH1 and NH3.

Figure 5 shows the proportion of the investigated OMPs that were eliminated to three different degrees in the ozonation plant (0–50%, 50–80%, and >80%) for each trial. The applied ozone dosages and the corresponding specific ozone consumption c_{spec} are shown. The specific ozone consumption refers to the specific mass of ozone consumed per g of inlet DOC and is calculated from the difference of ozone transferred from the gaseous into the liquid phase minus the ozone remaining in the liquid phase of the reactor (Gottschalk 2010). The eliminations refer to an HRT of 12.8 min and the effluent of the second reactor.

The varying total number of investigated OMPs per trial is due to the fact that elimination degrees could not be determined for each investigated OMP for every trial. For instance, the influent concentration of SMX was below the LOQ of 10 ng L⁻¹ for trial NH2 whereas trial NH2 with a dosage of 5 mg O₃ L⁻¹ was the only trial with influent ALL concentrations exceeding the LOQ. The three trials show quite a homogenous elimination of OMPs. At a dosage of 5 O₃ mg L⁻¹, almost all of the substances were eliminated to at least 50%. Applying a dosage of 2.5 mg O₃ L⁻¹ for NH3 did achieve significantly lower elimination: 12 of the...
18 OMPs investigated were eliminated to less than 50%. Increasing the dosage led to higher elimination degrees; this could also be observed for ATL and the corrosion inhibitors BTA and 5-MBT. Some PhACs could not be eliminated to more than a certain degree because the LOQ had already been reached (e.g. N-Ac-SMX for NH2) and are annotated in bold italics in brackets in the figure. Specific ozone consumptions and influent DOC concentrations (8.2–9.5 mg L\(^{-1}\)) were in similar ranges for all three trials.

The tested ozonation plant was able to successfully eliminate PhACs from NH wastewater. For trials NH2 and NH3, the average ozone input was 4.84 mg O\(_3\) L\(^{-1}\) for ozone dosages of 5 mg O\(_3\) L\(^{-1}\), and 9.36 mg O\(_3\) L\(^{-1}\) for all ozone dosages of 10 mg L\(^{-1}\). Yet in the effluent of the trial plant,
residual ozone concentrations (with an average of 0.33 mg O₃ L⁻¹ for trials NH2 and NH3 at a total HRT of 12.8 min) were measured in the liquid phase. Hence, an optimized reactor design with a better ozone input and thus a higher transferred ozone dose might still increase PhAC elimination or lead to a lower specific ozone consumption for achieving the same degree of elimination.

The degree of elimination varied for the different substances. Table 5 shows an overview of the required specific ozone consumption (c_{spec}) that was necessary to achieve elimination of more than 80% of the respective PhACs at an HRT of 12.8 min. With a specific ozone consumption of 0.27 g O₃*(g DOC)⁻¹ CBZ, DCF and SMX were transformed to more than 80%. This corresponds to the high specific reaction constants (k: 10⁴–10⁶ Ms⁻¹) of these PhACs with ozone found in other studies (Huber et al. 2005; Dodd et al. 2006; Mathon et al. 2017). For an elimination above 80% of BUP, Hy-BUP, the metimazole metabolites (AAA, AA and FAA), N-Ac-SMX and TMD a specific ozone consumption of 0.37 g O₃*(g DOC)⁻¹ was required. The reaction constants found in other studies for N-Ac-SMX and TMD (Dodd et al. 2006; Zimmermann et al. 2012) show a high reactivity with OH-radicals, in the range of those found for CBZ, DCF, SMX, but have a lower reactivity with ozone than the afore-mentioned PhACs. Kovalova et al. (2013) observed elimination of >85% for AA and of 96% and 99% for FAA and AA, respectively, at their lowest investigated specific ozone dosage of 0.64 g O₃*(g DOC)⁻¹. For IBU, PAN, MET and VAL the necessary specific ozone consumption in the current research was ca. 0.6 g O₃*(g DOC)⁻¹. These PhACs either show a moderate (i.e. MET) or low reactivity with ozone and a high reaction constant with OH-radicals (e.g. IBU). Further explanations can be found in von Sonntag & von Gunten (2012). Accordingly, with a specific ozone consumption of 0.59 g O₃*(g DOC)⁻¹, a high number of PhACs were eliminated satisfactorily. The anti-diabetic MTF proved to be refractory towards ozone, even at a specific ozone consumption of 1.40 g O₃*(g DOC)⁻¹. Nevertheless, its concentration in the wastewater after the MBR pretreatment was max. 300 ng L⁻¹. Its biological degradability and resistance to ozone has already been shown in a previous study (Scheurer et al. 2012).

**Combined MBR and ozonation**

Even though the primary task of the MBR was to pre-treat the wastewater and decrease the nutrient and organic load, a partial elimination of some PhACs in the MBR was also observed and increased the overall elimination of PhACs in the combination of MBR with subsequent ozonation. Figure 2 shows on the right axis the mean elimination percentages of PhACs for a combination of MBR and ozonation at an ozone dosage of 5 mg L⁻¹ and a HRT of 12.8 min. As shown previously, only a few PhACs were eliminated significantly in the MBR whereas the subsequent ozonation achieved a more or less significant elimination of all PhACs shown, with the exception of MTF. Mean effluent concentrations of all PhACs were below 250 ng L⁻¹, except for VAL (894 ng L⁻¹). Seven PhACs (AAA, AA, FAA, CBZ, DCF, BUP and TMD) even had effluent concentrations below 20 ng L⁻¹. The combination of the MBR and an ozone dosage of 5 mg O₃ L⁻¹ achieved an elimination of more than 90% for each PhAC, with the exception of PAN and BUP, which nevertheless had low effluent concentrations of 47 ng L⁻¹ and 10 ng L⁻¹ (corresponding to the LOQ), respectively.

The results obtained show that with a combination of pre-treatment in an MBR and ozonation, a very good elimination of PhACs can be achieved at a dosage of 5 mg O₃ L⁻¹, which corresponds to an specific ozone consumption of 0.6 g O₃*(g DOC)⁻¹ and relates to results from municipal WWTPs (Abegglen & Siegrist 2012; Antiou et al. 2013; Lee et al. 2015). The combination of MBR and ozonation is therefore an effective solution to remove PhACs. However, due to a smaller plant size, the specific costs and the energy demand (cf. Kovalova et al. 2013; Mousel et al. 2017) for treating NH wastewater would significantly exceed those of treating municipal sewage. Also, the low abatement of DOC in the ozonation step indicates the formation of transformation products that ought to be retained for a further treatment step. Since research (Hübner et al. 2015; Bourgin et al. 2018) has shown that some of the transformation products may not even be retained in these treatment steps, suitable bioassays to evaluate the performance of ozonation and possible post-treatment are needed prior to implementing full-scale ozonation of NH wastewater.

**CONCLUSIONS AND OUTLOOK**

With the investigated trial plant consisting of a combination of MBR and ozonation, a high removal of PhACs from the wastewater of a nursing home specializing in psychiatric diseases was achieved at a dosage of 5 mg O₃ L⁻¹ and an HRT of 12.8 min. The investigated PhACs showed similar behavior to previous studies on ozonation, yet the investigations...
on NH wastewater were new compared to previous studies that focused on municipal or general hospital wastewater. The MBR proved to be an adequate pre-treatment for subsequent PhAC removal even though continuous feeding of the MBR with the NH wastewater could still lead to an increased performance regarding both wastewater parameters and PhACs. A lower ozone dosage and lower specific ozone consumption, respectively, might even be allowed for with an optimized design of the ozonation plant. Yet, in this study, transformation products that might require a further post-treatment were not considered but are to be expected, as they have been detected in other studies and are indicated by the low elimination of organic content in the ozonation plant. Moreover, a full-scale treatment of NH wastewater would involve high treatment costs due to the small plant size. Maintenance of the plant is also a question to be addressed. Thus, no general recommendation for treating NH wastewater can be stated, as in this study the influent PhAC concentrations into the MBR did not show a significant difference from those detected in municipal wastewater. However, for nursing homes with large capacities connected to small WWTPs, (pre)-treating the wastewater could prove useful in order to discharge lower PhAC loads to the municipal WWTP. Potential transformation products could be degraded in the subsequent municipal WWTP. Also, investigations into the wastewater from other nursing homes, perhaps with different specialisms than the one in our study (i.e.

<table>
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<tr>
<th>C_{spec} for 80% elimination [g O_3 (g DOC)^{-1}]</th>
<th>PhAC</th>
<th>K_{O_3} [M s^{-1}]</th>
<th>Literature</th>
<th>Source</th>
<th>Comment</th>
<th>K_{OH} [M s^{-1}]</th>
<th>Literature</th>
<th>Source</th>
<th>Comment</th>
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<td>0.27</td>
<td>CBZ</td>
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<td>8.8 ± 10^9</td>
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<td>pH7, T = 25 °C</td>
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<td></td>
<td></td>
<td>&gt;10^6</td>
<td>Mathon et al. (2017)</td>
<td>T = 17 °C</td>
<td>7.5 ± 10^9</td>
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<td>T = 17 °C</td>
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<td>DCF</td>
<td>1×10^6</td>
<td>Huber et al. (2005)</td>
<td>pH7, T = 20 °C, dissociated</td>
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<td></td>
<td>5.5×10^5</td>
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<td>N-AcSMX</td>
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<td>pH7, T = 20 °C, neutral</td>
<td>6.8 ± 0.1×10^9</td>
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<td>TMD</td>
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<td>4×10^3</td>
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<td>9.6 ± 1.0</td>
<td>Huber et al. (2005)</td>
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<td>7.4 ± 1.2×10^9</td>
<td>Huber et al. (2005)</td>
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<td></td>
<td>MET</td>
<td>2 ± 0.6×10^5</td>
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<td>Benner et al. (2008)</td>
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<td>T = 17 °C, p-CBA decay</td>
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</table>
psychiatric diseases) could prove useful, especially taking into account demographic changes and the related expected increases in drug consumption. Whereas the combination of MBR and ozonation can be retained as a suitable option for removing PhACs from NH wastewater as from hospital wastewater, a full-scale implementation ought to be performed after a thorough case-specific effort/benefit assessment.

**ACKNOWLEDGEMENTS**

This work was supported by the German Federal Ministry of Education and Research within the research program ‘Risk Management of Emerging Compounds and Pathogens in the Water Cycle’ (RiSKWa), Project Sauber (+, 02WRS1280A-J). The authors would like to express their thanks to all the project partners. Special thanks go to Dr Wilhelm Gebhardt and the Analytical Laboratory of the Institute of Environmental Engineering as well as to student assistants Vivien Lee, Jan-Hendrik Ehlm and Jens Mesenholl.

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