Influence of effluent particles and particle-bound micropollutants on the removal of micropollutants and UVA$_{254}$ in wastewater effluent ozonation

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ABSTRACT

This study systematically investigated the influence of effluent particles and activated sludge (AS) particles on the removal of micropollutants via wastewater effluent ozonation within typical effluent total suspended solids (TSS) concentrations. A series of batch experiments revealed that particle concentrations up to 30 mg/L had a minor impact on the removal of organic micropollutants (OMPs) in the aqueous phase. Moreover, the reduction of UV absorbance at 254 nm (UVA$_{254}$) was negatively correlated to the level of particle concentration at ozone doses higher than 0.5 gO$_3$/gDOC. It indicates that UVA$_{254}$ abatement was more sensitive to the presence of particles compared to OMP removal. Organic micropollutants (OMPs) sorbed on effluent particles and sludge particles were extracted before and after ozonation. OMP sorption in effluent particles was 2–5 times higher than that in sludge particles. During the ozonation of raw secondary effluent, particle-bound micropollutants were removed comparably to the micropollutants in the aqueous phase. This suggests that the boundary layer surrounding the particle didn't affect the removal of OMPs in the particle phase. Furthermore, the removal of existing OMPs (irbesartan, sulfamethoxazole, and metoprolol) in the effluent was used to assess the ozone and •OH exposure. In water samples with and without particles, the elimination of OMPs could be reliably predicted (R^2 > 0.95) by calculated ozone and •OH exposures.

1. Introduction

Ozone degrades many organic micropollutants (OMPs) in wastewater efficiently and is widely used for advanced treatment of municipal and industrial wastewater (Lee et al., 2014; Huber et al., 2005; Alsager et al., 2018). The OMP removal during ozonation is mainly achieved by its reaction with ozone and hydroxyl radicals (•OH); the latter is produced from the ozone decomposition (von Sonntag and von Gunten, 2012; Lee et al., 2014).

According to ozone and •OH rate constants, Lee et al. categorized the OMPs into five groups (Lee et al., 2013). Group I and II are compounds with high ($k_{O_3} \geq 10^5$ $M^{-1}s^{-1}$) or relative high ozone reaction rates ($10 \leq k_{O_3} < 10^5$ $M^{-1}s^{-1}$); Group III contains compounds with low ozone rate constants, but high •OH rate constants

($k_{O_3} < 10$ $M^{-1}s^{-1}$ and $k_{\bullet OH} \geq 5 \times 10^9$ $M^{-1}s^{-1}$); and compounds with low •OH rate constants belong to Group IV ($1 \times 10^9 \leq k_{\bullet OH} < 5 \times 10^9$ $M^{-1}s^{-1}$) and Group V ($k_{\bullet OH} < 1 \times 10^9$ $M^{-1}s^{-1}$) (Lee et al., 2013). More often, OMPs were divided into different groups such as ozone-reactive and ozone-refractory contaminants (Pocostales et al., 2010); fast-reacting, moderately-reacting, and slowly-reacting contaminants (Zucker et al., 2015; Sauter et al., 2021), based on the levels of removal by ozonation.

The efficiency of ozonation in municipal wastewater treatment plants (WWTPs) for OMP removal depends on the ozone and •OH exposures, which are influenced by factors such as dissolved organic and inorganic matter, temperature, and pH in wastewater (Wert et al., 2009; Lee and Gunten, 2010; Hoigné et al., 1985; Mathon et al., 2021). Inorganic and organic matter may promote and inhibit the ozone chain

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reaction and thus affect the ozone and •OH exposures (Johannes Staehelin et al., 1985; Guo et al., 2023; Ma and Graham, 1999; Gonzales et al., 2012).

However, there is limited and sometimes controversial information regarding the impact of particles on ozonation. Juárez et al. reported that elevated total suspended solids (TSS) concentrations, mainly from 50 to 200 mg/L by the addition of thickened activated sludge (AS), had a negative effect on the removal of OMPs compared to that in the filtered secondary effluent (Juárez et al., 2021). Zucker et al. claimed that particles in secondary effluent (<50 μm) may adversely affect ozonation (Zucker et al., 2015). Contrary to the above-mentioned studies, Huber et al. found that the effluent particles and the addition of 15 mg/L AS had a minor influence on the oxidation efficiency of micropollutants during ozonation of raw effluent (RE) in a pilot plant at ozone doses from 0.07 - 0.7 mgO$_3$/gDOC (Huber et al., 2005). They suggested that ozone absorption on particles was limited by ozone diffusion across the boundary layer surrounding the sludge particles (Huber et al., 2005). Based on the previous work, more studies are necessary to address the impact of native effluent particles and native AS particles at typical effluent concentrations on the OMP removal during ozonation of RE. Investigations of the impact of particles on ozonation are of research interest for the application in practice. The necessity of pre-filtration or even post-filtration is to be determined.

The effluent and sludge particles are flocs containing mainly microorganisms and extracellular polymeric substances (EPS). EPS are a complex mixture of high molecular weight polymers secreted by microorganisms (Staudt et al., 2004; Wagner et al., 2009). EPS in the matrix of biofilms protect the microbial communities from harsh environments and chemicals such as antimicrobial agents (Mittelman, 1998; De Beer et al., 1994).

Particles play different roles during the ozonation of wastewater. Particles may compete with the dissolved substances for ozone and •OH during the oxidation reactions (Zucker et al., 2015). At high particle concentrations, less ozone and •OH are thus available for OMP oxidation. Secondly, OMPs can be sorbed to AS particles (Mailler et al., 2014; Gonzalez-Gil et al., 2016; Lajeunesse et al., 2012; Svahn and Björklund, 2015; Xiao et al., 2022). In fewer studies, OMP sorption (such as benzotriazole) in effluent particles was analyzed (Asimakopoulos et al., 2013; Stasinakis et al., 2013). It is still unclear if sorbed OMPs in the particle phase may desorb into the aqueous phase after ozonation.

This study aimed to determine the impact of particles at typical effluent concentrations on the removal efficiency of OMPs during ozonation. For that, this paper examines the OMP removal and the reduction of ultraviolet absorbance at the wavelength of λ = 254 nm (UVA$_{254}$) in the aqueous phase at different ozone doses and TSS concentrations up to 30 mg/L. Specifically, this study extends the knowledge of the fate of OMPs in the particle phase during ozonation by evaluating the sorption of eleven OMPs on the effluent particles and AS particles, as well as the removal of particle-bound OMPs.

2. Materials and methods

2.1. Wastewater and suspended solids samples

Grab water samples were taken at the secondary effluent of WWTP-A and WWTP-B in Germany.

In the catchment area of WWTP-A (13,000 PE), there are around 12,000 inhabitants and six rehabilitation clinics with almost no industrial wastewater input. The conventional treatment in WWTP-A includes sand and grease traps and no primary clarifier. The total sludge retention time (SRT) of the subsequent AS process is between 20 to 25 days.

WWTP-B has a capacity of 350,000 PE. The inflow consists of around 65% domestic and 35% industrial wastewater. The WWTP-B is equipped with screens, sand and grease traps, primary clarifiers, conventional activated sludge tanks, and secondary clarifiers. The SRT of the AS process in WWTP-B is between 10 to 14 days.

Water and AS samples were taken in polyethylene containers and stored in the dark at 4 °C before use. The samples were tested within a month. The characteristics of the water samples are listed in Table S1, Supplementary Information.

2.2. Wastewater types

To study the influence of particles on OMP removal during ozonation, three wastewater types with different TSS concentrations were prepared in the study. They were:

1) the permeate from membrane filtration with a pore size of 0.45 μm prepared from secondary effluent (cellulose acetate filter, Sartorius GmbH, Goettingen, Germany). TSS concentration was 0 mg/L;
2) raw effluent (RE) with original TSS concentration in the effluent (Table S2, Supplementary Information);
3) raw effluent + activated sludge (RE+AS): native AS was dosed into the unfiltered effluent in order to achieve a TSS concentration of 30 mg/L, simulating an AS treatment with suboptimal clarification. Effluent samples and sludge samples from the same WWTP were mixed together.

2.3. OMP removal in the water phase

The three wastewater types with different TSS concentrations from WWTP-A and WWTP-B were doped with the following OMPs at a concentration of 2 μg/L shortly before ozonation: benzotriazole, carbamazepine, diclofenac, 4-/5-methyl-benzotriazole, metoprolol, and sulfamethoxazole. The three water types were ozonated at six ozone doses, and the OMP removal in the water phase was analyzed.

The specific ozone doses were achieved by adding ozone stock solution into each water sample with gas-tight ozone-resistant syringes. A detailed description of the production and dosage of the ozone stock solution can be found in Text S1 in the Supplementary Information. The ozone concentration of the stock solution was determined by the indigo method (Bader and Hoigné, 1981; envilab, 2021). Detailed measurement protocol can be found in Text S2 in the Supplementary Information.

The abatement of an OMP can be predicted by a second-order kinetic equation (Eq. 1) consisting the ozone and •OH rate constants ($k_{O_3,OMP}$ and $k_{•OH,OMP}$) as well as the ozone and •OH exposures ($\int [O_3]dt$ and $\int [•OH]dt$).

$$-\ln\left(\frac{[OMP]}{[OMP]_0}\right) = k_{O_3,OMP} \times \int [O_3]dt + k_{•OH,OMP} \times \int [•OH]dt \qquad (1)$$

2.4. Particle-bound OMPs

The particle-bound OMPs were extracted by ultrasound-assisted extraction adopted from the studies of Ternes et al. and Boix et al., who focused on the extraction of OMPs from sludge and sediments (Ternes et al., 2002; Boix et al., 2016). To be more detailed, 4000 ml RE or 500 ml RE+AS were filtered with cellulose acetate filters (100 mm, 0.45 μm, Sartorius Corporate Administration GmbH, Goettingen, Germany). Each filter was carefully cut into small pieces after filtration, and the OMPs in the filter were extracted with 20 ml of MeOH:Water (50:50) 0.5% HCOOH, using an ultrasonic bath for 10 min. The supernatants were collected into a glass bottle, and the extraction procedure was repeated. Both supernatants were mixed and filtered through a syringe filter (0.45 μm, cellulose acetate filter, Sartorius GmbH, Goettingen, Germany). The filtered supernatants were evaporated to dryness at 60 °C and finally reconstituted with 20 ml of water with 0.1% HCOOH.

2.5. Removal of particle-bound OMPs

In order to study the removal of particle-bound OMPs, RE and

RE+AS were ozonated at two ozone doses: 0.2 gO$_3$/gDOC and 0.5 gO$_3$/gDOC. The OMPs in the particle phase after ozonation were extracted using the same method described above.

2.6. Analytical methods

DOC measurements were performed on equipment DIMATOC 2000 (DIMATEC Analysetechnik GmbH, Essen Germany) as described by DIN EN 1484. NO$_2^-$-N was determined by the photometric method according to DIN EN 26777. TSS was measured according to DIN 38414–2 with glass filters. pH was measured by TitroLine alpha (Schott Instruments GmbH, Germany) according to DIN 38409–7. The measurement of acid capacity to pH 4.3 was also performed by the equipment TitroLine alpha. Organic micropollutants were determined using HPLC-MS/MS and performed by a certified lab, IUTA, Germany. The following OMPs were analyzed in the study: 4 N-Acetylsulfamethoxazole, benzotriazole, candesartan, carbamazepine, clarithromycin, diclofenac, hydrochlorothiazide, irbesartan, metoprolol, Σ4,5-methyl-benzotriazole, and sulfamethoxazole. These micropollutants were measured with an Agilent 1100 LC system (Agilent Technologies Deutschland GmbH, Germany) coupled to a Sciex QTRAP 6500 mass spectrometer (AB Sciex Germany GmbH, Germany) according ISO 21676 (2018). LC-MS-grade water and acetonitrile (both with 0.1% formic acid) were used as solvents. The limit of quantification (LOQ) of these compounds is listed in Table S3 in the Supplementary Information.

3. Results and discussion

3.1. Extraction of micropollutants from particles

To comprehensively investigate the role of particles on OMP removal via ozonation, the OMP sorption on effluent and sludge particles was analyzed and presented in this section.

Fig. 1 shows that the OMP concentration in the effluent particles from the two WWTPs (columns with diagonal design) ranged from 0.1 - 40 μg/gTSS. Benzotriazole, 4- and 5-methyl-benzotriazole, and carbamazepine were among the most sorbed OMPs. For instance, 12 and 37 μg benzotriazole were found in one gram of effluent particles in WWTP-A and WWTP-B, respectively. Since industrial wastewater contributed ca. 40% of the whole influent in WWTP-B, more than three times of benzotriazole was measured in the effluent particles in WWTP-B than that in WWTP-A. Similar was found for 4- and 5-methyl-benzotriazole, which are also corrosion inhibitors like benzotriazole. On the other hand, higher concentrations of pharmaceutical residues were detected in the effluent particles from WWTP-A compared to that in WWTP-B since city A has many rehabilitation clinics.

Comparing the OMP sorption on raw effluent (RE) particles (columns with diagonal design in Fig. 1) and that in the effluent plus AS (RE+AS) particles (columns in blue), the effluent particles were more loaded with OMPs compared to that in the RE+AS particles. Based on the OMP sorption on RE and RE+AS, the OMP sorption on sludge particles alone was calculated. Table S4 in the Supplementary Information shows the ratio between extracted OMPs in effluent particles [μg/g] and OMPs in AS particles [μg/g]. It can be seen that the effluent particles contained 2 - 5 times more OMPs compared to sludge particles, except for carbamazepine, which was 16 - 18 times more sorbed in effluent particles than in the sludge in the two WWTPs.

The effluent particles were more loaded than the sludge flocs. This is because effluent particles are, on average, smaller than sludge flocs. The reported peak particle size for volume distribution was about 50 μm for effluent particles (Khanam et al., 2016; Puig-Bargués et al., 2005), whereas that for sludge flocs was between 80 - 130 μm (Kuśnierz, 2018; Li and Ganczarczyk, 1991). More OMPs could be sorbed on the effluent particles' surface due to the larger surface area of the smaller particles.
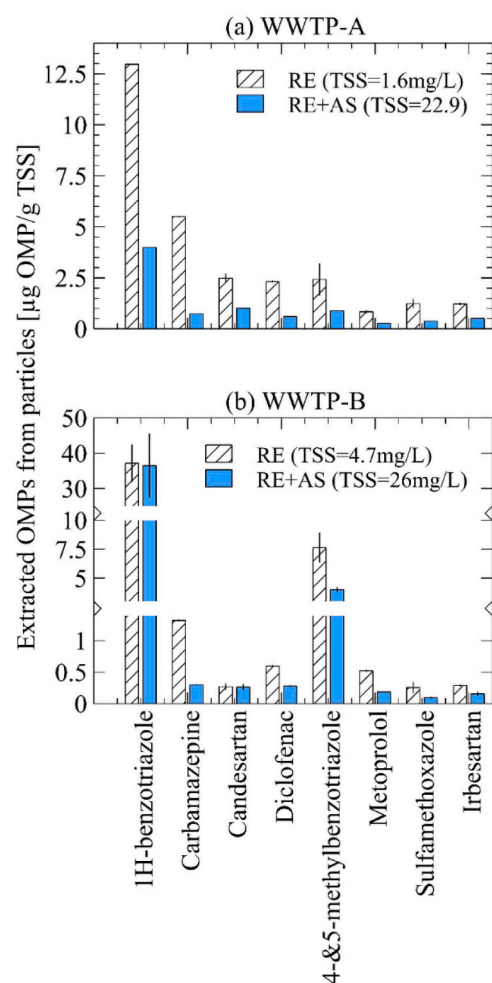

Fig. 1. Extracted OMPs from raw effluent (RE) particles and RE+AS particles in (a) WWTP-A and (b) WWTP-B. Error bars indicate standard deviations based on double measurements (n = 2).

3.2. Removal of particle-bound OMPs

Fig. 2 compares the OMP removal in aqueous and particle phases from RE samples of WWTP-B. The OMP removal in the solid phase was analyzed after ozonation of the raw effluent at 0.2 or 0.5 gO$_3$/gDOC, followed by OMP extraction from the particles. Fig. 2 reveals that the percentages of OMP removal in the aqueous phase were similar to that in the particles. Data regarding WWTP-A can be found in the Supplementary Information (Fig. S1) and demonstrates comparable results to those of WWTP-B. To the authors' knowledge, no other study has investigated the OMP removal in effluent particles by ozonation. Huang et al. evaluated the removal of endocrine-disrupting chemicals in the colloidal and soluble phases by ozone (Huang et al., 2019). Their research found that the respective removal efficiencies of endocrine-disrupting chemicals in colloidal and soluble phases were similar (Huang et al., 2019), which is, to a certain extent, similar to the results of this study.

Similar to the experiments regarding the OMP removal in the effluent particles, the OMP removal in the effluent doped with AS particles (RE+AS) was also investigated and presented in Figs. S2 and S3 (Supplementary Information). The removal of OMPs in the aqueous phase and RE+AS particle phase were similar, except for benzotriazole. The concentrations of metoprolol and irbesartan in the particle phases were relatively low (≤ 0.5 μgOMP/gTSS) in the RE+AS samples of WWTP-B (see Fig. 1), and thus, the lower removal in the particle phase compared to that in the aqueous phase may due to the measurement uncertainty.
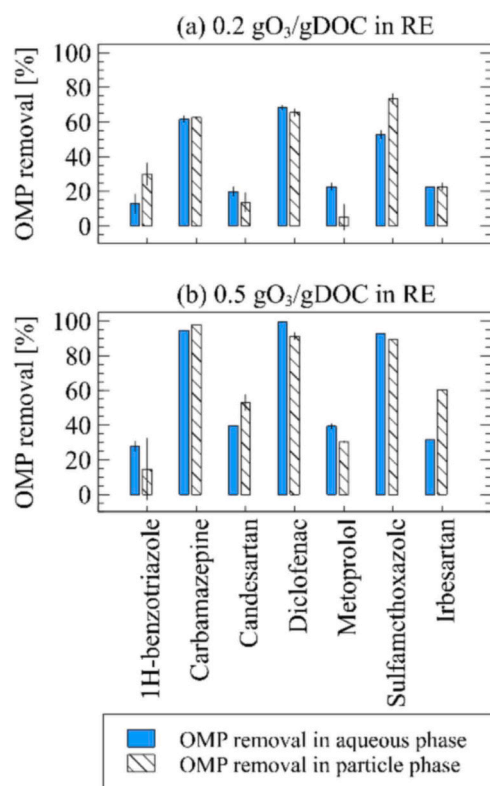
Fig. 2. Removal of OMPs in the aqueous and particle phases from RE samples of WWTP-B at ozone dose of (a) 0.2 gO3/gDOC and (b) 0.5 gO3/gDOC. Error bars indicate standard deviations based on double measurements (n = 2).

Fig. 3. OMP distribution in aqueous and particle phase from RE samples of WWTP-B before and after ozonation at ozone dose of 0.2 $gO_3/gDOC$ and 0.5 $gO_3/gDOC$. Error bars indicate standard deviations based on double measurements (n = 2).

However, benzotriazole was abundant in the particle phase (RE+AS particles), and the concentration of benzotriazole even increased by 10 - 25% in the particle phase (RE+AS particles) after ozonation at an ozone dose of 0.5 $gO_3/gDOC$ in WWTP-A and WWTP-B (Fig. S2 and Fig. S3). Part of the soluble benzotriazole seemed to turn into the particle phase after ozonation. Studies have proven that ozonation at low doses (≤ 0.5 $gO_3/gDOC$) can destabilize organic particles and dissolved organic matter and promote aggregation of particles (Chandrakanth and Amy, 1996; Zucker et al., 2015). The aggregation of organic matter induced by ozonation was, to a large extent, due to the presence of metal cations (Chandrakanth and Amy, 1996). Since benzotriazole can chelate metal ions (Hart et al., 2004; Kuśnierz, 2018), and ozonation causes precipitation of metal-DOM complexes (Reckhow et al., 1992; Chandrakanth and Amy, 1996), the authors hypothesize that benzotriazole may co-precipitate with the metal-DOM complexes. However, more detailed studies shall be carried out to investigate these phenomena.

Distribution of OMPs in aqueous and particle phases

The partition of OMPs in the aqueous and particle phase was calculated as a ratio between the amount of OMPs in the aqueous phase [μg/L] and the amount of OMPs in the particle phase per liter effluent sample [μg/L]. Fig. 3 demonstrates that OMP distribution in the aqueous and particle phase had a minor change after ozonation in RE samples from WWTP-B. The aqueous concentrations of carbamazepine, diclofenac, and sulfamethoxazole were below the detection limit after ozonation at the dose of 0.5 $gO_3/gDOC$, and the corresponding data points are not displayed in Fig. 3. The load of candesartan and diclofenac in the aqueous phase was three orders of magnitude higher than in the particle phase (Fig. 3). At the same time, carbamazepine, methyl-benzotriazole, and benzotriazole display the lowest ratio between the aqueous and the particle phases. The results in WWTP-A display similar results (Fig. S4 in the Supplementary Information). Candesartan displays poor affinition to effluent particles, probably due to its negative charge and low $logD_{ow}$
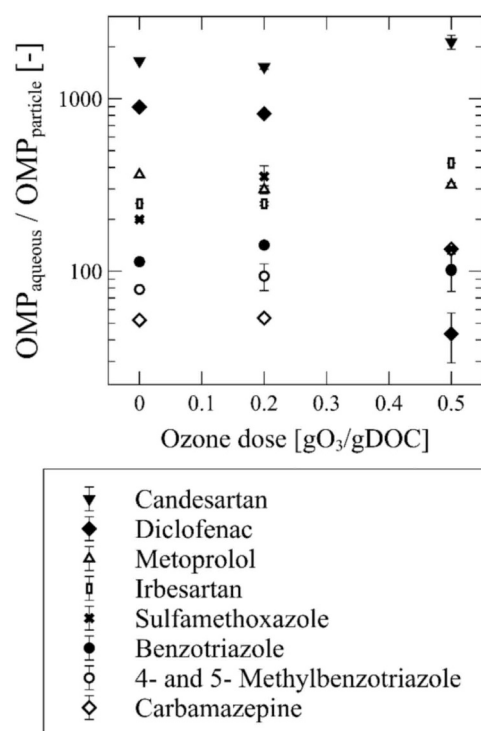
value ($logD_{OW} = 1.04$ at pH = 7). To be mentioned, candesartan is considered as a substance with variable or low PAC affinity (Decrey et al., 2020; Atallah Al-Asad et al., 2022). Although irbesartan is also negatively charged at pH = 7, this substance shows relatively high abundance in the effluent particles, probably due to its high hydrophobicity ($logD_{OW} = 4.46$ at pH = 7). Carbamazepine, on the other hand, shows a very good affinity to particles due to its neutral charge and high $logD_{OW}$ value ($logD_{OW} = 2.77$ at pH = 7) (Sbardella et al., 2018).

According to the literature, the lipophilicity and acidity of OMPs correlate to their sorption to sludge (Carballa et al., 2005; Carballa et al., 2008; Vieno and Sillanpää, 2014). When studying the DOM-organic pollutant interactions, the polarity and aromaticity of DOM are critical parameters (Caupos et al., 2015; Gauthier et al., 1987; Chiou et al., 1986; Zietzschmann et al., 2015). This study suggests that high $logD_{OW}$ and low polarity are critical to the high distribution of OMPs to effluent particles.

This study reveals that OMPs in the aqueous phase were one to three orders of magnitude higher than that in the particle phase, and ozone treats OMPs in both aqueous and particle phases. However, discharging treated wastewater may still lead to the accumulation of OMPs, such as carbamazepine and benzotriazole, via effluent particles in receiving water bodies.

3.3. UVA254 abatement

Fig. 4 shows that UVA_{254} abatement correlates well with the ozone doses at all three TSS concentrations: Filtrate (TSS = 0), RE (native TSS concentration, 1,6 - 4,7 mg/L), and RE+AS (TSS between 22 - 26 mg/L). The presence of effluent particles and activated sludge displayed a minor effect at lower ozone doses (< 0.4 $gO_3/gDOC$). At the doses higher than 0.5 $gO_3/gDOC$, a negative correlation between UVA_{254} abatement and TSS concentration was observed. The UVA_{254} abatement at the ozone dose of 0.75 $gO_3/gDOC$ decreased from 49% (Filtrate) to 47% (RE) and
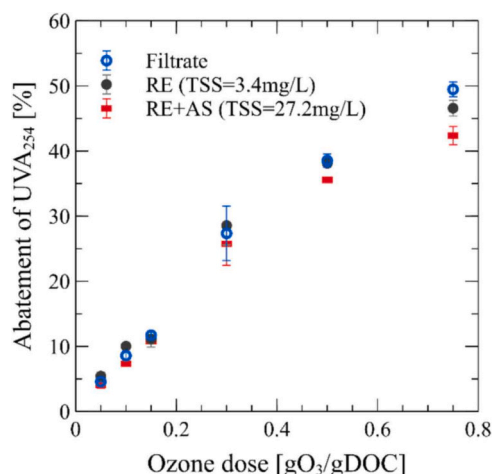
Fig. 4. Abatement of UVA at 254 nm at different ozone doses and TSS concentrations. Error bars indicate standard deviations based on double measurements (n = 2).

42% (RE+AS) (Fig. 4). Zucker et al. also reported an adverse effect of particles on the reduction of the effluent UVA$_{254}$ at a dose of 0.93 gO$_3$/gDOC (Zucker et al., 2015), as the UVA$_{254}$ abatement reduced from ca. 57% in the 0.45 µm-filtrated water samples to ca. 46% in unfiltered samples.

In this study, the lowered UVA$_{254}$ abatement at 0.75 gO$_3$/gDOC may have resulted from two mechanisms. Firstly, particles react with ozone and •OH and depleted part of the reactive oxygen species. Therefore, less ozone and •OH were available for the oxidation of the DOM. Secondly, ozone transforms suspended particles into dissolved organic matter, contributing to UVA$_{254}$. The rise of DOC after the ozone disintegration of sludge has been observed at ozone doses from 0.005 to 0.08 gO3/gTSS in literature (Meng et al., 2015; Fatoorehchi, 2016). This was due to cell lysis and the release of intracellular organic matter (Meng et al., 2015; Zhang et al., 2009; Gu et al., 2020) and the transformation of non-soluble EPS into soluble DOM after sludge disintegration (Li et al., 2021).

Compared to the literature study, this study examined the UVA$_{254}$ abatement at six ozone doses as well as the impact of both effluent particles and AS particles. This study reveals that particles had only a minor impact at ozone doses lower than 0.4 gO3/gDOC on UVA$_{254}$ abatement. This is caused by the preferential reactions between ozone and dissolved substances at low ozone doses (Dietrich et al., 2007) and
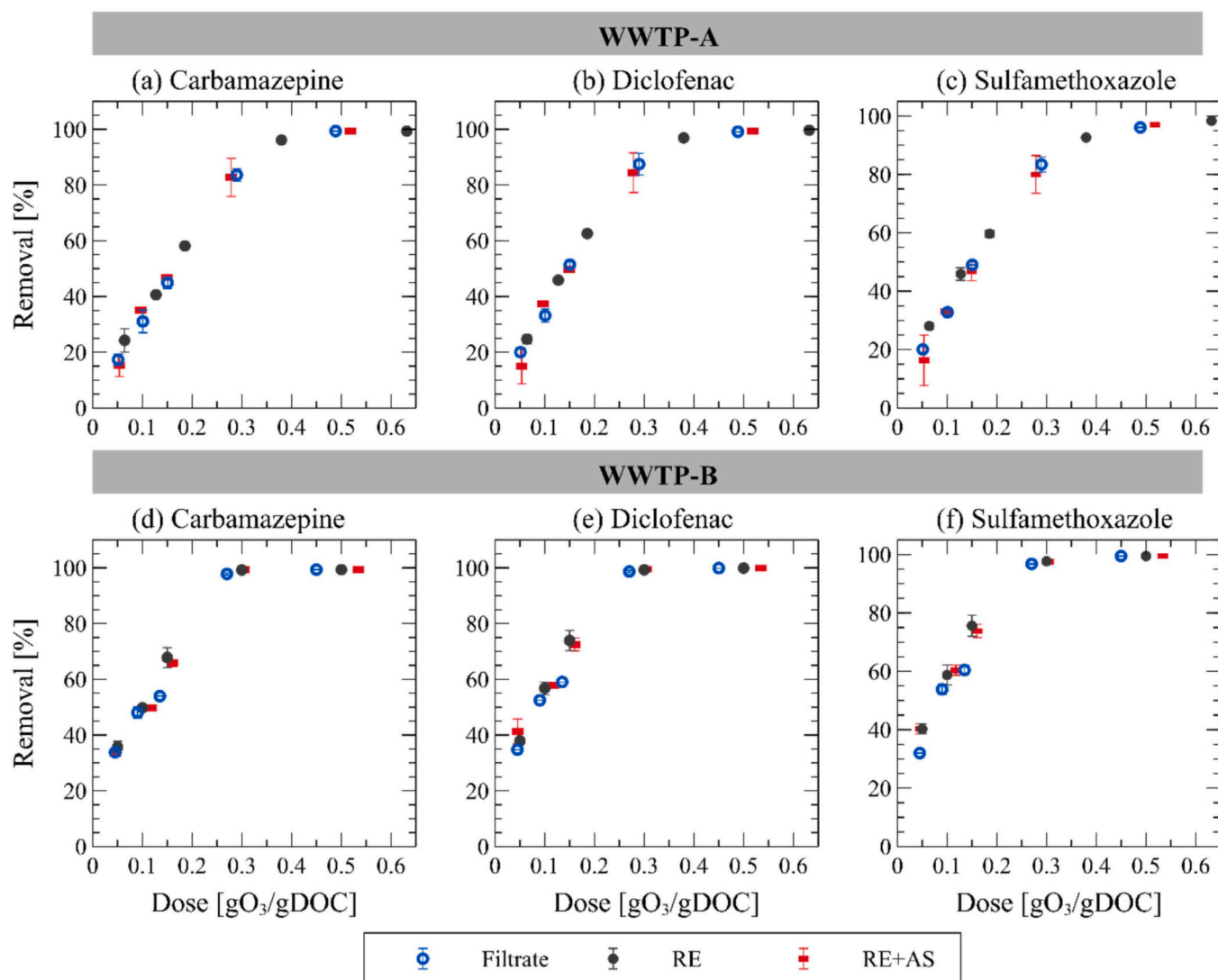

Fig. 5. Removal of the fast-reacting OMPs in effluents with different TSS concentrations in WWTP-A and WWTP-B. (a) and (d): the removal of carbamazepine; (b) and (e): the removal of diclofenac; and (c) and (f): the removal of sulfamethoxazole. Error bars indicate standard deviations based on double measurements (n = 2).

the low reaction rate between ozone and particles. In the sludge particles, the bacterial cells make up a minor part (5 - 20% according to different methods) of the organic material, and the largest remaining part are EPS (Nielsen et al., 2004). EPS have been reported to be resistant to antimicrobial agents such as chlorine and ozone (Brown and Gilbert, 1993; De Beer et al., 1994). A biofilm chlorination experiment shows that chlorine concentrations measured 10 μm deep in the biofilms were typically only 20% or less of the concentration in the bulk liquid after 1–2 h of chlorine treatment (De Beer et al., 1994), indicating the resistance of biofilm and EPS to disinfectants.

3.4. OMP removal in the water phase with different particle concentrations

The removal of fast-reacting OMPs such as carbamazepine, diclofenac, and sulfamethoxazole at different ozone doses and particle concentrations in samples from two WWTPs was investigated. Fig. 5 shows that a particle concentration of up to 30 mg/L had a minor impact on removing these compounds. Like the fast-reacting substances, the moderately-reacting substances including benzotriazole, candesartan and metoprolol were similarly removed in the presence or the absence of particles (Fig. S1 in the Supplementary Information). Therefore, results indicate that the effluent particles and AS particles have negligible impact on removing fast- and moderately-reacting OMPs in the water phase via ozonation till a concentration of 30 mg/L TSS.

This finding is consistent with the previous evidence reported by Huber et al., who studied the removal of OMPs in raw effluent or effluent spiked with 15 mg/L AS (Huber et al., 2005). Minor effects of the addition of AS on OMP removal were observed (Huber et al., 2005). On the other side, Juárez et al. reported that suspended solids (mainly from 50 - 200 mg/L) had a negative effect on OMP removal (Juárez et al., 2021). If a linear correlation between the TSS concentrations and reduced OMP removals was assumed, the impact of TSS at common effluent concentrations (<10 mg/L) was between 1.6% and 3.7% in the study of Juárez et al. (Juárez et al., 2021), which is among the measurement uncertainty of the experiments.

This study suggests that the neglectable impact of particles up to 30 mg/L on ozonation was owing to the low distribution of OMPs in the particle phase compared to the water phase as shown in Sections 3.1 and 3.2. No critical reaction competition thus occurred between the OMPs in water and particle phases. Another argument is the relatively low reaction rate between ozone and the components of particles, such as EPS. A previous study has proposed that the low ozone transfer (0.4%) across the boundary layer surrounding the particle was the mechanism of the minor effect of particles during effluent ozonation (Huber et al., 2005). In their study, a particle surface area of 2.4 m²/gTSS was estimated with the assumption of a spherical particle/floc (50 μm) to evaluate the ozone transfer to particles (Huber et al., 2005). This study demonstrates that OMPs sorbed on particles were comparably removed during ozonation compared to OMPs in the aqueous phase. This implies that ozone transfer from bulk to the particle surface didn't noticeably hinder the ozonation of the particles. Andreadakis reported that the specific surface areas of sludge flocs (porous structure) were measured to be typically 100 - 200 m²/g dry sludge, which was one to two orders of magnitude higher than the corresponding geometric floc surface areas (Andreadakis, 1993). Therefore the ozone diffusion to particle surface was probably underestimated by Huber et al. (Huber et al., 2005). However, more studies are necessary to investigate the ozone transfer and reactions within the porous structure of the sludge particles.

3.5. OH and ozone exposure

3.5.1. OH exposure

The abatement of an OMP can be predicted by a second-order kinetic equation (Eq. 1). Based on Eq. 1, para-chlorobenzoic acid (pCBA, $k_{\bullet OH} =$

5×10^9 $M^{-1}s^{-1}$) is usually used as a probe compound to calculate •OH exposure. This study uses the removal of irbesartan to determine the •OH exposure, because irbesartan mainly reacts with •OH ($k_{O_3} = 23$ $M^{-1}s^{-1}$, $k_{\bullet OH} = 10^{10}$ $M^{-1}s^{-1}$) (Bourgin et al., 2018). A preliminary study revealed that irbesartan removal was well predicted by

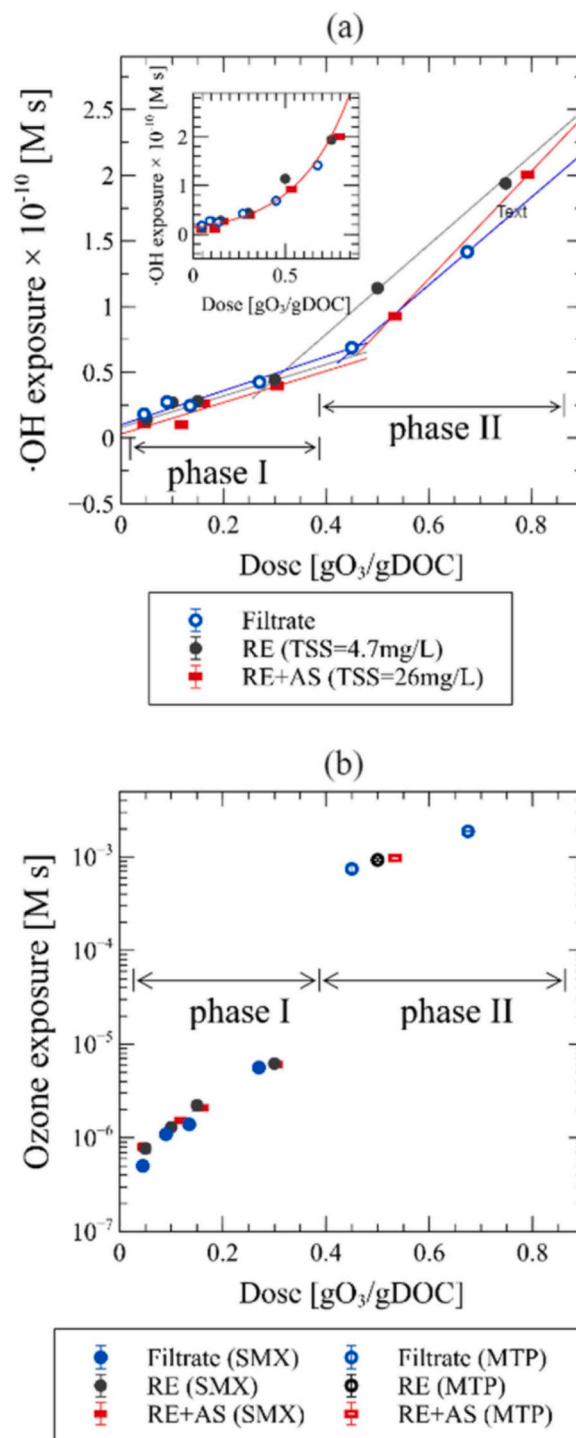**Fig. 6.** (a) •OH exposure (a) and (b) ozone exposure determined for wastewater samples with different particle concentrations of WWTP-B. Inset of (a): Exponential regression of the same data points of three wastewater types. In Figure (b), the filled points were determined with the removal of sulfamethoxazole (SMX), and the hollow points were determined with the removal of metoprolol (MTP). Error bars indicate standard deviations based on double measurements (n = 2).

the removal of pCBA (data not shown).

Fig. 6(a) displays the correlation between •OH exposure and ozone doses ranging from 0.05 to 0.8 gO₃/gDOC in wastewater samples with different particle concentrations in WWTP-B. Only a minor difference was observed between the three water types: filtrate, RE, and RE+AS. Furthermore, the correlation between •OH exposure and ozone doses can be fit into two linear phases (main figure) or be described as an exponential regression (inset of Fig. 6(a)). Lee et al. (2014) reported a two-phase linear regression of •OH exposure with the first phase from 0.0 - 0.6 gO₃/gDOC and the second phase from 0.6 - 1.5 gO₃/gDOC, which is comparable to this study (Lee et al., 2014).

3.5.2. Ozone exposure

The ozone exposure as a function of the ozone doses for water samples from WWTP-B is demonstrated in Fig. 6(b). For the ozone doses from 0.05 to 0.3 gO₃/gDOC, the ozone exposure was calculated based on the removal of sulfamethoxazole ($k_{O_3} = 5.7 \times 10^5$ $M^{-1}s^{-1}$, $k_{•OH} = 5.5 \times 10^9$ $M^{-1}s^{-1}$). For the ozone doses from 0.4 to 0.75 gO₃/gDOC, the removal of metoprolol ($k_{O_3} = 2 \times 10^3$ $M^{-1}s^{-1}$, $k_{•OH} = 7.3 \times 10^9$ $M^{-1}s^{-1}$) was applied to determine the ozone exposure. Metoprolol was not used for doses lower than 0.4 gO₃/gDOC, because metoprolol elimination was low at these doses ($\leq$ 20%) and was mainly removed by •OH. These two substances were chosen due to their abundance in the wastewater effluent samples and their reaction rate with ozone: sulfamethoxazole as a fast-reacting substance and metoprolol as a moderately-reacting substance.

Ozone exposure increased exponentially, ranging from 10^{-7} to 10^{-3} (M s) as a function of the ozone doses. Similar results have been reported by Lee et al. (2014), who have also determined similar ozone exposure ranging from 10^{-7} to 10^{-3} (M s) in hospital wastewater at similar ozone doses. It can be seen that there was a jump in the ozone exposure when the substance for exposure calculation was changed from sulfamethoxazole to metoprolol (Fig. 6(b)). This may be because the •OH and ozone rate constants chosen from the literature (listed in Table S5 in Supplementary Information) don't align with the real rate constants during ozonation in this study.
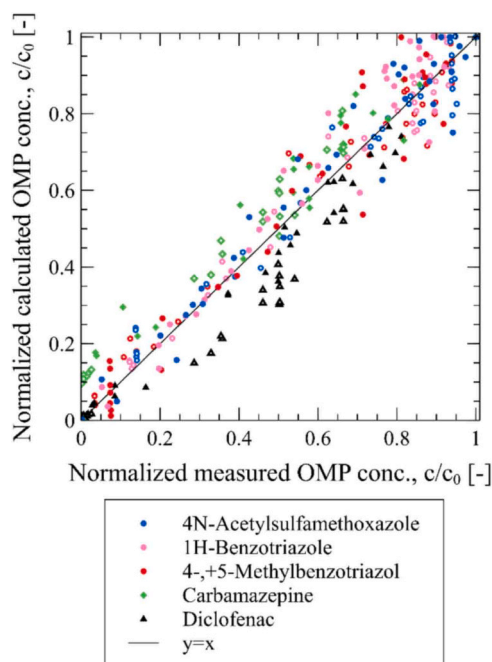

Fig. 7. Calculated and measured OMP concentrations after ozonation of wastewater samples from WWTP-A and WWTP-B at ozone doses from 0.05 to 0.8 gO3/gDOC.

3.6. Prediction of micropollutant removal efficiency

Fig. 7 shows the calculated and measured OMP removal for all samples of both WWTPs. The calculated removal was assessed based on the •OH and ozone exposure reported in 3.5, the ozone and •OH rate constants of these compounds (Table S5 in the Supplementary Information), and Eq. 1. It can be seen that using irbesartan for the determination of •OH exposure as well as sulfamethoxazole and metoprolol for the calculation of the ozone exposure resulted in a good prediction of the other OMPs.

The data points in Fig. 7 are scattered above or under the line y = x for benzotriazole and methyl-benzotriazole. The slight inconsistency of these substances between the measured and calculated removal can result from measurement uncertainty of the OMPs. Moreover, the concentrations of carbamazepine were generally overpredicted, and the concentrations of diclofenac were generally underestimated. The two reaction constants were determined in Milli-Q water in literature (Table S5) and may deviate from the actual rate constants in wastewater in this study. In this case, the ozone rate constant for carbamazepine applied in the calculation was underestimated.

The impact of TSS concentration on the prediction of the OMP concentrations has also been assessed (Fig. S6). Results show that the TSS concentration up to 30 mg/L didn't play a role in predicting the OMP concentrations.

4. Conclusions

This study investigated the impact of effluent particles and secondary sludge up to a TSS concentration of 30 mg/L on removing organic micropollutants during wastewater effluent ozonation. In order to evaluate the impact of OMPs in the particle phase on the OMP removal in the aqueous phase, particle-bound OMPs were extracted and analyzed before and after ozonation.

It was determined that OMP sorption in effluent particles was 2 - 5 times higher than that in sludge particles. The OMPs in the particle phase were 1 - 3 orders of magnitude lower than that in the aqueous phase. During ozonation, OMPs sorbed on particles were removed comparably to OMPs in the aqueous phase.

The particle concentrations within common secondary effluent ranges had a minor effect on the removal of OMPs in the aqueous phase, probably due to the low distribution of OMPs in the particle phase and low reaction rate between ozone and the components of particles, such as EPS, in the investigated ozone concentrations. The reduction of UVA₂₅₄ during ozonation was not affected by particles (TSS $\leq$ 30 mg/L) when the ozone dose was lower than 0.4 gO₃/gDOC. However, the reduction of UVA₂₅₄ was negatively affected by particles at higher ozone doses. It suggests that UVA₂₅₄ abatement was more sensitive to the presence of particles compared to OMP removal.

Moreover, the calculated ozone and •OH exposure at different TSS concentrations and two WWTP effluents can reliably predict the elimination of other OMPs analyzed in this study.

CRediT authorship contribution statement

Jueying Qian: Conceptualization, Methodology, Investigation, Data Curation, Writing, Review and Editing; **Hana Atallah Al-asad:** Conceptualization, Review; **Janna Parniske:** Conceptualization, Review; **Andrea Brandl:** Methodology, Investigation; **Monika Degenhardt:** Methodology, Investigation; **Tobias Morck:** Conceptualization, Methodology, Validation, Supervision, Writing, Review and Editing

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Janna Parniske, Hana Atallah Al-asad, Jueying Qian reports financial

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Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2023.115915.

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