



Research article

Influence of operational conditions and wastewater properties on the removal of organic micropollutants through ozonation

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ABSTRACT

The objective of this study was to evaluate the influence of operational conditions and wastewater properties on the removal of pharmaceuticals, contrast media and antibiotics through ozonation, in order to facilitate the optimization of treatment and its implementation on a full scale. Pilot-scale ozone oxidation trials were performed on treated wastewater, before and after post-precipitation, over a seven-month period, including summer and winter months. Hydraulic retention times as short as 7 min were found to be sufficient for organic micropollutant removal. A short hydraulic retention time reduces both investment costs and land use. Neither the choice of ozone dispersion method, a static mixer or a Venturi injector, nor the wastewater temperature had any significant effect on the removal efficiency of organic micropollutants, however, higher removal was achieved after on-site post-precipitation with aluminum chloride.

1. Introduction

The reduction of ecological effects and risks to human health posed by the release of treated wastewater containing organic micropollutants has been a high priority for researchers and policymakers for the past decades (Carvalho et al., 2015; EU WFD, Directive 2000/60/EC; Joss et al., 2008; Loos et al., 2013; Nguyen et al., 2021). Wastewater treatment plants (WWTPs) have been identified as point sources of organic micropollutants such as pharmaceuticals, contrast media and antibiotics (Guilossou et al., 2019; Joss et al., 2008; Ruff et al., 2015; Stangroom et al., 1998). The first national policy on the introduction of advanced treatment for the removal of organic micropollutants was adopted in Switzerland in 2016 (Eggen et al., 2014), and full-scale plants have already been, or are currently being, realized in Switzerland (Bourgin et al., 2018), Germany (Itzel et al., 2017, 2020), Sweden (Baresel et al., 2016), and other countries. Several treatment options have been evaluated, and two of the most promising techniques are activated carbon and ozonation, applied separately or in combination (Abegglen and Siegrist, 2012; Altmann et al., 2014). While both techniques are used in drinking water treatment (Audenaert et al., 2010; Camel and Bermond, 1998; Gibert et al., 2013; Kasuga et al., 2010), the treatment of wastewater has posed new challenges due to the difference in quality and

variation in quantity (diurnal fluctuations and rain events).

Ozone is a highly reactive but selective oxidant that reacts with electron-rich moieties such as secondary and tertiary amines, activated aromatic rings, and olefins (von Sonntag and von Gunten, 2012). This means that the removal of organic micropollutants is substance-specific, for example, carbamazepine and diclofenac have a higher reactivity with ozone than oxazepam and iodinated contrast media (Lee et al., 2014). Ozone also forms hydroxyl radicals in water, which are non-selective oxidants. In addition to the micropollutant reactivity with ozone, other parameters affect the overall removal efficiency, for example the properties of the wastewater, e.g. the concentrations of nitrite and organic carbon, pH, and water temperature (Antonioni et al., 2013; Ekblad et al., 2019; Hansen et al., 2016; Zucker et al., 2015). Although it is difficult to change the properties of the wastewater entering the ozonation plant without re-designing the wastewater treatment process, operational and design parameters such as the ozone dose, dispersion method, hydraulic retention time (HRT), and coagulant addition for post-precipitation prior to ozonation can be adjusted.

Many WWTPs are located in areas with little or no room for expansion. Thus, reducing contact volumes and land requirements is important. WWTPs using ozone for organic micropollutant removal, both pilot- and full-scale, currently apply HRTs between about 15 and 70 min

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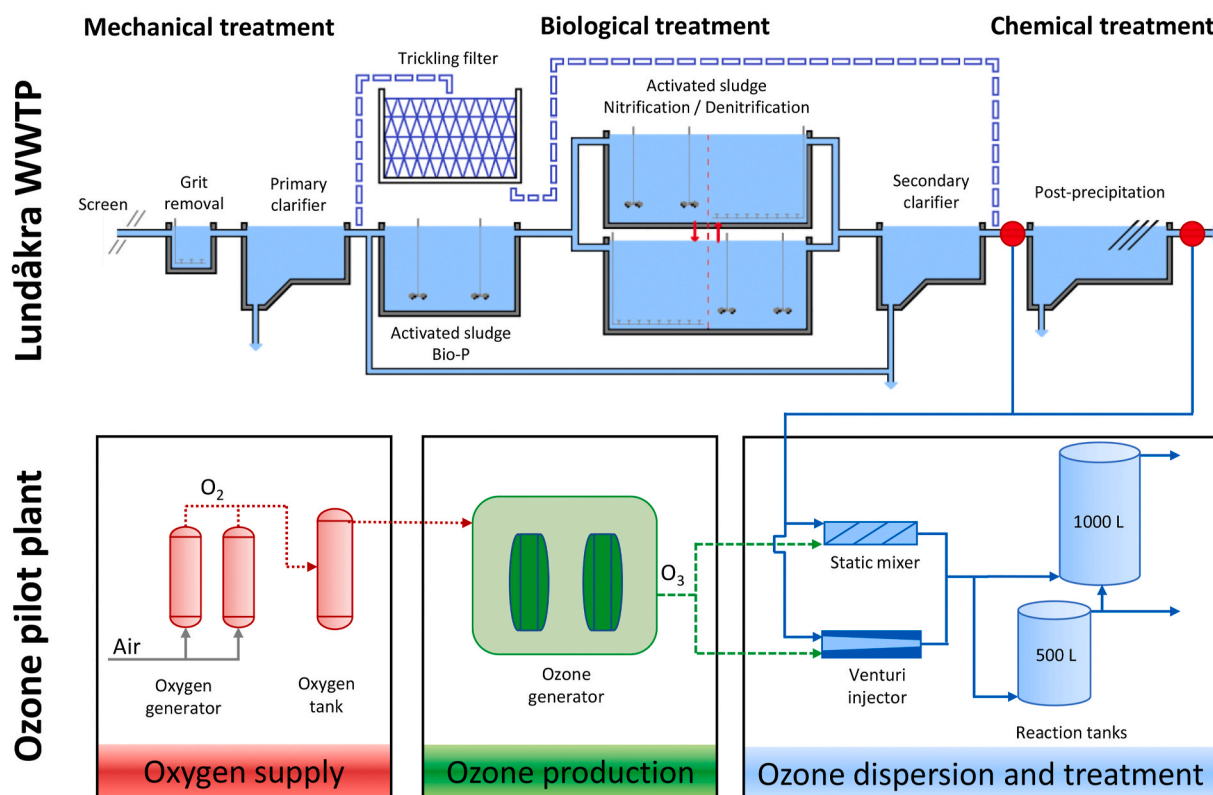


Fig. 1. Overview of the Lundåkra WWTP and the ozone pilot plant. The large red dots before and after post-precipitation indicate extraction points for wastewater pumped to the pilot plant. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Mean values of dissolved organic fractions (DOC and COD), nitrogen species, SS, UV absorption (UVA_{254}) and pH \pm standard deviation in the wastewater before post-precipitation ($n = 35\text{--}46$) and after post-precipitation ($n = 22\text{--}25$).

Quantity	Units	Before post-precipitation	After post-precipitation
DOC	[mg/L]	10.6 ± 1.0	10.0 ± 0.8
COD	[mg/L]	35.1 ± 9.8	27.5 ± 1.8
NO_2^- -N	[mg/L]	0.15 ± 0.05	0.17 ± 0.06
NO_3^- -N	[mg/L]	2.5 ± 0.9	4.4 ± 2.8
NH_4^+ -N	[mg/L]	0.98 ± 0.66	1.47 ± 1.03
SS	[mg/L]	7.5 ± 6.9	1.8 ± 0.9
UVA_{254}	[m^{-1}]	20.4 ± 3.3	20.4 ± 2.1
pH	[-]	7.6 ± 0.3	7.6 ± 0.1

(Bourgin et al., 2018; Lee et al., 2012; Margot et al., 2013; Schollée et al., 2018; Östman et al., 2019). If the HRT could be shortened, then investment costs and space requirements could be reduced. The implementation of ozone oxidation at WWTPs increases the energy consumption of the plant. The main reason for this is the energy-intensive process of ozone production (Abegglen and Siegrist, 2012). Therefore, means of reducing the amount of ozone needed to achieve sufficient removal efficiency should also be investigated, for example, the method of dosing the ozone gas.

The amount of ozone required to achieve sufficient organic micropollutant removal can be reduced by reducing the amount of total organic carbon (TOC) in the wastewater before ozone treatment (Zucker et al., 2015). To ensure that the requirements for phosphorus removal are met, some WWTPs employ post-treatment steps in which the wastewater is further polished before being released to the receiving waters, while others have integrated coagulant dosing with pre- or co-precipitation. Since chemical precipitation is a common practice, it is interesting to investigate the effects this may have on the removal efficiency when using ozone oxidation.

The natural fluctuation in wastewater temperature may also affect organic micropollutant removal. In areas with a temperate climate, the temperature of wastewater may vary between roughly $20\text{ }^\circ\text{C}$ in the summer and $10\text{ }^\circ\text{C}$ in the winter (Davis, 2010). It is thus also important to study the effect of temperature.

This study was carried out to evaluate the effects of HRT, ozone dispersion method, post-precipitation, and wastewater temperature on the removal of organic micropollutants by ozone oxidation, in order to facilitate full-scale optimization and implementation of the process. We performed pilot-scale trials with ozone oxidation over a seven-month period, including summer and winter months, with water before and after post-precipitation.

2. Methods

2.1. Wastewater treatment plant

An ozonation pilot plant was operated at Lundåkra WWTP in Landskrona, Sweden. The wastewater treatment plant has stringent treatment requirements on phosphorus (Tot-P 0.5 mg/L), nitrogen (Tot-N 10 mg/L) and BOD ($BOD_7\text{ }10\text{ mg/L}$). An overview of the WWTP and ozonation pilot plant is shown in Fig. 1. Domestic wastewater from about 40 000 inhabitants, together with some industrial wastewater, is first treated mechanically, by screening, grit removal and settling, then biologically. The biological treatment is based on a Biotenipho™ process with activated sludge for denitrification, nitrification, and biological phosphorus removal. Under high flow conditions part of the inflow is treated in a nitrifying trickling filter. All wastewater is treated in a post-treatment step with lamella sedimentation after the addition of aluminum chloride.

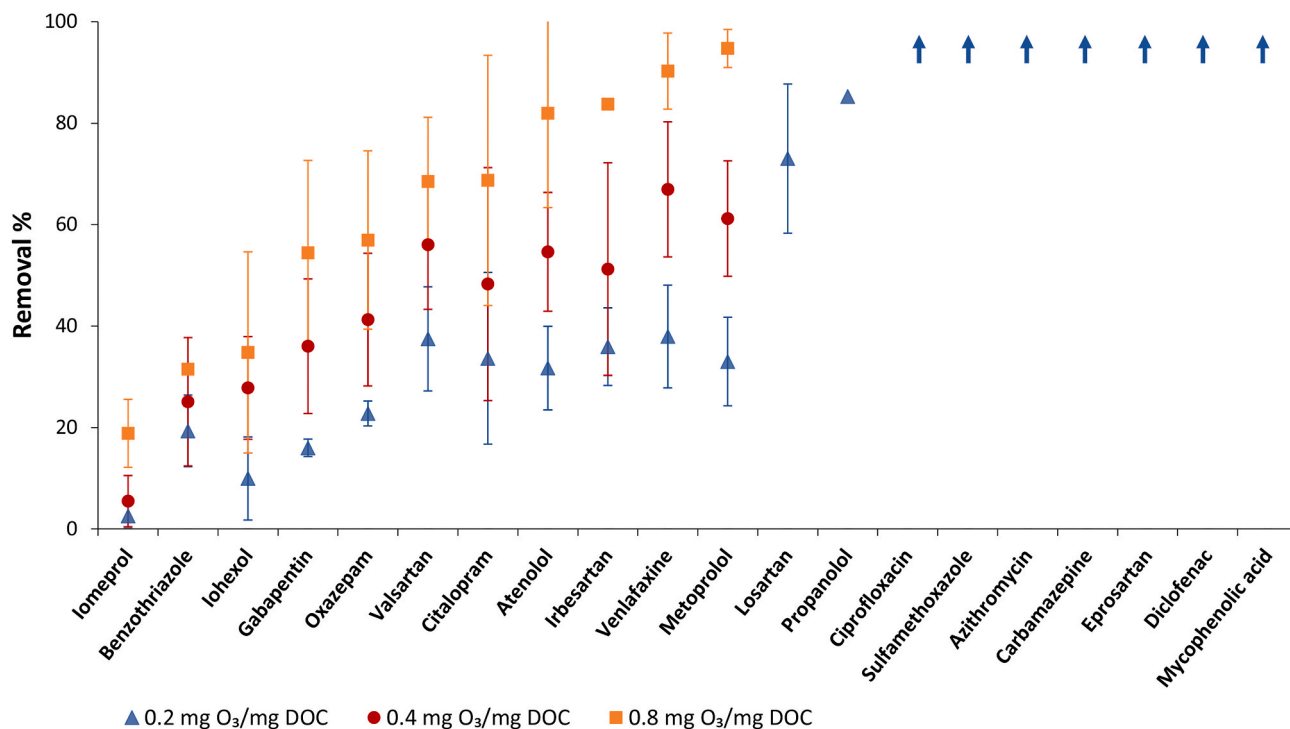


Fig. 2. Average removal efficiency for 20 organic micropollutants, together with standard deviations, at three ozone doses. No rates could be calculated for values below LOQ, and the blue arrows indicate substances detected before, but not after, ozonation at the lowest applied ozone dose. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

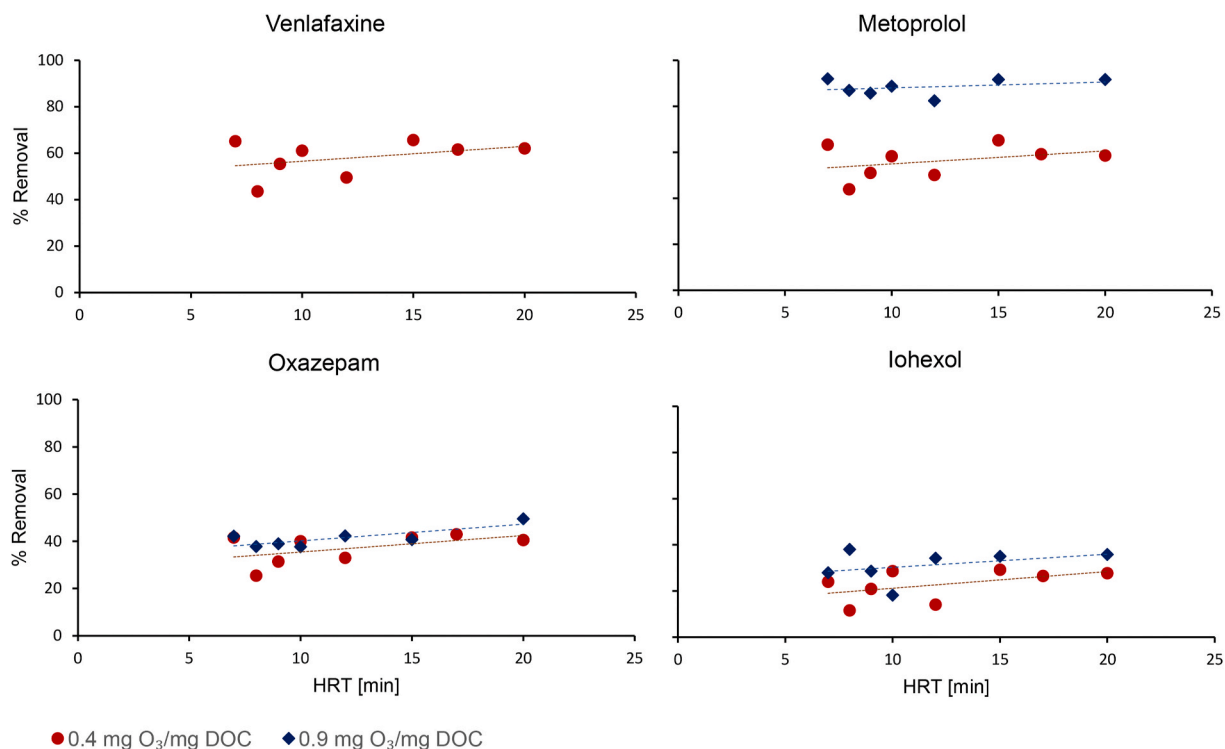


Fig. 3. Dose-response curves for the four selected organic micropollutants, comparing two ozone doses and eight hydraulic retention times. No data are presented for post-ozonation concentrations below LOQ.

2.2. Operation of the ozonation pilot plant

Ozonation of organic micropollutants in the wastewater was performed on water extracted both before and after post-precipitation. The

ozonation pilot plant, built in an insulated standard 20-foot container, consisted of a pump (PC Transfer, Sulzer Ltd, Winterthur, Switzerland), a flow meter (IFM Electronic GmbH, Essen, Germany), a modular PSA oxygen generator (Oxymat A/S, Helsingør, Denmark), an ozone

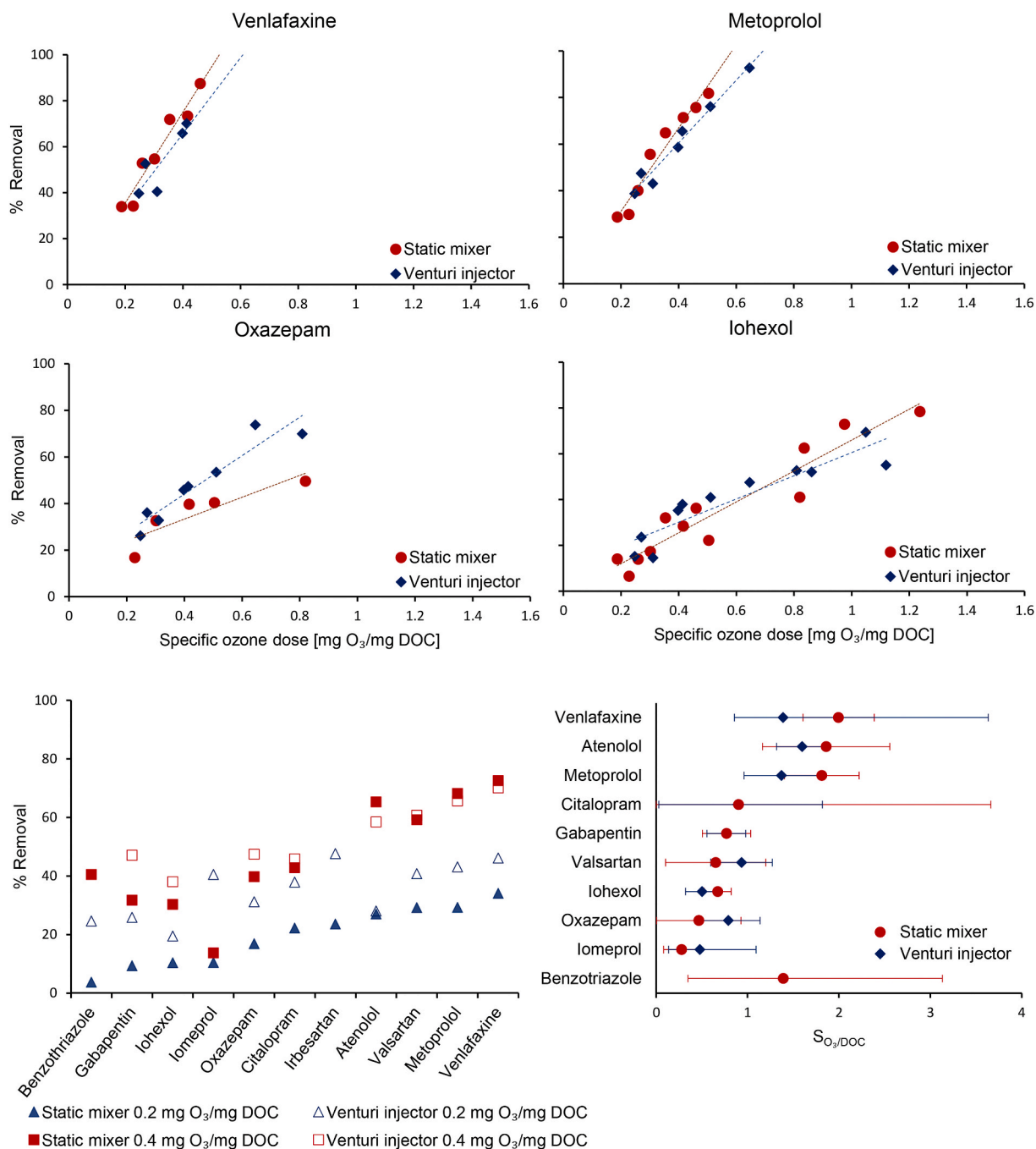


Fig. 4. Dose-response curves for the four selected organic micropollutants, comparing two dispersion methods, a static mixer and a Venturi injector. Two separate sampling campaigns were conducted for each dispersion method. The graph on the lower left shows the percental removal at 0.2 and 0.4 mg O₃/mg DOC. The graph on the lower right shows the calculated S_{O₃/DOC} values, and the error bars represent the 95% confidence intervals. No data are given for post-ozonation concentrations below LOQ.

generator (GM2, Primozone®, Löddeköpinge, Sweden) connected to a chiller (Ultracool, Lauda®, Lauda-Königshofen, Germany), an ozone concentration meter (BMT 964C, BMT Messtechnik GmbH, Berlin, Germany), a static mixer (WEM-80-3, Noritake Co. Limited, Nagoya, Japan), a Venturi injector (1" injector, Model 1078 3, Mazzei®, Bakersfield, CA, USA) (details on the Venturi injector and static mixer in Table S1-S2) and two pressurized reaction tanks (0.5 m³ and 1 m³, 0.2–0.4 bar) that could be used separately or in series. For safety reasons, the ozonated water was released to the inlet of the WWTP. The whole system was controlled by a fully automated PLC system.

2.3. Sampling

The water flow was set to 50 L/min, resulting in a 10-min HRT in the 500-L pressurized reaction tank during all sampling, except in the HRT experiments (see Section 2.3.1). A lag time of at least 3 times the HRT (i. e. 30 min) was applied between changing the ozone dose (or HRT) and sampling. Samples of incoming water to the pilot plant were collected at the same time as the effluent samples. Samples for micropollutant analysis were collected in 15-mL glass bottles and stored at -18 °C until analysis. Samples for the analysis of all parameters except organic micropollutants, were collected in plastic bottles, stored at 4 °C, and analyzed within 24 h. Wastewater temperature and pH were measured

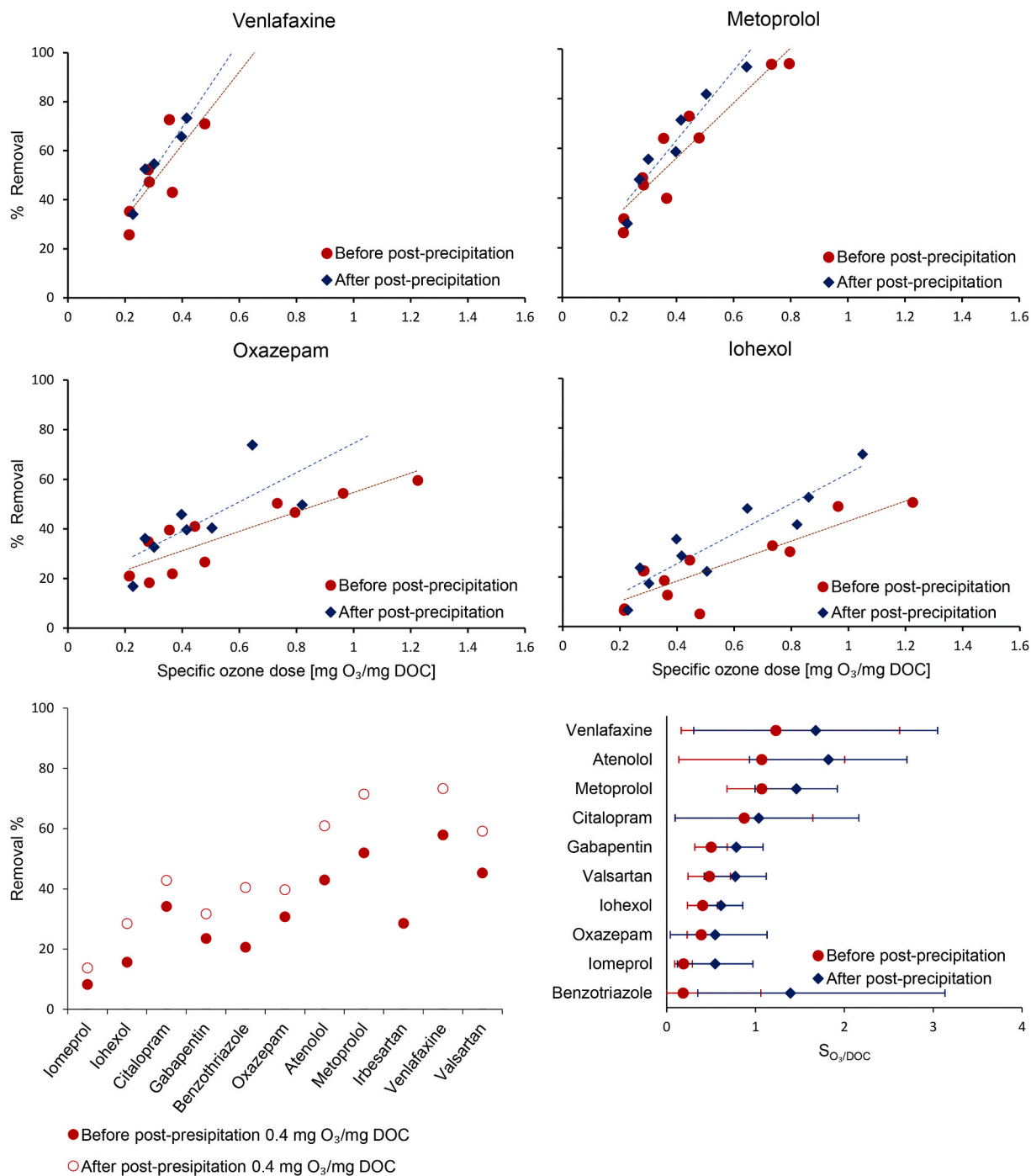


Fig. 5. Comparison of the dose-response curves for ozonated wastewater before and after post-precipitation for the four selected organic micropollutants. The graph on the lower left shows the percental removal at 0.4 mg O₃/mg DOC. The graph on the lower right shows calculated S_{O₂/DOC} values, and the error bars represent the 95% confidence intervals. No data are given for post-ozonation concentrations below LOQ.

at the time of sampling.

The term applied ozone dose, here used for the amount of ozone added in the pilot plant, refers to the calculated value based on gas flow, ozone concentration in the gas and water flow. Concentrations of dissolved ozone in the outgoing water was measured with AccuVac® ampules from Hach (Düsseldorf, Germany) to ensure depletion. Ozone concentrations in the off-gas were not measured in this set up. However, there was no detectable smell of ozone emitting from any of the samples suggesting that no ozone was left in the off-gas as humans can detect the smell of ozone down to 20 µg/m³ (Cain et al., 2007).

2.3.1. Hydraulic retention time

HRTs of 7, 8, 9, 10, 12, 15 and 20 min were tested at two different applied ozone doses (5 and 9 mg O₃/L) dispersed with a static mixer. Residual ozone concentrations in the effluent water were measured using AccuVac® ampules from Hach (Düsseldorf, Germany) to ensure the ozone had been depleted in the reaction tank.

2.3.2. Ozone dispersion method

Two dispersion methods were used to investigate the influence of ozone dispersion on the removal of organic micropollutants: a static mixer and a Venturi injector. Six different applied ozone doses (3, 4, 5, 6,

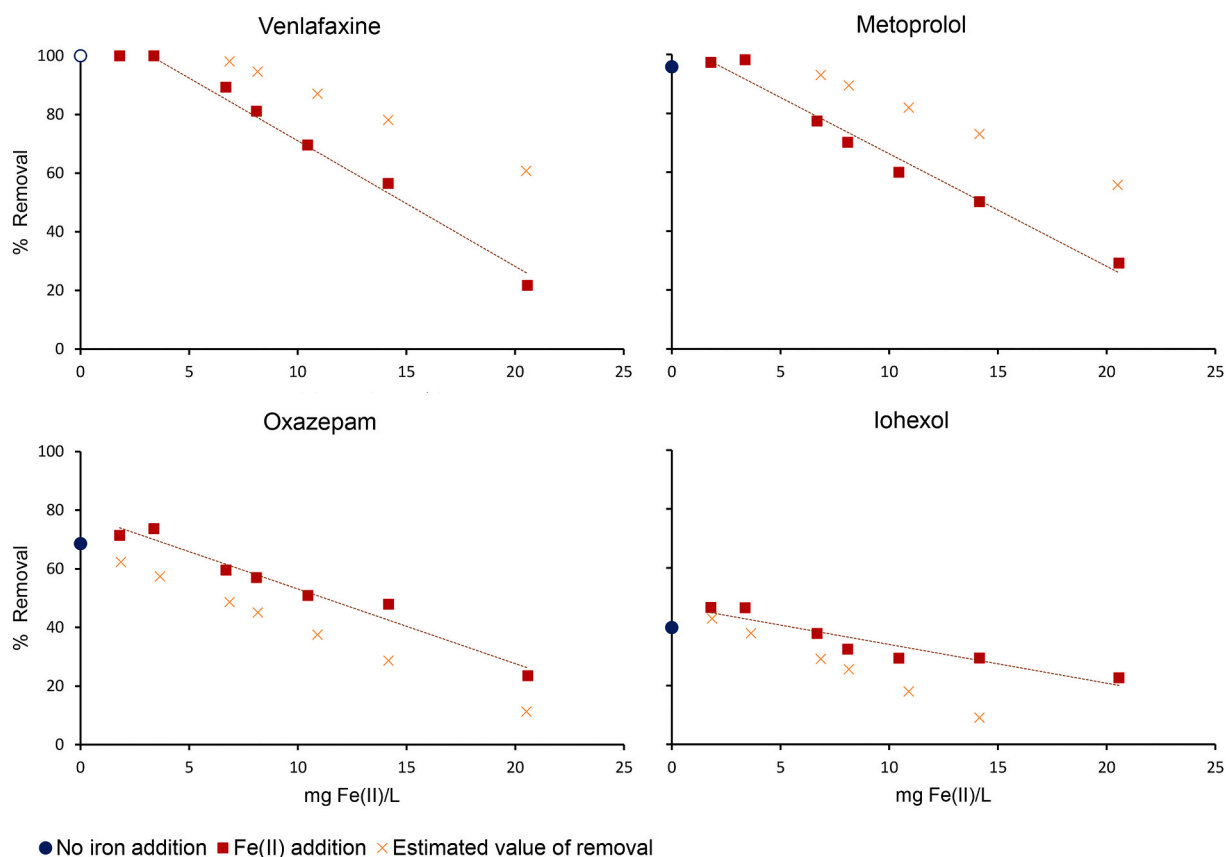


Fig. 6. Dose-response curves for the four selected organic micropollutants with increasing Fe(II) doses and a fixed ozone dose of 0.7 mg O₃/mg DOC, together with the estimated removal based on the stoichiometric relationship between ozone and Fe(II). Concentrations of venlafaxine after ozonation with no iron addition were below LOQ, indicated by the open dot.

9 and 12 mg O₃/L were administered using the two different dispersion methods, on 4 separate occasions.

2.3.3. Effects of post-precipitation prior to ozonation

The possible effects of post-precipitation of phosphorus following activated sludge treatment on micropollutant removal were investigated by running water extracted before and after post-precipitation through the ozonation pilot plant (see extraction points in Fig. 1). These experiments were conducted with applied ozone doses of 3, 4, 5, 6, 9, 12 and 15 mg O₃/L using a static mixer. During the course of these experiments, the aluminum chloride dose varied between 2.2 and 4.8 mg Al³⁺/L.

2.3.4. Effects of iron dosing prior to ozonation

Laboratory-scale ozonation of biologically treated wastewater was performed to assess the possible effects of two other commonly used coagulants, Fe(III) and Fe(II), on the ozone oxidation of organic micropollutants. Ferric iron, Fe(III), and ferrous iron, Fe(II), doses of 10 mg Fe/L were used, and samples without iron were used as references. To ensure measurable concentrations of the organic micropollutants, the water samples were spiked with 5 µg/L without organic solvent. (A complete list of the organic micropollutants is given in Table S3). The lab set up included an ozone generator (GM1, Primozone®, Löddeköpinge, Sweden), oxygen gas in tubes (Linde, Guildford, United Kingdom), an air filter (ultrafilter, Donaldson, Bloomington, Minnesota, USA), a tap water cooling system, a glassware backflow protector, a reaction flask (2 L) with a glass infuser and sampling point cooled with ice, an ozone destructor (Primozone®, Löddeköpinge, Sweden), and an ozone monitor (C-30ZX, EcoSensors®, Newark, California, USA). Iron was added immediately before the addition of a concentrated ozone stock solution (50–79 mg dissolved O₃/L) to the wastewater to achieve

dissolved ozone doses of 2, 3, 4, 5, 8 and 10 mg O₃/L. Note the difference between dissolved ozone dose, used in the laboratory-scale experiment, and applied ozone dose, used in the pilot-scale experiments. A gastight glass syringe (No. 1010, Hamilton Ltd, Reno, NV, USA) was used to add the ozone stock solution within seconds of adding the iron. The dissolved ozone doses were calculated based on triplicate measurements before and after each experiment (six measurements in total). The ozone concentration in the stock solution was determined according to Bader (1982) using a spectrophotometer (Cary® 100, Varian Inc., Palo Alto, CA, USA).

To further investigate the effects of Fe(II) we performed an experiment with stepwise dosing of between 2 and 20 mg Fe(II)/L using biologically treated wastewater and a fixed dissolved ozone dose of 0.7 mg O₃/mg DOC. Water samples were spiked with 2 µg/L (Table S4) before the addition of iron and ozone dosing with 2, 3, 4, 5, 8 and 10 mg dissolved O₃/L, as described above.

2.3.5. Wastewater temperature

Experiments were conducted over a seven-month period, between July 2018 and January 2019, in order to study the effects of the seasonal change in water temperature between summer and winter. Experiments were carried out on biologically treated wastewater (extracted before post-precipitation) and ozone was added at 3, 4, 5, 6, 9, 12 and 15 mg O₃/L using the static mixer.

2.4. Analytical methods

Analysis of the organic micropollutants was performed with high-performance liquid chromatography with tandem mass spectrometry (HPLC/MS-MS). Water samples were injected directly as 100 µL

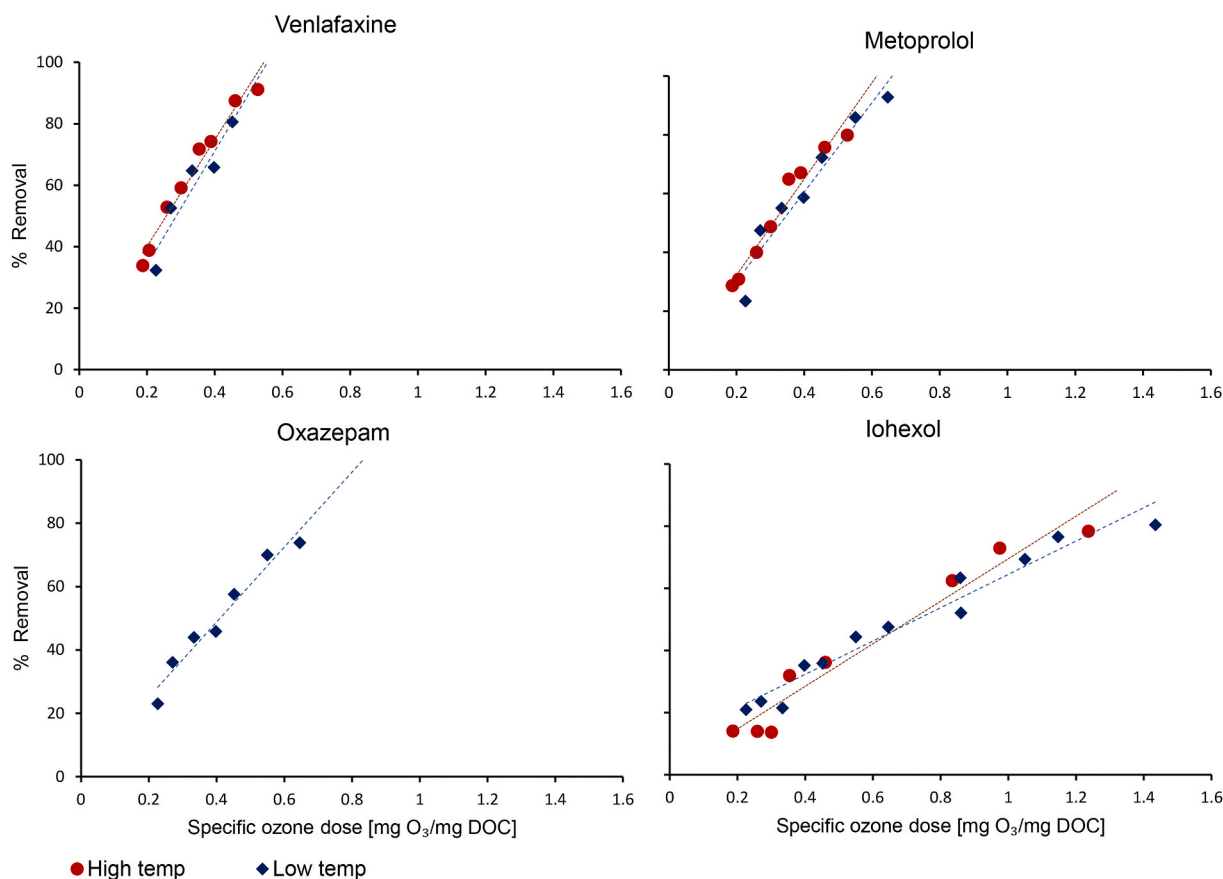


Fig. 7. Dose-response curves for the four selected organic micropollutants under warm and cold weather conditions. No data are presented for post-ozonation concentrations below LOQ.

dispersions using an Ultimate 3000 dual-gradient low-pressure mixing HPLC system with an Ultimate 3000 autosampler (Dionex, Sunnyvale, CA, USA) coupled to an API 4000 triple-quadrupole mass spectrometer (AB Sciex, Framingham, MA, USA). Chromatographic separation was achieved using a Synergi Polar-RP column (150 × 2 mm I.D., particle size 4 μm, Phenomenex, Torrance, CA, USA) with acidic elution using formic acid (0.2%) in both mobile phase A (water) and B (methanol). Multiple reaction monitoring was used to quantify the analytes. Data processing was performed with Analyst 1.6.3 (AB Sciex, Framingham, MA, USA). Limits of quantification were usually around 0.04 μg/L (Table S5) while starting concentrations were around 1 μg/L (Table S3). Details of the methods are provided in the supplementary material in Tables S6-S9.

Nitrogen, phosphate and COD fractions were analyzed spectrophotometrically (Hach-Lange DR 2800, Hach, Düsseldorf, Germany) using Hach-Lange cuvettes: PO₄³⁻-P (LCK 349), Tot-N (LCK 138), NH₄⁺-N (LCK 303), NO₃⁻-N (LCK 339), NO₂⁻-N (LCK 341), COD (LCK 314), and DOC (LCK 385). DOC and soluble COD were measured after filtration through 0.45 μm Whatman cellulose nitrate membrane filters (GE Healthcare, Chicago, IL, USA). Suspended solids (SS) were determined according to SS-EN 872:2005. UV absorption at 254 nm (UVA₂₅₄) was measured with a 1 cm path length cuvette using a Hach-Lange DR 6000 spectrophotometer (Hach, Düsseldorf, Germany).

2.5. Data handling

Linear removal rate constants were estimated according to Ekblad et al. (2019) using the least squares regression and Equation (1):

$$R = S_{O_3/DOC} \cdot (O_3 / A) \cdot 100 \quad \text{Eq. 1}$$

where R is the estimated removal efficiency (%), A the concentration of DOC (mg/L), O_3 the applied concentration of ozone (mg/L), and $S_{O_3/DOC}$ the removal constant (mg O₃/mg DOC).

Ozone concentrations in the pilot plant were calculated based on measured gas flow and ozone concentration in the gas (Calculations S1). In addition, all specific ozone doses were corrected based on the nitrite concentration of each wastewater sample in accordance with Equation (2):

$$\text{corrected } S_{O_3/DOC} = (O_3 - 3.43 \cdot NO_2 - N) / DOC \quad \text{Eq. 2}$$

where O_3 is the applied concentration of ozone (mg/L), $NO_2 - N$ the concentration of nitrite nitrogen in the wastewater (mg/L), DOC the concentration of DOC (mg/L) and 3.43 the ozone demand for oxidation of nitrite to nitrate.

Organic micropollutant concentrations below the level of quantification (LOQ, Table S9) were omitted from calculations of the dose-response curves.

3. Results and discussion

3.1. Wastewater characteristics

The characteristics of the wastewater, before and after post-precipitation, are summarized in Table 1. The properties of the wastewater leaving the WWTP was rather stable, indicating a well-functioning treatment. The measured properties of the wastewater before and after post-precipitation was very similar with respect to DOC, nitrogen species and pH, but differed with regard to COD and SS. Edefell et al. (2020) have reported bromide concentrations between 0.3 and 0.5 mg/L in treated wastewater and bromate concentrations above the permissible

level for drinking water (10 µg/L) after ozone doses of 0.7 mg O₃/mg DOC. According to reports from Switzerland, these values are considered relatively high (Soltermann et al., 2016; Soltermann et al., 2017; von Gunten and Hoigne, 1994).

3.2. Pilot-plant micropollutant removal efficiency

Fig. 2 shows the mean removal efficiency of 20 organic micropollutants during 8 sampling campaigns from biologically treated water (before post-precipitation) using the static mixer for the dispersion of ozone. Some of the micropollutants most readily reactive with ozone, such as carbamazepine and diclofenac, showed concentrations below LOQ at the lowest applied ozone dose of 0.2 mg O₃/mg DOC. More than 80% removal was achieved for many of the moderately reactive micropollutants, such as atenolol, metoprolol, and venlafaxine, at the highest applied ozone dose of 0.8 mg O₃/mg DOC. However, the maximum removal of iodinated contrast media at the highest applied ozone dose was only 40%. The low removal of contrast media is consistent with the results of previous studies (Kovalova et al., 2013; Margot et al., 2013).

To further compare the effects of the parameters studied in this work, four organic micropollutants, representing groups of micropollutants with different reactivity with ozone, in accordance with the classification proposed by Lee et al. (2014), were selected as indicator substances. Venlafaxine and metoprolol were selected as they represent a group of substances that are relatively easy to oxidize through direct reactions with ozone (second-order reaction rate constant > 10⁴ M⁻¹ s⁻¹). Oxazepam represents a group of organic micropollutants with low reactivity with ozone (<50 M⁻¹ s⁻¹), but with a moderate reactivity with hydroxyl radicals (≥5 × 10⁹ M⁻¹ s⁻¹). Iohexol was selected to represent the group of iodinated contrast media that has negligible reactivity with ozone and low reactivity with hydroxyl radicals, as previously reported for iopromide with a similar iodinated structure (<50 M⁻¹ s⁻¹ for ozone; < 5 × 10⁹ M⁻¹ s⁻¹ for hydroxyl radicals) (Lee et al., 2014). The removal efficiencies for these compounds were: venlafaxine 90 ± 7%; metoprolol 95 ± 4% and iohexol 35 ± 20%, all at 0.8 mg O₃/mg DOC, and are in good agreement with the values reported in previous studies (Ekblad et al., 2019; Margot et al., 2013).

3.3. Hydraulic retention time

Fig. 3 shows the results of the pilot trials for venlafaxine, metoprolol, oxazepam, and iohexol with varying HRTs at 0.4 and 0.9 mg O₃/mg DOC. The results show no significant increase in the removal of organic micropollutants with increasing HRT. (All dose-response curves are shown in Figure S1). The results suggest that ozone oxidation can be run with an HRT of 7 min without compromising the removal efficiency. Previous studies have also shown that high removal efficiency can be obtained with short HRTs (Ekblad et al., 2019; El-taliawy et al., 2017; Nilsson et al., 2017). Since ozone poses a human health risk, it is important to ensure that no residual ozone is released after treatment. The AccuVac® tests showed that there was no residual ozone in the water at any HRT (<0.01 mg O₃/L). Both Nöthe et al. (2009) and Hansen et al. (2016) reported that the lifetime of ozone (10 mg/L) in wastewater at pH 7–8 was less than 4 min.

3.4. Ozone dispersion method

We compared the two dispersion methods, a static mixer and a Venturi injector. Only minor differences in removal efficiencies were observed (Fig. 4). (All dose-response curves are shown in Figure S2). This was verified by the calculated removal constants (S_{0₃/DOC}) and 95% confidence intervals (Fig. 4). However, comparing percental removal (Figure S3), the use of a Venturi injector seems to result in somewhat higher removal (15 ± 8%) at the lowest applied ozone dose (0.2 mg O₃/mg DOC) while this difference is no longer apparent at higher ozone

doses (3 ± 7% at 0.4 mg O₃/mg DOC).

3.5. Effects of post-precipitation on ozonation

The properties of the wastewater before and after post-precipitation were stable during the sampling period (Table 1). Higher concentrations of SS and COD were observed before post-precipitation than after. Aluminum doses of 2.2–4.8 mg Al³⁺/L was applied based on the varying PO₄-P concentrations of 0.19–0.41 mg/L. This aluminum dose corresponds to molar ratios of 13.2–13.8 mol Al³⁺/mol PO₄-P.

Fig. 5 shows the dose-response curves for the four selected organic micropollutants after the ozonation of wastewater before and after post-precipitation. (All dose-response curves are given in Figure S3). A trend towards higher removal constants (S_{0₃/DOC}) after post-precipitation can be seen in the lower graph in Fig. 5, although the uncertainty is high, as indicated by the broad confidence intervals. This difference can also be seen when calculating the percental removal (13 ± 5% at 0.4 mg O₃/mg DOC). A positive correlation has previously been reported between the removal of suspended solids with coagulation and flocculation, and the removal of organic micropollutants (Zucker et al., 2015). In addition, our previous study (Ekblad et al., 2019) suggests that the decrease in COD (~7 mg/L) could correspond to an estimated decrease in the required applied ozone dose of ~2 mg O₃/L to achieve 80% removal of metoprolol and venlafaxine. The specific ozone dose required to achieve a removal efficiency of 80% of metoprolol and venlafaxine before and after post-precipitation differs by 0.1–0.2 mg O₃/mg DOC (Fig. 5), which agrees well with the estimated decrease in the required applied ozone dose of 2 mg O₃/L for wastewater containing 10 mg DOC/L (Table 1).

3.6. Effects of iron addition prior to ozonation

The lab-scale experiments on the addition of Fe(III) and Fe(II) salts show that adding Fe(II) reduces the efficiency of ozone oxidation of all the organic micropollutants analyzed, while no clear trend could be seen when adding Fe(III) (Figure S4). The theoretical amount of ozone needed to oxidize 1 mg of Fe(II) is 0.48 mg (Langlais et al., 1991).

To investigate the relationship between iron dose and ozone consumption, we increased the Fe(II) dose stepwise from 2 to 20 mg/L at a dissolved ozone dose of 0.7 mg O₃/mg DOC (Fig. 6). (All dose-response curves are shown in Figure S5). These results confirm the linear relationship between iron dose and lower removal efficiency for the organic micropollutants analyzed in this study. In an attempt to describe this effect, we estimated the removal based on the initial concentration of micropollutants, the iron dose, and the stoichiometric relationship between Fe(II) and ozone (see Calculations S2), similar to the corrections made for nitrite. The calculated removal based on the corrected ozone dose (Fig. 6) indicates that there is no universal explanation, as the removal of individual substances is affected differently. One explanation could be that the pH is lowered from 7.9 before adding Fe(II) to 7.2 after adding the highest dose of 20 mg Fe(II)/L. This decrease in pH would affect the reaction rate of metoprolol and venlafaxine with protonatable amine moieties (Benner et al., 2008; Zucker et al., 2018). In addition, the addition of Fe(II) has a positive effect on the formation of hydroxyl radicals (Zhang et al., 2013). This could explain why the experimental values of the removal of substances that predominantly react with these radicals, e.g. oxazepam and iohexol, is higher than the theoretical values.

Although the addition of Fe(II) had an evident effect on organic micropollutant removal in the lab, in practice, the addition of Fe(II) salts would be carried out in, or just before, aerated treatment steps. Morgan and Lahav (2007) have shown that the oxidation of Fe(II) to Fe(III) by dissolved oxygen occurs within minutes at pH 7.6. This suggests that the risk of negative effects arising from the addition of iron is limited.

3.7. Wastewater temperature

The temperature of the wastewater varied between 12.7 °C and 21.4 °C over the study period. The mean temperature was 13.0 ± 0.4 °C during the colder winter months, and 20.2 ± 1.7 °C during the warmer summer months. The solubility of ozone in water increases with decreasing water temperature. Lowering the temperature from 20 °C to 0 °C almost doubles the solubility (von Sonntag and von Gunten, 2012). At the same time, the water temperature affects the depletion rate of ozone; a higher depletion rate being observed with increasing temperature (Elovitz et al., 2000; Hansen et al., 2016; Nöthe et al., 2009). This means that the reaction between organic micropollutants and ozone is faster at higher water temperatures. Although reactivity rates increase, and the solubility of ozone decreases, with increasing temperature, we found no measurable effects of seasonal temperature changes on the dose-response curves for the organic micropollutants (Fig. 7). (All dose-response curves are shown in Figure S6). This suggests that temperature has little or no direct effect on organic micropollutant removal in wastewater treatment with ozone oxidation in the applied temperature and HRT range.

4. Conclusions

We have performed pilot-scale trials with ozone oxidation to evaluate the effects of HRT, ozone dispersion method, post-precipitation, and wastewater temperature on the removal of organic micropollutants, and have drawn the following conclusions.

- An HRT of only 7 min could be used without compromising the removal efficiency of the organic micropollutants evaluated.
- The choice of dispersion method, static mixer or Venturi injector, did not affect removal efficiency at applied ozone doses above 0.4 mg O₃/mg DOC.
- Post-precipitation with aluminum chloride seems to result in a slight improvement in the removal efficiency of organic micropollutants.
- Adding iron salts in the lab showed that Fe(II) affected the removal of micropollutants negatively, while Fe(III) had no observed effect.
- The seasonal changes in wastewater temperature (13–21 °C) did not affect the removal efficiency significantly at the ozone doses (0.2–1.4 mg O₃/mg DOC) and HRTs (7–20 min) studied.

Although site specific, the evaluated parameters are universal, and the results can be applied in other contexts. The long-term nature of the experiments, stretching over nine months, gives important knowledge for future expansions of WWTPs for removal of organic micropollutants.

CRedit author statement

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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

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