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Effect of ozonation on the biodegradability of urban wastewater treatment plant effluent

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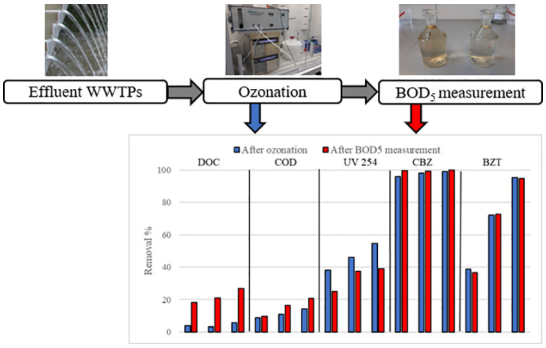
HIGHLIGHTS

- Exposure for BOD_5 measurement is used to assess biodegradability after ozonation.
- Ozonation induces further biodegradation of recalcitrant effluent organic matter.
- An ozone dose-dependent pattern is observed; absolute numbers differ with matrix.
- The results imply abatement of ozonation byproducts and organic micropollutants.
- The results support the relevance of biological post treatment after ozonation.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work aimed to study the effect of ozonation on the organic sum parameters linked to enhanced biodegradability. Laboratory experiments were conducted with the effluent of four Austrian urban wastewater treatment plants with low food to microorganism ratios and different matrix characteristics. Biochemical oxygen demand over 5 days (BOD_5) was measured before ozonation and after application of different specific ozone doses (D_{spec}) (0.4, 0.6 and 0.8 g O_3/g DOC). Other investigated organic parameters comprised chemical oxygen demand (COD), dissolved organic carbon (DOC), UV absorption at 254 nm (UV_{254}), which are parameters that are applied in routine wastewater analysis. Carbamazepine and benzotriazole were measured as reference micropollutants. The results showed a dose-dependent increase in biological activity after ozonation; this increase was linked to the enhanced biodegradability of substances that are recalcitrant to biodegradation in conventional activated sludge treatment. The highest relative change was determined for BOD_5, which already occurred between 0 and 0.4 g O_3/g DOC for all samples. Increasing the D_{spec} to 0.6 and 0.8 g O_3/g DOC resulted in a less pronounced increase. DOC was not substantially decreased after ozonation, which was consistent with a low reported degree of mineralization, while partial oxidation led to a quantifiable decrease in COD (7 to 17%). Delta UV_{254} and the decline in specific UV absorption after ozonation clearly correlated with D_{spec}. In contrast, for COD and biodegradable DOC (BDOC), a clear dose-response pattern was identified only after exposure to BOD_5 measurement. Indications for improved biodegradability were further supported by the rise in the BOD_5/COD ratio. The results indicated that subsequent biological processes have a higher degradation potential after ozonation. The further reduction in biodegradable organic carbon emission by the combination of ozonation and biological post treatment represents another step towards sustainable water resource management in addition to micropollutant abatement.

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1. Introduction

Biological processes, such as the conventional activated sludge process, currently represent the majority of applied processes in wastewater treatment plants (WWTPs) worldwide. However, while conventional organic sum parameters such as COD and BOD are removed to a high degree, others comprising micropollutants are released into the environment unchanged or metabolized (Krzeminski et al., 2019; Quintana et al., 2005). To mitigate this release, particular attention has been directed towards advanced treatments, such as ozonation. The application of ozone is considered a suitable technology to further remove organic micropollutants from urban wastewater and is already implemented on full scale in several countries (Switzerland, Germany, and Sweden) (Baresel et al., 2016; Bourgin et al., 2018; Itzel et al., 2017). The removal efficiencies of various organic micropollutants are influenced by their reactivity with ozone and spontaneously formed hydroxyl radicals (Zimmermann et al., 2011), the ozone dose (Lee et al., 2013) and the composition of the wastewater (Schindler Wildhaber et al., 2015). To reduce ozone scavenging by the organic fraction in wastewater, ozonation is usually applied after biological treatment (Schaar et al., 2010). In biologically treated wastewater, ozone reacts with micropollutants (Lee and von Gunten, 2016; Rizzo et al., 2019) and targets electron-rich moieties, such as olefins, aromatic rings, and amines (von Sonntag and von Gunten, 2012).

During ozone treatment, recalcitrant organic compounds undergo a transformation into more readily biodegradable species, thus increasing their biodegradability.

The aim of this study was to evaluate the impact of ozonation on the biodegradability change of recalcitrant COD in treated urban wastewater. The main parameters of interest were the organic sum parameters BOD, COD, DOC and UV absorption at 254 nm. Additionally, two micropollutants were analysed to validate the experimental setup for ozonation batch tests. Specifically, the study aimed to answer the following research questions:

1) Will an increase in the specific ozone dose typically applied for micropollutant abatement from urban wastewater affect organic sum parameters commonly assessed in wastewater treatment and used as quality criteria and treatment targets for conventional treatment?
2) Does ozonation result in an increase in biodegradability, and is there a correlation with the specific ozone dose?

2. Materials and methods

2.1. Investigated wastewaters

Effluent samples from four Austrian urban wastewater treatment plants (WWTPs) operating at full nitrification and denitrification (high sludge retention time and low food to microorganism ratio) were investigated in this study. Samples were collected in a polyethylene tank (20 L) and filtered with glass fibre filters (0.45 μm) before the experiments for reasons of reproducibility of measurements at the low concentrations expected. Parameter values relevant for this study are listed in Table S1.

Effluent samples were collected as 24-h volume proportional composite samples (CVVT: constant volume, variable time) or grab samples. As the goal of the study was to demonstrate the change in biodegradability due to the effects of ozone on the water matrix, representative daily composite samples were not taken for all experiments.

2.2. Set-up of ozonation experiments

Due to the relevance of the organic matrix for ozone consumption, ozone was dosed in relation to the DOC of the WWTP effluent (specific ozone dose, D_{spec}) in g O_3/g DOC, which has been established as a reference variable and control parameter (Altmann et al., 2014; Buffle et al., 2006; Stapf et al., 2016). Nitrite is another relevant parameter for ozone consumption; thus, the specific ozone dose was compensated by the stoichiometric consumption of 4.34 mg O_3/mg NO_2-N (von Sonntag and von Gunten, 2012). In this study, varying nitrite-compensated D_{spec} in the range of 0.4 to 0.8 g O_3/g DOC was investigated (see Table S3). Three different wastewaters were investigated in the dose-specific experiments (specific target doses of 0.4, 0.6 and 0.8 g O_3/g DOC), while in total, seven effluent samples were studied in detail at a targeted ozone dose of 0.6 g O_3/g DOC, which is considered a typical specific ozone dose for advanced wastewater treatment (Rizzo et al., 2019).

The experimental setup applied to answer the research questions is shown in Fig. S1. Ozone was generated through silent electrical discharge by an ozone generator (Fischer technology model OZ200/5; with flow rate 10 L/h and power 35 W) with oxygen used as feed gas. The generated O_3 is fed to a reactor for the ozone stock solution via ozone-resistant hose material (PTFE) and an aeration stone. The ozone reactor (glass bottle, 2 L) was filled with deionized water that was cooled in an ice bath following the procedure by Lee and von Gunten (2010). The ozone concentration was determined by the indigo method and photometry (ε = 2950 L/mol·cm and λ = 258 nm) (Bader and Hoigné, 1981; von Sonntag and von Gunten, 2012). The ozone concentration in the stock solution varied between 40 and 55 mg O_3/L, depending on the experiments. Different amounts of the stock solution were mixed with deionized water to obtain specific target doses of 0.4, 0.6 and 0.8 g O_3/g DOC.

The ozonation experiments were conducted as batch tests. The wastewater (effluent) was mixed with the O_3 stock solution in 0.5 L-Schott bottles. The mixing ratio of wastewater and O_3 stock solution was based on the targeted D_{spec}, the ozone concentration in the ozone stock solution and the DOC and nitrite in the wastewater (see Table S2). To ensure that the volume and dilution of wastewater was the same in every batch for the dose-specific experiments, the sum of the ozone stock solution and the deionized water was kept constant, as shown in Table S2. Typically, 450 mL of wastewater was diluted by 50 mL of the ozone stock solution and deionized water. Exact values are given in Table S3. All experiments were carried out in triplicate. After a reaction time of approximately 1 h, the samples were aerated with a fine ceramic aerator for 15 min to remove possible residual ozone.

2.3. Analysed parameters

In this study, wastewater samples were analysed for organic sum parameters, nitrite and micropollutants before ozonation, after ozonation and after BOD_5 measurement (see Fig. S1).

Dissolved organic carbon (DOC) was measured with a Total Organic Carbon Analyser TOC-L CPH from Shimadzu using direct method. This method is also known as NPOC (non-purgeable organic carbon), removed, after acidification, TIC from sample and after thermal-catalytic combustion carbon dioxide was detected with Non-dispersive infrared (NDIR) cell. The measured value of the carbon dioxide concentration corresponded to the DOC. A Continuous Flow Analyzer (CFA) - SAN Plus System from Skalar company was used to analyse the nitrite. The concentration was determined based photometric principles. The chemical oxygen demand (COD) was analysed with small tube test (STT) (Hach-Lange DR 2800; Hach-Lange COD Test LCK 314). The biochemical oxygen demand (BOD) was measured after 5 days as BOD_5. ATU was added as a nitrification inhibitor to ensure that the consumed oxygen measured as BOD_5 was limited to respiration for organic matter oxidation. Oxygen was measured with luminescence-based measurement (SP-PSt3-NAU-D5-YOP, PreSens Precision Sensing GmbH) to obtain daily results (Table S8). The sensor (luminophore) was attached to the inner surface of a BOD-bottle (see Fig. S2) and the signal was measured with electro-optical components without direct contact. To validate this method, parallel measurements for the determination of residual oxygen after 5 days were conducted with an oxygen probe (WTW), see Table S5. The spectral absorbance coefficient at 254 nm (SAC_{254} or UV_{254}, respectively) was measured with a UV/VIS spectrometer (Dr. Lange – Cadas 100). Measurements were carried out according to the standardized methods listed in Table S4.

Carbamazepine (CBZ) and benzotriazole (BZT) were analysed as process control parameters to evaluate the validity of the ozonation experiments. This was done by comparing the observed abatement with values expected from literature and own experiments. In that regard, both substances are recommended as process indicator substances for ozonation by Jekel et al. (2015). The two micropollutants show different reactivity during ozonation: CBZ is an indicator substance for highly reactive compounds, whereas BZT represents moderately reactive compounds, reflected by their second-order rate constants $k_{O3} = 3 \times 10^5\ M^{-1}\ s^{-1}$ for CBZ and $k_{O3} = 230\ M^{-1}\ s^{-1}$ for BZT (Huber et al., 2003). Based on the high k_{O3} for CBZ an abatement of ≥80–90% is expected for D_{spec} above 0.4 g O_3/g DOC. A lower abatement can be considered an indication for methodological or experimental shortcomings.

For the analysis of the trace substances, automated online solid-phase extraction (SPE) coupled with LC-MS/MS analysis was used. The signal to noise ratio (S/N) and lower limit of detection (LOD) are given in Table S6.

2.4. Data processing

For reasons of comparison, relative rather than absolute decrease (elimination) or increase of the investigated parameter (P) was calculated according to the following equation:

$$Change\ of\ P_{by\ treatment}\ [\%] = \frac{P_{initial} - P_{after\ treatment}}{P_{initial}} \times 100$$

$P_{initial}$ represents the WWTP effluent, while $P_{after\ treatment}$ can be i) after ozonation experiments or ii) after 5 days of exposure for BOD_5 measurement.

Regression analysis was performed in SigmaPlot 14 (Systat Software, Inc.) with global curve fitting. For increases in the BOD_5 and the BOD_5/COD ratio, nonlinear regression fit with exponential rise to maximum, single, 3 parameters ($y = y_0 + a \times (1 - e^{-bx})$) was applied.

3. Results

3.1. Effect of ozonation on organic sum parameters

3.1.1. BOD_5

To assess the increase in biodegradability, BOD experiments were performed, as increased oxygen consumption indicates higher levels of respiration for the biological oxidation of organic carbon. To assess only the oxygen demand for organic carbon respiration, ATU was added as a nitrification inhibitor. The results of the BOD measurements over a period of 5 days demonstrated the expected increase due to the oxidation of refractory organic matter present in the ozonated WWTP effluent. The BOD_5 concentrations of the 7 investigated samples originating from 4 different WWTPs before and after ozonation with 0.4 to 0.8 g O_3/g DOC (nitrite compensated D_{spec}) are shown in Table S7. BOD concentrations between day 1 and day 5 are listed in Table S8. Before ozonation, the BOD_5 ranged between 0.60 and 1.99 mg/L. This is typical for Austrian WWTPs operating at full nitrification and denitrification with a high sludge retention time (SRT) corresponding to a low food to microorganism (F/M) ratio. The oxidative effect of ozone resulted in a higher BOD_5, ranging from 1.46 to 3.40 mg/L.

In Fig. 1, the relative increase in BOD_5 during the dose-specific experiments is depicted as % of the initial concentration in the effluent samples before ozonation. The highest change already occurred between zero and the lowest investigated ozone dose of 0.45 ± 0.02 g O_3/g DOC for all samples (88.75% for WWTP2c, 21.23% for WWTP3, and 67.46% for WWTP4). A further increase in D_{spec} to 0.65 ± 0.03 g O_3/g DOC resulted in a less pronounced increase. This slight increase in BOD_5 further continued at 0.83 ± 0.05 g O_3/g DOC (96.67% for WWTP2c, 31.70% for WWTP3, and 77.98% for WWTP4).

Fig. 2 shows the relative increase in BOD_5 for the targeted D_{spec} of 0.6 g O_3/g DOC (0.65 ± 0.03), analysing all samples to obtain a broader view of changes to be expected at a D_{spec} typically applied for organic micropollutant abatement. The average BOD_5 concentration reached 94.44 ± 58.23%, with a minimum of 27.47% (WWTP3) and a maximum of 192.78% (WWTP1b), indicating the significance of the different matrices encountered in treated urban wastewater.

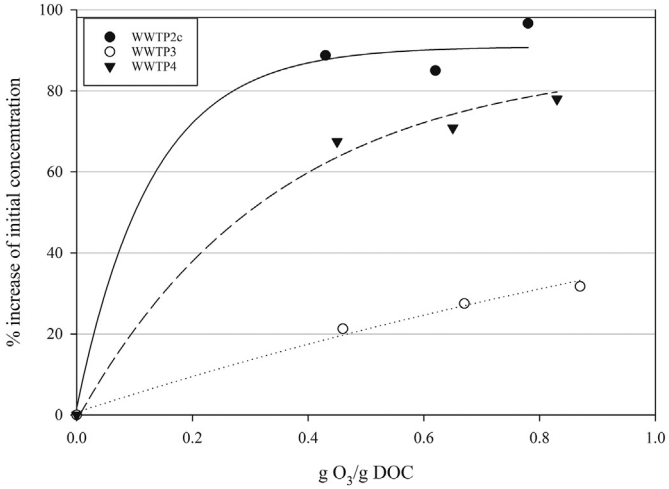

Fig. 1. Dose-specific increase in BOD_5 in WWTP2c, WWTP3, and WWTP4.

3.1.2. DOC

Fig. 3a shows the results of the dose-specific investigation for DOC elimination between 0.45 ± 0.02 (minimum) and 0.83 ± 0.05 (maximum) g O_3/g DOC. Immediately after ozonation, the DOC elimination varied between 2.13% (0.45 g O_3/g DOC for WWTP2c) and 6.71% (0.87 g O_3/g DOC for WWTP3), and a correlation with D_{spec} could not be observed.

In contrast, after the exposure time for the BOD_5 measurement, the elimination of DOC correlated with D_{spec} for all investigated samples (see also Fig. S3). The lowest elimination was 12.06% at 0.43 g O_3/g DOC (WWTP2c), and the highest was 29.44% at 0.83 g O_3/g DOC (WWTP4).

Fig. 3b shows the DOC decrease for the targeted D_{spec} of 0.6 g O_3/g DOC (0.65 ± 0.03), analysing all samples at a D_{spec} typically applied for organic micropollutant abatement. Immediately after ozonation, the mean DOC elimination was 3.36 ± 1.58%, with a minimum at 1.27% (WWTP2a) and a maximum at 6.67% (WWTP4). The decreases of the three samples (WWTP2c, WWTP3, and WWTP4) were on a similar order of magnitude at approximately 4.7%.

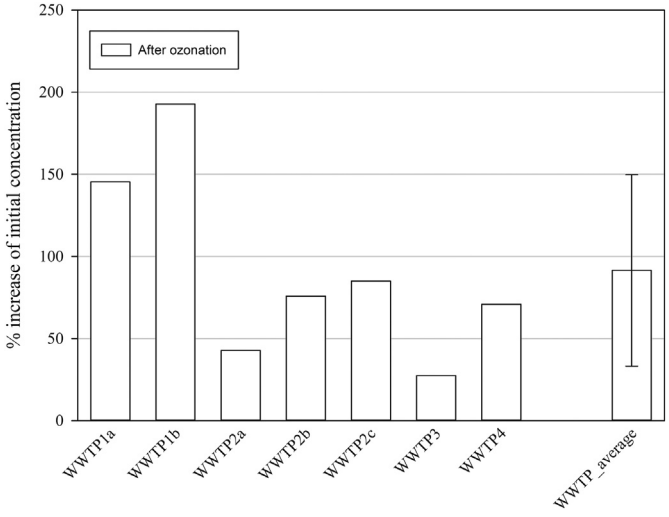

Fig. 2. Increase in BOD_5 at an average D_{spec} of 0.65 ± 0.03 g O_3/g DOC (n = 7).

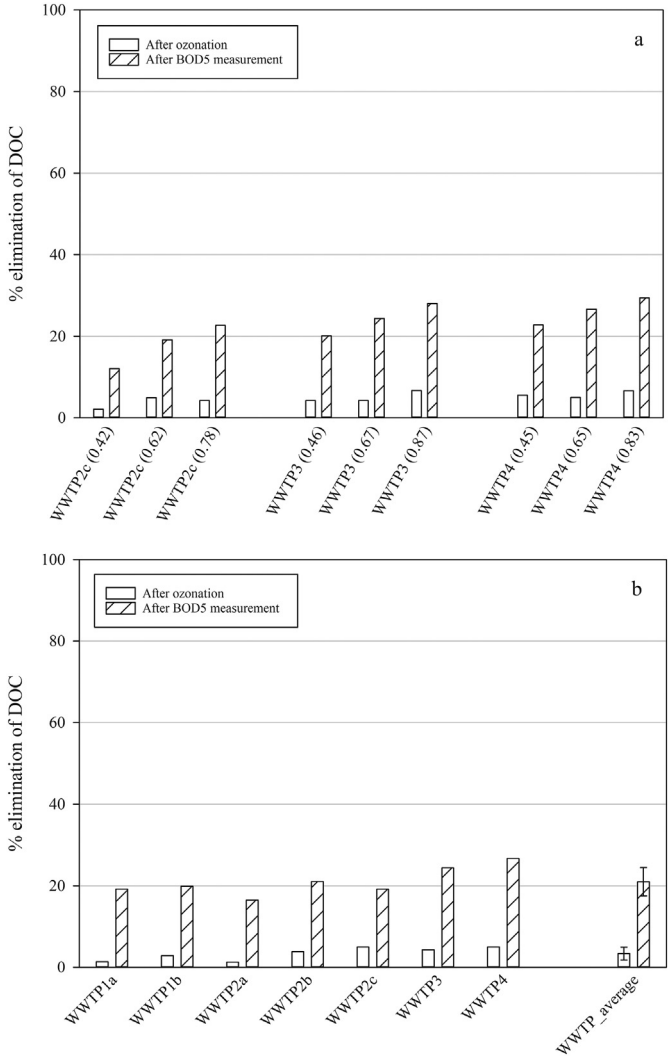

Fig. 3. Dose-specific elimination of DOC (a) and elimination of DOC at 0.65 ± 0.03 g O_3/g DOC (n = 7) (b).

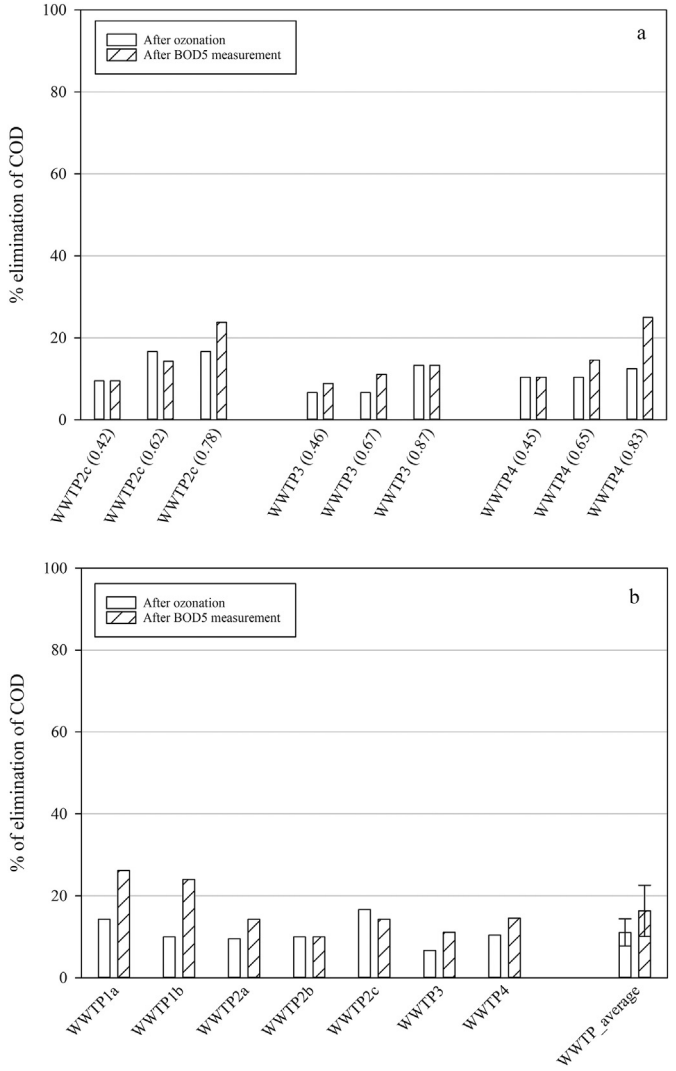

Fig. 4. Dose-specific elimination of COD (a) and elimination of COD at 0.65 ± 0.03 g O_3/g DOC (n = 7) (b).

After the exposure time for the BOD_5 measurement, the mean removal of DOC increased to 20.97 ± 3.47%, and in accordance with the results after ozonation, the lowest value was obtained for WWTP2a (16.46%) and the highest for WWTP4 (29.44%).

3.1.3. COD

The dose-specific elimination of COD is presented in Fig. 4a. After ozonation, the lowest elimination was 6.67% (WWTP3), and the highest was 16.67% (WWTP2). The correlation with D_{spec} was not immediately obvious: while the lowest COD elimination was always observed at the minimum applied D_{spec} and the highest elimination at the maximum D_{spec}, varying results were obtained at the medium D_{spec} of 0.6 g O_3/g DOC. For WWTP2c and WWTP4, it corresponded to the results obtained for a D_{spec} of 0.4 g O_3/g DOC and for WWTP3 to the results obtained for a D_{spec} of 0.8 g O_3/g DOC. The most likely reasons for this observation are the small differences in the COD that result from low absolute concentrations and the resolution of the applied method.

In contrast, after five days of exposure for BOD_5 measurement, a dose-dependent increase in COD elimination was detected for all WWTPs, which was more significant for the higher ozone doses. The minimum COD elimination was 9.52% at 0.43 g O_3/g DOC (WWTP2c) and the maximum 25.00% at 0.83 g O_3/g DOC (WWTP4).

Fig. 4b shows the COD abatement for the targeted D_{spec} of 0.6 g O_3/g DOC (0.65 ± 0.03). After ozonation, the mean removal of COD was 11.08 ± 3.32%, with a minimum of 6.67% (WWTP3) and a maximum of 16.67% (WWTP2c).

After the exposure time for the BOD_5 measurement, the mean removal of COD was 16.35 ± 6.25%, with 10.00% as the lowest value (WWTP2b) and 26.19% (WWTP1a) as the maximum.

3.1.4. BOD_5/COD ratio

The BOD_5/COD ratios before and after ozonation are given in Fig. S6 and Table S12. Ozonation resulted in an increase from 0.08 to 0.17 (mean values over all investigated samples). As shown in Fig. S6, in the dose-specific investigation, there was a clear increase in the ratio with increasing D_{spec}. This was caused by a dose-specific increase in BOD_5 and a simultaneously occurring decrease in COD. The starting values were typical for WWTPs characterized by a low F/M ratio.

3.1.5. UV_{254}

The change in UV_{254} for the dose-specific experiments during ozonation and BOD_5 measurement – caused by the oxidative effect of ozone on the aromatic ring structures absorbing at 254 nm and the effects of further biological activities – is shown in Fig. 5a. Corresponding numbers are given in Table S13. An increase in delta UV_{254} is a consequence of a higher decrease in UV_{254} during ozonation. The relative decrease in UV_{254} correlated with the increase in the specific ozone dose. Immediately after ozonation, the

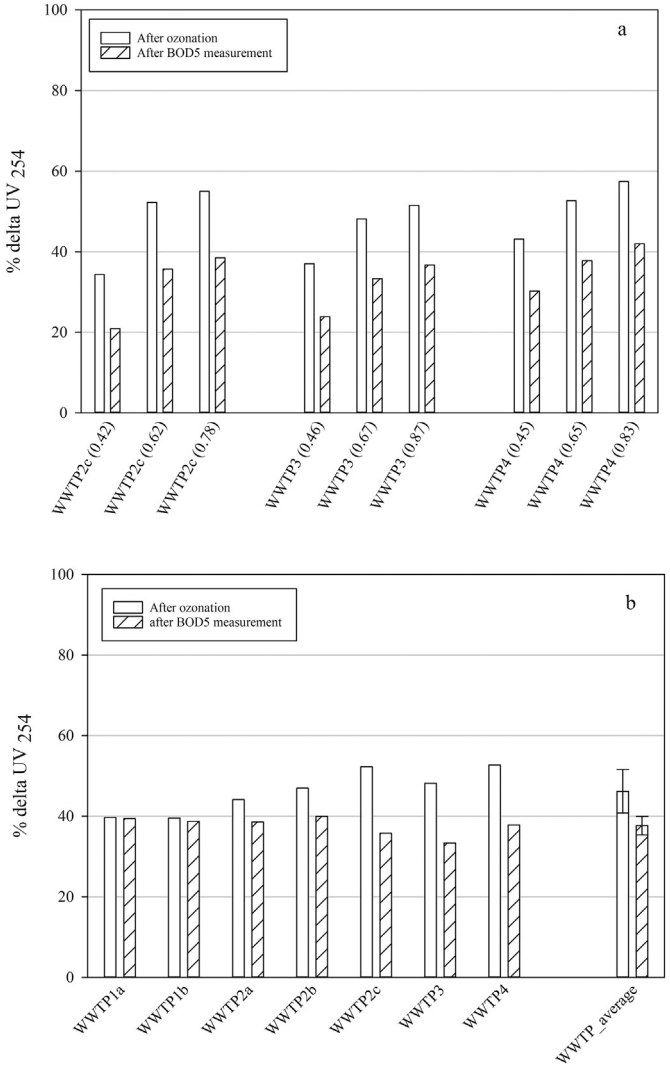

Fig. 5. Dose-specific decrease of UV_{254} (a) and decrease of UV_{254} at 0.65 ± 0.03 g O_3/g DOC (n = 7) (b).

lowest delta UV_{254} was 34.36% (0.43 g O_3/g DOC for WWTP2c), and the maximum delta UV_{254} was 57.42% (0.83 g O_3/g DOC for WWTP4).

After the exposure time for the BOD_5 measurement, the delta UV_{254} correlated with D_{spec} as well; however, an increase in UV_{254} resulted in a lower delta UV_{254} than after ozonation. Again, the lowest delta UV_{254} was determined for WWTP2c at 0.43 g O_3/g DOC (20.96%), and the highest was determined at 0.87 g O_3/g DOC for WWTP4 (42.02%).

The delta UV_{254} for the targeted D_{spec} of 0.6 g O_3/g DOC (0.65 ± 0.03) is presented in Fig. 5b. After ozonation, the mean change in UV_{254} was 46.17%, with a minimum of 39.52% at 0.61 g O_3/g DOC (WWTP1b) and a maximum of 52.66% at 0.65 g O_3/g DOC (WWTP4).

After the exposure time for BOD_5 measurement, the mean decrease in UV_{254} was 37.64%, the lowest value obtained was 33.33% at 0.67 g O_3/g DOC (WWTP3), and the highest was 39.94% at 0.67 g O_3/g DOC (WWTP2b). Except for WWTP1 (similar results as after ozonation), the results from Fig. 5a can be confirmed, showing a lower delta UV_{254} after BOD_5 measurement.

3.2. Effect of ozonation on organic micropollutants

The results for the two organic micropollutants investigated primarily for process validation of the experimental ozonation setup are depicted in Fig. 6a and b and in the supporting information (Figs. S8–S11, Tables S15 and S16).

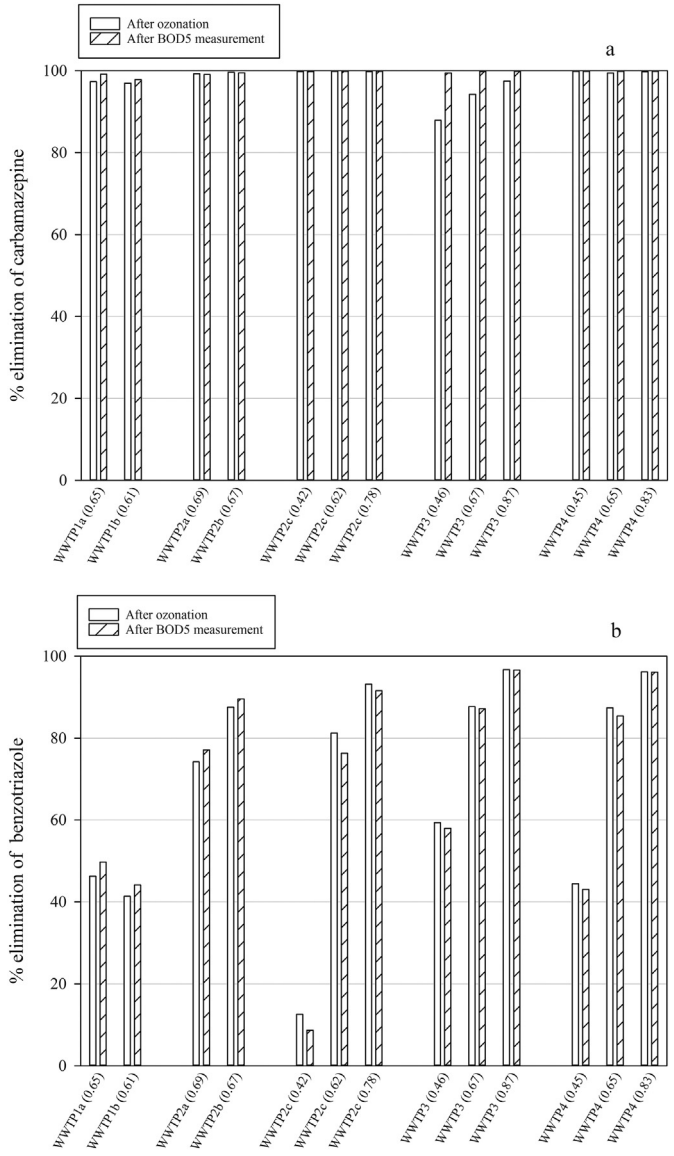

Fig. 6. Dose-specific abatement of CBZ (a) and BZT (b).

Fig. 6a shows the dose-specific abatement of CBZ for all samples. As expected, a high CBZ abatement was already achieved at the lowest D_{spec} of 0.42 g O_3/g DOC investigated. For WWTP3, the abatement was slightly lower (approximately 90%), and it increased with a D_{spec} up to 98%. After the exposure time for the BOD_5 measurement, even in WWTP3, the CBZ concentration was < LOQ at 0.46 g O_3/g DOC.

Fig. 6b shows the dose-specific abatement of BZT. It followed a dose-specific pattern, typical for moderately reactive substances. After exposure for BOD_5 measurement, no further removal was observed.

4. Discussion

4.1. Effect of ozonation on micropollutants

To prove the validity of the ozonation experiments, the abatement of CBZ and BZT was assessed and compared to results from the literature.

The CBZ abatement was quite efficient because CBZ is a highly reactive compound ($k_{O3} = 3 \times 10^5\ M^{-1}\ s^{-1}$). In Fig. 7, the mean decrease was correlated with increasing D_{spec}, and it was higher than 90% for all investigated D_{spec}. This finding coincided with the results of previous studies, which indicated a CBZ decline of at least 90% for an ozone dose of only

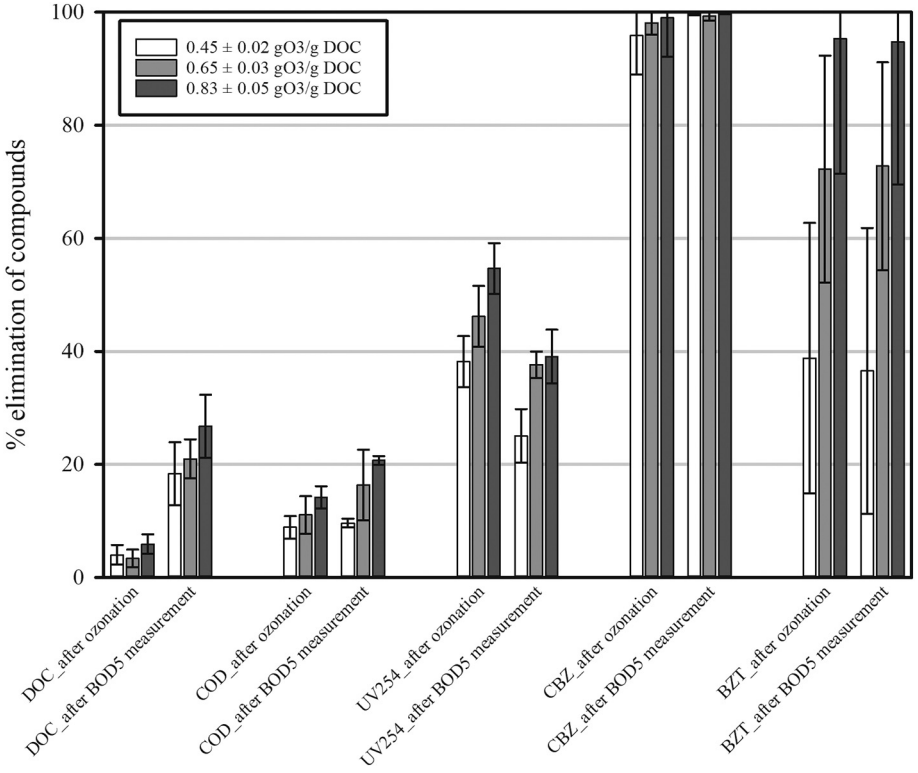

Fig. 7. Dose-specific elimination of organic sum parameters and micropollutants after ozonation and exposure time for BOD_5 measurement. Average values over all investigated samples (n = 3 for D_{spec} of 0.45 and 0.83 g O_3/g DOC; n = 7 for 0.65 g O_3/g DOC).

0.45 g O_3/g DOC (Bourgin et al., 2018; Lee et al., 2013; Schaar et al., 2010; Zimmermann et al., 2011; Rizzo et al., 2019).

The BZT abatement was lower than that of CBZ, which is in line with its lower k_{O3} value (k_{O3} = 230 M^{-1} s^{-1}). BZT showed a moderate average abatement of approximately 60–80% at a targeted D_{spec} of 0.6 g O_3/g DOC, mainly due to reaction with the strong and unselective OH radical originating from the reaction of ozone with the organic wastewater matrix (Rosal et al., 2010). Moreover, OH radical exposure varies with the ozone dose and wastewater quality, such as the presence of ozone and hydroxyl radical scavengers or competitors, pH, and alkalinity (Lee et al., 2013). Such varying exposure resulted in the typical dose-specific elimination pattern for BZT shown in Fig. 7. The higher standard deviations observed for BZT are in line with results presented in a review paper by Rizzo et al. (2019).

As a consequence of the abatement obtained for the two selected reference substances, the ozonation experimental setup was considered valid.

4.2. Effect of ozonation on organic sum parameters

Ozonation as an advanced treatment step is applied for the abatement of organic micropollutants. The effect of ozonation on conventional organic sum parameters that are routinely measured for the evaluation of treatment efficiency and legal compliance is not assessed at the same intensity. Based on the obtained results, the question of whether an increase in the specific ozone dose that is typically applied for micropollutant abatement from urban wastewater affects organic sum parameters is addressed. Thus, the change in organic sum parameters at different specific ozone doses is discussed, and a special focus is placed on the subsequent biological activities assessed via the 5-day exposure for conventional BOD_5 measurement. In the comparison of different wastewater matrices, relative rather than absolute changes were determined absolute changes are given in the supplementary data.

Fig. 7 represents a summary graph for the outcomes after ozonation and exposure time for BOD_5 measurement that are presented in detail in the Results section.

Over the measurement period of five days, the oxidative effect of ozone resulted in a higher BOD_5 of the ozonated WWTP effluent samples (Figs. 1 and 2). The observed increase in BOD_5 can be attributed to a transformation of organic compounds into less complex species (Siddiqui et al., 1997). Compounds with higher molar masses are considered to be less biodegradable than lighter compounds (Testolin et al., 2020). Ozonation results in a higher availability of these partially oxidized products for further biological processes, e.g., microbial energy sources for aerobic respiration, which is indeed assessed by the parameter BOD. A rise in BOD_5 after ozonation indicates a higher biodegradability of matrix substances that are recalcitrant to biodegradation in conventional activated sludge treatment, as reported in the literature (Nishijima et al., 2003; Nöthe et al., 2009).

Due to the mean increase of approx. 90% at 0.6 g O_3/g DOC, indicating a final value of 190% or roughly a doubling of the BOD_5, an effluent value that is close to the legal standards before ozonation could result in noncompliance with BOD limits. This result indicates the necessity of a high level of elimination of biodegradable substances in the preceding biological stage, which is typically achieved at low F/M ratios (high-SRT) in activated sludge plants with full nitrification and denitrification. Therefore, implementing ozonation at high-SRT WWTPs with lower effluent organic matter (Khan et al., 1998) is crucial not only for limiting oxidant competition between organic compounds and micropollutants but also to ensure legal compliance of BOD, a conventional wastewater parameter.

In general, an observed decrease in DOC during biological wastewater treatment can be considered equivalent to biodegradable DOC (BDOC). In the ozonation stage, there was only a slight, dose-independent decrease in DOC (Fig. 7), which was in line with the partial oxidation and a degree of mineralization of <10% at the D_{spec} that is usually applied for micropollutant abatement (Sauter et al., 2021; von Sonntag and von Gunten, 2012). During ozonation, molecular structures are attacked, which means that the DOC usually becomes more bioavailable and can be broken down in a subsequent biological process, e.g., in biologically activated carbon (BAC) filters, sand filters or even receiving water bodies. DOC removal and modification of chemical structures by ozonation

predominantly depend on the DOC composition, which explains the differences encountered for the various samples investigated. Values obtained in this study are comparable with those in the published literature. The study by Molnar et al. (2012) showed DOC reductions from 5% to 25% at a D_{spec} of 0.4–3 g O_3/g DOC. Mao et al. (2014) reported DOC reductions up to 20% achieved by ozonation in conventional treatment plants at D_{spec} of 0.6–1.6 g O_3/g DOC. High values were not reproducible in our experiments but can be connected to the higher D_{spec} and higher initial DOC values and DOC composition in these studies, respectively. Our results are in line with Sauter et al. (2021), who reported a DOC decline of 5% at 0.65 ± 0.09 g O_3/g DOC, and Stapf et al. (2017) who showed an average DOC decrease of 5% for various WWTPs. Additionally, Nöthe et al. (2009) reported a low impact of ozonation on the DOC (4–9% decrease between 0.4 and 0.8 g O_3/g DOC). Nöthe et al. (2009) attribute the low impact to the low degree of decarboxylation, since DOC is only eliminated when decarboxylation reactions occur or when substances that are already substantially oxidized are further oxidized.

The increase in DOC elimination we determined in our study after the exposure for the BOD_5 measurement was also observed by Khan et al. (1998), who studied BDOC in high- and low-SRT WWTPs as well as in water reclamation plants using ozonation and subsequent BAC, applying the same methodological approach as in the present paper. Similar results are reported by Nishijima et al. (2003). Moreover, we were able to demonstrate a correlation of BDOC and D_{spec}, which is in accordance with the dose-dependent structural changes determined by delta UV_{254} and SUVA, respectively (see Fig. 7). The BDOC in the effluent of the conventional WWTPs was calculated as the difference between the initial DOC and the DOC after BOD_5 exposure with an average share of 4% (96% refractory DOC). After ozonation, this share increased to 15, 18 and 22%, corresponding to applied D_{spec} values of 0.4, 0.6 and 0.8 g O_3/g DOC, respectively.

The COD measurement provides information about the degree of oxidation in organic compounds but also comprises oxygen required for inorganics that are not fully oxidized (e.g., nitrite). In contrast, the DOC measurement only provides information on the amount of carbon that could be mineralized to CO_2. Thus, it appears possible that COD could supply additional information regarding ozone scavenging by the wastewater matrix compared to the information that can be obtained from DOC. Furthermore, COD is a parameter typically used in wastewater treatment for process design and evaluation as well as for regulation. The fact that COD is reduced while DOC only changes slightly during ozonation indicates that ozone treatment transforms the structure of organic matter and mainly forms transformation products via direct oxidation (Ekblad et al., 2019; Liu et al., 2015; Pešoutová et al., 2014). For this reason, dose-dependent elimination can be expected after ozonation, as summarized in Fig. 7. Exposure to biological processes simulated by BOD measurement only indicated a slightly greater dose-dependent removal.

The COD/DOC ratio is a measure of the average degree of oxidation of organic compounds. For low F/M, WWTPs a COD/DOC ratio of approx. 3 typically can be expected, as reported by Nöthe et al. (2009). In our wastewater samples, the average COD/DOC ratio before ozonation was 2.76 ± 0.14 (Table S11). After ozonation (0.65 ± 0.03 g O_3/g DOC), the ratio decreased to 2.54 ± 0.10, indicating a higher degree of oxidation and fewer oxidation equivalents required for full oxidation to CO_2. After exposure to the BOD_5 measurement, the ratio increased again to a value of 2.92 ± 0.23, which resulted from a different change in COD compared to DOC. Obviously, the high degree of BDOC disappearance (higher removal of DOC, as shown in Fig. 7) indicates the predominant removal of higher oxidized carbon species that are characterized by a comparably lower COD, resulting in the low change of COD observed during exposure for BOD_5 measurement. This line of argument results in the expectation of an even lower COD/DOC ratio with increasing D_{spec}. Indeed, data for 0.83 ± 0.05 g O_3/g DOC indicate a lower ratio for the individual wastewater samples and again a substantial increase after BOD measurement (see Supplementary data).

UV_{254} generally corresponds to the content of organic carbon (DIN_38404-3, 2005). The typical shoulder in the UV absorbance pattern of WWTP effluents at approximately 260 nm is due to the absorbance of aromatic structures or conjugated double bonds, among others present in non-readily biodegradable compounds, e.g., humic substances, or products of microbial metabolism and lysis (Schaar et al., 2010). Because ozone attacks double bonds, active aromatic constituents, and organic functional groups, such as carboxylic groups (von Gunten, 2003), ozonation effectively reduces the UV_{254}. The dose-specific UV_{254} decline correlates with micropollutant abatement (cf. Fig. S7); which makes the delta UV_{254} a suitable surrogate parameter and parameter for process control of ozonation, respectively (Bahr et al., 2007; Chon et al., 2015; Dickenson et al., 2009; Nanaboina and Korshin, 2010; Stapf et al., 2016). The dose-response curve of delta UV_{254} is illustrated in Fig. 7.

Interestingly, after exposure to BOD_5 measurement, the absolute UV absorption increased again (see Table S13), resulting in a delta UV_{254} constantly lower than that directly after ozonation. This phenomenon was independent of the applied D_{spec}. Higher DOC elimination compared to oxidation equivalents (COD) was observed, as discussed above, indicating the potential transformation of organic substances by processes other than biological respiration (oxidation). Transformation can involve the assimilatory formation of complex organic compounds with aromatic structures that increase aromaticity and thus can result in an increase in UV_{254} (Weishaar et al., 2003).

Following up on the UV measurement, the specific UV absorbance at 254 nm (SUVA) as ratio of the UV_{254} and the DOC is a measure for the aromaticity of a water sample and is considered useful for the estimation of the aromatic carbon content (Weishaar et al., 2003). In the WWTP effluent samples, the SUVA ranged from 1.8–2.3 L/(mg·m) and decreased by 44% (arithmetic mean for 0.65 ± 0.03 g O_3/g DOC) after ozonation (Table S14). This decrease is a result of the partial oxidation of the UV-active moieties. The constant DOC content and the dose-dependent reduction in SUVA demonstrate the structural alterations of the organic matrix.

After the exposure time for the BOD_5 measurement, a dose-dependent increase in SUVA was observed as a result of both the increase in UV_{254} absorbance and a simultaneous decrease in DOC. In combination with a predominating degradation of nonaromatic organic carbon, this increase in aromaticity strongly supports the hypothesis on the assimilatory formation of complex organic compounds comprising aromatic structures (Hoppe-Jones et al., 2010).

The BOD_5/COD ratio can be used as a further indicator for biodegradability. Based on the population-specific organic loads in the inflow of an urban WWTP, a BOD_5/COD ratio of 0.5 can be assumed. Biological treatment results in a decrease in this ratio depending on the SRT. While the BOD_5/COD ratio in the effluent of high F/M (low-SRT) plants ranges between 0.25 and 0.35, high-SRT plants with nutrient removal usually achieve a ratio of approx. 0.1, indicating greater removal of BDOC compared to the removal of refractory organic compounds. In the current study, the BOD_5/COD ratios were calculated for wastewater before and after ozonation (see Table S12 and Fig. S6). There was a steady, dose-dependent increase in the BOD_5/COD quotient from 0.09 (before ozonation) to 0.17 (average value after ozonation), indicating enhanced biodegradability. This finding corroborates the results of Van Aken et al. (2015), who reported that the biodegradable fraction increases during ozone treatment and that the amount of refractory COD decreases because of the partial degradation of the pollutant. The enhanced biodegradability is attributed to the transformation of the effluent organic matter into readily biodegradable compounds by ozonation, such as aldehydes and carboxylic acids (Siddiqui et al., 1997).

5. Summary and conclusion

The current paper dealt with the assessment of biodegradability after ozonation, focusing on the changes of BOD_5 and the impact of exposure time for BOD measurement on other relevant conventional organic sum parameters indicating enhanced bioavailability. Enhanced biodegradability of wastewater by ozonation can be evaluated by an increase in BOD_5 for carbon removal. Based on the parameter set measured (BOD_5, COD, DOC,

UV_{254}), additional indications of increased biodegradability can be obtained from parameters such as the BDOC or a change in the BOD_5/COD ratio, the BDOC and the correlation of BOD_5 increase and D_{spec}. Summarized the results showed:

- There was a dose-dependent BOD_5 increase that varied among the investigated WWTPs. The minimum increase was 21%, and the maximum was 193%.
- The DOC did not substantially decrease after ozonation; this result was consistent with the low reported degree of mineralization, while partial oxidation led to a quantifiable decrease in COD from 7 to 17%.
- Delta UV_{254} (34–57%) and the decline in SUVA (33–54%) after ozonation indicated structural changes by oxidation, clearly correlating with D_{spec}. In contrast, for COD and DOC (BDOC), a clear dose-response pattern was observed only after exposure to BOD_5 measurement.
- The rise in BDOC (from 4% to a maximum of 22%) is another indication for the improved biodegradability, which was further supported by the change in the BOD_5/COD ratio (from 0.08 to a maximum of 0.21).
- The reference micropollutants CBZ and BZT were removed in accordance with the literature (>88% for CBZ, 13–97% for BZT), proving the validity of the experimental setup for ozonation.
- The results showed a dose-dependent increase in biological activity after ozonation, which was linked to the enhanced biodegradability of substances that are recalcitrant to biodegradation in conventional activated sludge treatment.

While the changes in traditional organic sum parameters have been reported in literature, the higher degradation potential for a subsequent biological process due to the increase in biodegradability has not been systematically investigated. This aspect is important for any kind of technical post treatment step involving biological processes, such as sand filtration, BAC filtration, soil aquifer treatment (SAT) and even processes that promote reuse in agricultural irrigation and receiving waters in general. Without biological post treatment, the additional degradation of organic matter would be shifted to downstream environments as soil or receiving water bodies (groundwater and surface water). In the case of technical processes, the further reduction in biodegradable organic carbon emissions equivalent to approximately 20% of DOC, as determined in this study, is another step towards sustainable water resource management in addition to micropollutant abatement.

CRediT authorship contribution statement

Lam Thanh Phan: conceptualization, laboratory experiments, analysis, preparation of manuscript.
Heidemarie Schaar: review & editing, supervision.
Ernis Saracevic: chemical analysis, supervision of laboratory work.
Jörg Krampe: project supervision, review.
Norbert Kreuzinger: review & editing, supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152466.

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