Improving the ozone-activated peroxymonosulfate process for removal of trace organic contaminants in real waters through implementation of an optimized sequential ozone dosing strategy

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ABSTRACT (max. 300 words)

The ozone-activated peroxymonosulfate process (O_3/PMS) has received increasing attention for the removal of trace organic contaminants (e.g. pesticides and pharmaceuticals) from water bodies. However, the ozone dosing strategy has not yet been properly investigated, especially in real water matrices. Typically one-step dosing is applied in literature. Nevertheless, optimal dosing is an important step for improving the process. This study investigates the effect of sequential ozone dosing on the PMS activation, atrazine (ATZ) removal, residual ozone concentration and radical exposure, and compares the results to those of a one-step ozone dosing approach. Experiments were performed in three water matrices with a different (in)organic content, i.e., secondary effluent, surface water and groundwater. In all matrices, the highest PMS activation was reached when applying three sequential ozone doses (3 x 5 mg O_3/L). This resulted in a 3 times higher ATZ removal efficiency (up to 46%) in secondary effluent compared to that obtained with a one-step ozone dosing (15 mg O_3/L). In surface water and groundwater, similar ATZ removal (> 90%) was observed among the different ozone dosing strategies. However, the sulfate radical ($SO_4^{\bullet-}$) exposure increased after each ozone addition. After three ozone additions of 5 mg/L, $SO_4^{\bullet-}$ contributed for 9%, 26% and 54% to ATZ removal in respectively secondary effluent, surface water and groundwater. This high $SO_4^{\bullet-}$ contribution compared to $^{\bullet}OH$ contribution is an advantage as the selectivity of $SO_4^{\bullet-}$ gives rise to less radical scavenging by bulk organic matter and thus increases the (cost-)effectiveness of the O_3/PMS process.

Key-words: ozone, peroxymonosulfate, dosing, micropollutant, water, advanced oxidation

1. INTRODUCTION

Trace organic compounds (TrOCs) such as pharmaceuticals, pesticides and personal care products are often found in water bodies at low concentrations (ng/L – µg/L), and are associated with long-term toxicity, endocrine disrupting effects and antibiotic resistance (Luo et al., 2014; Rogowska et al., 2020). The ozone-activated peroxymonosulfate process (O_3/PMS) is an advanced oxidation process, and has been gaining increasing interest for the removal of TrOCs in water (Cong et al., 2015; Deniere et al., 2022, 2018; Shao et al., 2019; Wu et al., 2019; Yang et al., 2015). The O_3/PMS process relies on the production of two types of radicals, i.e. hydroxyl ($^{\bullet}OH$) and sulfate ($SO_4^{\bullet-}$) radicals, via the reaction of O_3 with PMS (SO_5^{2-}) (Yang et al., 2015). For now, most research is focused on its application in spiked deionized water. Compared to the conventional ozonation process, enhanced removal efficiencies of TrOCs were observed due to the addition of PMS. Both radicals were detected, and $SO_4^{\bullet-}$ were identified as the main radical contributors to TrOC removal (Cong et al., 2015; Deniere et al., 2018; Yang et al., 2015). Although limited research has been performed in real water matrices, some important observations were recently made. The instantaneous ozone demand (IOD) of the water, which represents the consumed ozone by highly ozone reactive organic compounds within 5 seconds of reaction, was increased by the addition of PMS (Deniere et al., 2022). This increase (ΔIOD) was higher in surface water and groundwater than in secondary effluent. This suggests that the PMS activation by ozone is hindered in secondary effluent by matrix constituents, which results in a more limited improvement of TrOCs removal. Furthermore, in real water matrices, $^{\bullet}OH$ were identified as the main radical contributors which is the opposite from the results obtained in deionized water. This shift was attributed amongst others to the presence of chloride, which is a radical scavenger of $SO_4^{\bullet-}$ and results in extra production of $^{\bullet}OH$ (Deniere et al., 2022; Yang et al., 2015).

As such, the full potential of O_3/PMS is not reached as the total amount of added PMS is not activated in either deionized water or real water samples (Deniere et al., 2018; Milh et al., 2021). In deionized water, the amount of activated PMS can be boosted by increasing the pH of the matrix. Also the molar ratio between ozone and PMS can be optimized by decreasing the PMS concentration and keeping the ozone concentration constant. At a PMS:O_3 ratio of 1:10, complete activation of PMS could be reached, but a 1.3 – 1.5 times lower removal efficiency of TrOCs was noticed compared to that at a PMS:O_3 ratio of 1:1 (Deniere et al., 2018). However, in real water matrices, such as secondary effluent, surface water and groundwater, it is challenging to increase the pH as the water contains a certain buffering capacity, and extra chemicals are an additional cost during treatment. A more realistic alternative could be a multiple activation of PMS. This approach has already been investigated during the iron-activated persulfate (Fe^{2+}/PS) process, showing that a sequential dosing of ferrous iron activated a similar amount of PS during every dosing step (Milh et al., 2021). At the end, more PS was activated during sequential dosing than during single time dosing because less scavenging reactions took place that arise with high Fe^{2+} concentrations. The higher PS activation resulted in 25% extra removal of sulfamethoxazole (Milh et al., 2021). Although multiple PMS activation by ozone during the O_3/PMS process has not been explored yet, it is of importance to investigate the different dosing techniques of the oxidants during ozone-based processes. For example, Cruz-Alcalde et al. (2020) noticed promising results during the peroxone process (O_3/H_2O_2) for different dosing strategies of H_2O_2. Cruz-Alcalde et al. (2020) compared continuous with single addition of H_2O_2, while continuously adding ozone, in order to maximize the oxidation efficiency during O_3/H_2O_2. Results showed that the continuous addition of H_2O_2 improved the removal of acetamiprid (ACMP) compared to single H_2O_2 addition due to less $^{\bullet}OH$

scavenging by H_2O_2. However, the degree of improvement in ACMP removal was dependent on the load of the (in)organic matrix: up to 15% difference was noticed in wastewaters with a relatively low load (DOC = 7.1 – 13.3 mg/L), while only up to 5% difference was observed in heavily loaded wastewaters (DOC = 21.7 mg/L) (Cruz-Alcalde et al., 2020).

These studies show that it is of high interest – in view of process improvement – to investigate the optimization of the dosing strategy in the O_3/PMS process. Therefore, the goal of this work was to evaluate 4 ozone dosing strategies, i.e. single ozone addition versus 3 different sequential ozone additions. As the total amount of ozone that is applied in each ozone dosing strategy is kept the same, the operating expense (OPEX) is assumed to be similar among the different strategies. Experiments were performed in three different water matrices, i.e. secondary effluent from a municipal wastewater treatment plant (WWTP), surface water and groundwater, as previous research showed that the performance of O_3/PMS is dependent on the (in)organic matrix load (Deniere et al., 2022). The target compound selected in this work was atrazine (ATZ), which is often used as a reference compound in O_3/PMS degradation experiments (Deniere et al., 2022, 2018; Guan et al., 2013; Yang et al., 2015). Furthermore, para-nitrobenzoic acid (pNBA) and ATZ were used as radical probes in radical exposure experiments. As such, the specific objectives of this research are two-fold: (1) to evaluate the performance of single and sequential ozone dosing strategies in terms of PMS activation, ATZ removal and residual ozone concentration in 3 different water matrices, and (2) to determine the impact of the ozone dosing strategy on radical exposure during O_3/PMS.

2. MATERIALS AND METHODS

2.1 Chemicals

Atrazine (ATZ, ≥ 99%) and p-nitrobenzoic acid (pNBA, 98%) were provided by Sigma Aldrich (Belgium) as well as $NaNO_2$, ascorbic acid (AA), oxone (known as peroxymonosulfate or PMS) and indigo trisulfonate (≥ 60%). HPLC grade water, methanol (MeOH) and acetonitrile were obtained from VWR (Belgium). All solutions were made in deionized water.

2.2 Experimental setup & design

Ozone was produced from oxygen by an ozone generator (up to 8 g O_3 h^{-1}, COM-AD-O2, Anseros GmbH, Germany). Ozone stock solutions (80 – 100 mg/L) were prepared by bubbling ozone gas (150 mL/min) through a sintered glass filter in ice-cooled deionized water (Chys et al., 2017; Deniere et al., 2022; Liu et al., 2020). PMS stock solutions of 11.2 g/L were made by dissolving oxone in deionized water.

The secondary effluent was collected from a conventional activated sludge process at the WWTP Harelbeke, Belgium (operated by Aquafin NV, Belgium) (Chys et al., 2018; Deniere et al., 2022). Pre-treated surface water was collected after the coagulation-flocculation treatment step from a drinking water production site in Harelbeke, Belgium (operated by De Watergroep, Belgium) (Deniere et al., 2022; Van Hulle et al., 2006); while groundwater was sampled from a monitoring borehole of 30 m depth at Campus Sterre, Ghent University, Belgium (Deniere et al., 2022). The water samples were collected twice as the ATZ degradation experiments and the radical exposure experiments were performed separately in time. Prior to use, all water samples were filtered by a 0.45 µm Whatman nylon membrane. The characteristics of these water samples are summarized in Table 1.

All experiments were performed in batch using glass beakers. Each time, the matrix was diluted by 20% by the addition of the ozone stock solution. First, O_3/PMS

148 experiments were performed (all in duplicate) for the degradation of ATZ (5 µM or 1.1
149 mg/L) with 4 different ozone dosing strategies. In the first experiment, 15 mg/L of ozone
150 was directly added at 0 min reaction time (further referred as the one-step ozone
151 dosing technique or A1), while in the other experiments the ozone dose was
152 sequentially added according to the following dosing strategies: (1) addition of 7.5 mg/L
153 of ozone at 0 min and at 10 min reaction time (further referred as A2), (2) three times
154 addition of ozone (each time 5 mg/L) at 0 min, 10 min and 20 min reaction time (further
155 referred as A3), and (3) addition of 7.5 mg/L of ozone at 0 min reaction time, and three
156 times addition of 2.5 mg/L of ozone at 10 min, 20 min and 30 min (further referred as
157 A4). Table SI-1 summarizes the volumes of the stock solutions used during the
158 experiments. The theoretical total dosed ozone concentration was 15 mg/L in all
159 strategies. The actual added ozone doses can differ from the theoretical concentration
160 due to the actual ozone stock concentration, hence, these are further specified in the
161 figure captions. PMS (64 mg/L) was added at 0 min reaction time during all ozone
162 dosing strategies. The experiments were initiated by the addition of the PMS and ozone
163 stock solution to the beakers containing the ATZ solution. Samples were taken at
164 regular time intervals to determine the residual ozone, PMS and ATZ concentration.
165 The samples for the ATZ measurements (1 mL) were quenched with an excess of
166 $NaNO_2$, which quickly consumes all remaining ozone, PMS and radicals. To measure
167 the PMS concentration, samples (5 mL) were bubbled with nitrogen gas to remove
168 ozone and quenched with MeOH to stop radical reactions (Deniere et al., 2022). The
169 performed calculations in these degradation experiments are elaborated in the
170 supplementary information (Text SI-1).
171 To determine the radical exposure, the degradation of a mixture of pNBA (100 µg/L)
172 and ATZ (100 µg/L) was investigated at the sequential ozone dosing strategy providing

the best results in terms of PMS activation and ATZ removal (see Section 3.2.2 and 3.2.3). The added PMS concentration was again 64 mg/L. The experiment was performed in triplicate. Samples were taken to determine the residual pNBA, ATZ and PMS concentration at regular time intervals between 0.5 min and 10 min after each ozone addition. AA and MeOH were added to the samples (1 mL) used for pNBA and ATZ analysis. PMS samples (5 mL) were bubbled with nitrogen gas and quenched with MeOH. The calculations for data interpretation are explained in Text SI-1.

2.3 Analytical methods

The ozone concentration in the stock solutions and samples was measured by the indigo method (Bader and Hoigné, 1981). PMS concentrations were measured by a spectrophotometric method using potassium iodide (Liang et al., 2008).

The IOD represents the ozone demand (mg/L) of highly ozone reactive matrix components such as bulk organic matter and nitrite. IOD_{PMS} represents the IOD in case PMS (64 mg/L) was added to the water matrix. The IOD and IOD_{PMS} were determined by quenching the reaction after 5 s through the addition of an indigo solution (Bader and Hoigné, 1981). Other water parameters (nitrite concentration, COD, alkalinity, chloride and sulfate content) were measured according to the methods explained in Deniere et al. (2022).

ATZ and pNBA were analysed by a Surveyor HPLC system (Thermo Finnigan, Germany) coupled to a photodiode array detector (Thermo Finnigan, Germany). A Gemini C18 column (150 x 3.0 mm, 5 µm, Phenomenex) was kept at 35°C during the analysis. Details of the method are reported by (Deniere et al., 2022, 2018).

3.

4. RESULTS AND DISCUSSION

4.1 One-step ozone addition

Figure 1 shows the residual ozone concentration (C/C_0), the activation of PMS ($1 - n/n_0$) and the removal efficiency of ATZ ($1 - n/n_0$) during O_3/PMS, in case a single addition of ozone (16.0 ± 1.9 mg O_3/L) was applied.

The residual ozone concentration at 0.5 min in secondary effluent, surface water and groundwater was respectively 2%, 13% and 21% (Figure 1A). The higher residual ozone concentration in groundwater and surface water is the result of a lower oxidizable (in)organic content, which is represented by both lower COD and lower IOD values. The IOD of groundwater and surface water is up to 8 times lower than that of secondary effluent (see Table 1). Despite the high and rapid ozone decomposition in the different water matrices, the PMS activation was rather low. Up to 20%, 38% and 48% PMS activation was noticed in secondary effluent, surface water and groundwater (Figure 1B). This indicates that most of the added PMS was not activated by ozone, and hence, can be seen as a lost resource in the O_3/PMS process as well as a potential for secondary pollution. The activation of PMS mainly occurs during the first 0.5 min of reaction, which is exemplified by the fact that the values are not significantly different ($p > 0.05$) at any later sampling time. Furthermore, within the first 0.5 min, less than 20% ATZ was removed in secondary effluent, while almost complete removal (> 90%) occurred in surface water and groundwater (Figure 1C). The differences in removal efficiency between the 3 matrices can be explained by the availability of the oxidants and radicals. ATZ has low reactivity with ozone, hence, its removal is largely dependent on radical reactions. Indeed, the reaction rate constants of ATZ with ozone, $^{\bullet}OH$ and $SO_4^{\bullet-}$ are respectively 4 – 6.3 $M^{-1}s^{-1}$, (2.6 – 2.7) x 10^9 $M^{-1}s^{-1}$ and (1.4 – 3.5) x 10^9 $M^{-1}s^{-1}$ (Acero et al., 2000; Wojnárovits and Takács, 2019; Yang et al., 2015). Therefore, the

radical scavenging capacity of the water matrix is an important parameter during the ATZ removal. The higher amount of organic compounds in secondary effluent (represented by high COD and IOD values) leads to more scavenging of radicals which reduces the radical availability and hence, the ATZ removal. Through prolonged reaction time, no or only limited additional ATZ removal is observed, which is in agreement with our previous research (Deniere et al., 2022). Figure 1 clearly shows that the (produced) reactive species during O_3/PMS are quickly consumed in the one-step ozone dosing strategy and that all reactions originating from ozone and PMS take place during the first minute. However, this results in a far from complete PMS activation in all water matrices and a limited ATZ removal in secondary effluent, demonstrating the need for further optimization of the dosing strategy.

4.2 Sequential ozone addition

4.2.1 Ozone decomposition

The residual ozone concentration (mg/L) at 0.5 min in the 3 matrices and for all ozone dosing strategies is represented in the upper part of Figure 2. Overall, very low residual ozone concentrations are observed in secondary effluent compared to surface water and groundwater. The main reason for this is the higher amount of ozone-reactive species in the (in)organic matter of secondary effluent, as discussed in Section 3.1.

During the sequential ozone dosing strategies, increasing residual ozone concentrations were measured after each ozone addition, particularly for A2 and A3 in both surface water and groundwater. For example, in A3, the residual ozone concentration in surface water was 0.3 mg/L, 1.3 mg/L and 3.0 mg/L after 0.5 min of the 1st, 2nd and 3rd ozone addition, respectively. A similar effect was noticed by Park et al. (2001) when applying sequential ozone addition during ozonation of river water,

which they explained by a slower ozone decomposition after the second and third ozone addition. The sum of the consecutive residual ozone concentrations in A2, A3 and A4 were compared to the residual ozone concentration measured during one-step ozone dosing. Results are given in Table SI-2. In all matrices, the total residual ozone concentration in A2 is very similar to that of the one-step ozone dosing strategy, i.e. ≤ 0.1 mg/L difference. However, when applying A3, a 3.7 times higher residual ozone concentration is observed in secondary effluent compared to A1. In groundwater and surface water, the difference is approximately a factor of 2. Although the absolute values are rather low (0.3 mg O_3/L and 1.1 mg O_3/L), a larger effect is thus noticed in secondary effluent. The same is true for A4, where in secondary effluent the total residual ozone concentration was 2.3 times higher compared to that during the one-step ozone dosing, although the increase in surface water and groundwater was at maximum a factor of 1.3.

Overall, the ozone dosing strategy A3 shows the highest residual ozone concentrations, from which it is assumed that the least secondary ozone reactions (e.g. between ozone and $^{\bullet}OH$) took place during this dosing strategy. This is most probably because the ozone concentration dosed in the first step was lower than in A2 and A4. The contribution of secondary reactions increases if the applied ozone concentration exceeds the IOD of the water, which is more easily the case in waters with a low amount of oxidizable components (Von Sonntag and von Gunten, 2012). Therefore, the high ozone concentrations in A2 and A4 led to more secondary reactions which decreased the availability of residual ozone.

4.2.2 PMS activation

The activation of PMS ($1 - n/n_0$, %) during the 4 different ozone dosing strategies is presented in Figure 2 (middle section). Values shown are the averages of the PMS activation datapoints (n = 5) measured between 0.5 min and 10 min after each ozone addition (see Figure SI-1).

In secondary effluent, all sequential ozone dosing strategies improved the total PMS activation from 17% (single ozone addition) to at least 36%. In surface water and groundwater, A2 had no added value compared to single ozone addition as the same amount of PMS was activated. Nonetheless, A3 – and to a smaller extent also A4 – increased PMS activation efficiencies up to 65%.

When focusing on A3, it is clear that the amount of PMS activated increases each time when a new amount of ozone is dosed, e.g. values of 5%, 10%, 24% of additional PMS activation are observed after respectively the 1st, 2nd and 3rd ozone addition in secondary effluent. This is in good agreement with the increasing residual ozone concentrations when applying sequential ozone dosing (particularly A3) as shown in Section 3.2.1, and indicating that the amount of fast ozone reacting compounds in the matrix is decreasing after every ozone addition. Hence, there is less competition for ozone between these compounds and PMS after the consecutive ozone additions, which results in a more efficient PMS activation.

4.2.3 ATZ removal

The impact of the alternative ozone dosing techniques on the removal of ATZ in the three matrices is shown in Figure 2 (bottom part). After each ozone addition step, the ATZ removal remains constant between 0.5 min and 10 min of reaction (see Figure SI-1). Therefore, Figure 2 visualizes the average of these datapoints (n = 7) per ozone addition.

In secondary effluent, the removal efficiency of ATZ was enhanced by using sequential ozone dosing. The total ATZ removal was 16%, 22%, 46% and 47% for respectively single ozone addition (A1), A2, A3 and A4. The better ATZ removal during A3 and A4 compared to A1 is in line with the higher PMS activation, but the total amount of activated PMS, which is similar in the three sequential dosing strategies (Section 3.2.2), cannot explain the lower ATZ removal in A2 compared to A3 and A4. In each of the sequential ozone dosing strategies, the first ozone addition was below the IOD of secondary effluent, resulting in an incomplete oxidation of the fast ozone reactive compounds. In A3 and A4 – both reaching 10 mg/L ozone dosing after the second step – the second ozone dosing is lower than that of A2 but sufficient to exceed the IOD. Together with the 3rd (and 4th) ozone addition in A3 (and A4) and the higher residual ozone concentrations in those strategies (see Section 3.2.1), this most likely affects the occurrence of secondary scavenging reactions and increases the efficiency of ozone decomposition into radicals, explaining the higher ATZ removal in A3 and A4.

In surface water and groundwater, the ATZ removal obtained with one-step ozone dosing was already high (> 90%). Sequential ozone dosing did not change ATZ removal in a significant way, although a slight increase (up to 7% ATZ removal) was noticed for A3 and A4. The application of lower ozone concentrations could probably give a better view on the effect of sequential ozone dosing in groundwater and surface water. Furthermore, sequential ozone dosing could also be economically beneficial in groundwater and surface water. For example, if the aim is 80% ATZ removal, only 7.5 – 10 mg O_3/L is needed in A2, A3 and A4. This is 33% to 50% less ozone that is added in sequential ozone dosing techniques, compared to the single ozone dosing technique. Hence, the application of sequential ozone dosing techniques can lower the OPEX value of the O_3/PMS process and keeping the capital expenditures (CAPEX)

similar. For example, the choice can be made to use a plug flow reactor with multipoint injection instead of one point injection, as only a limited increase in CAPEX will be noticed.

4.2.4 Radical exposure

Overall, for the three investigated matrices, the total residual ozone concentration and PMS activation was the highest for the ozone dose strategy A3. Also the ATZ removal increased by a factor of 3 with A3 applied in secondary effluent, compared to a one-step ozone dosing. Therefore, additional radical exposure experiments were performed following the A3 ozone dosing approach, to gain more knowledge about $^{\bullet}OH$ and $SO_4^{\bullet-}$ production and contribution to ATZ removal. Figure SI-2 shows that the radical exposure remains constant between 0.5 min and 10 min because of the fast reactions during O_3/PMS in the three matrices. Hence, Figure 3 shows the averaged values of the radical exposure within each stage of ozone addition for the different types of water. The results of ATZ and pNBA removal, on which the calculations for radical exposure are based, as well as the PMS activation, are shown in Figure SI-3 and SI-4. pNBA is used as an $^{\bullet}OH$ probe ($k_{OH} = 2.6 \times 10^9\ M^{-1}s^{-1}$) as its reactivity with ozone and $SO_4^{\bullet-}$ is low ($k_{O3} < 0.15\ M^{-1}s^{-1}$, $k_{SO4} < 10^6\ M^{-1}s^{-1}$) .

Both $^{\bullet}OH$ and $SO_4^{\bullet-}$ exposures were boosted with every ozone addition (Figure 3). In all matrices, the first ozone addition generated the highest $^{\bullet}OH$ exposure, whereas the $SO_4^{\bullet-}$ exposure in this first stage was negligible despite a PMS activation of at least 20% (Figure SI-4). The slightly negative values for $SO_4^{\bullet-}$ exposure can be explained by small deviations in the reaction rate constants published in literature, next to experimental variability. To explain the results with respect to the radical exposure after the first ozone addition, two hypothesis are put forward. First, it can be assumed that

ozone reacts only with highly ozone-reactive organic matter in the first stage of the ozone process, which results into a high production of $^{\bullet}OH$. In this case, the direct reaction between ozone and PMS does not take place, and the PMS activation results from reactions with radicals and/or (ozonated) organic matter as was indicated by (Deniere et al., 2022) during the IOD phase of secondary effluent. As a second hypothesis, ozone reacts with both highly ozone-reactive organic matter and PMS, resulting in the production of both $^{\bullet}OH$ and $SO_4^{\bullet-}$. Since no $SO_4^{\bullet-}$ exposure is observed, $SO_4^{\bullet-}$ are most probably quickly consumed by remaining ozone-reactive organic matter ($SO_4^{\bullet-}$ reacts – similar as ozone – with aromatic and olefinic moieties (Sun et al., 2020)) or are transformed into $^{\bullet}OH$ via reactions with chloride. Due to the complex ozone chemistry during O_3/PMS, it is difficult to differentiate between both hypothesis and, most likely, both reaction pathways take place.

The second ozone addition induces a 4 times higher $SO_4^{\bullet-}$ exposure in groundwater than in surface water, and the differences between the matrices are even more pronounced after the third ozone addition. Figure 3 shows that the $SO_4^{\bullet-}$ exposure is up to 4 and 28 times higher in groundwater, compared to respectively surface water and secondary effluent. This clearly demonstrates that the $SO_4^{\bullet-}$ exposure can be drastically increased by multiple ozone dosing, especially in waters with a low (in)organic matrix content. Also the total $^{\bullet}OH$ exposure was 2.3 and 1.3 times higher in groundwater than in respectively secondary effluent and surface water. The higher total PMS activation in groundwater (Figure SI-4), resulting in extra radical production, can explain this difference among the matrices. In line with our results here for the O_3/PMS process, Hubaux et al. (2016) observed a more efficient conversion of O_3 into $^{\bullet}OH$ after a second ozone addition during ozonation of secondary effluent, favouring the application of sequential but lower ozone dosages.

Figure 4 shows the radical contributions to ATZ removal, calculated from Equations 3 and 4. The contribution of $SO_4^{\bullet-}$ to the ATZ removal was limited in secondary effluent, i.e. about 10%, and only appeared after the third ozone addition, which is in line with the low $SO_4^{\bullet-}$ exposure in this matrix. In surface water and groundwater, however, the $SO_4^{\bullet-}$ contribution increased after each ozone addition to respectively 26% and 54% in the last stage. $SO_4^{\bullet-}$ are more selective towards organic matter than $^{\bullet}OH$ (Ahn et al., 2017; Lee et al., 2020) and thus yield a more effective use of dosed oxidants for TrOCs removal. The higher $SO_4^{\bullet-}$ contribution in groundwater is most likely linked to the lower Cl^- content in that water matrix (Table 1). Indeed, $SO_4^{\bullet-}$ can be transformed into $^{\bullet}OH$ via scavenging reactions with chloride ions (Lutze et al., 2015), which was identified as a major reason why $^{\bullet}OH$ rather than $SO_4^{\bullet-}$ became the dominant species during O_3/PMS in real (waste)waters instead of deionized water (Deniere et al., 2022, 2018).

5. CONCLUSIONS

This research is the first to investigate the effect of the ozone dosing strategy during O_3/PMS. The results highlight several advantages of sequential compared to one-step ozone dosing. First, a higher PMS activation – i.e. an additional 17% (groundwater), 21% (secondary effluent) and 34% (surface water) – is obtained due to consecutive ozone dosing as a result of higher residual ozone concentrations available for reaction with PMS. Second, up to 3 times higher ATZ removal is achieved when applying sequential ozone dosing in secondary effluent. Third, the contribution of the more selective $SO_4^{\bullet-}$ (compared to $^{\bullet}OH$) to the ATZ removal can be controlled by the ozone dosing strategy and can be enhanced up to 54% in groundwater. Next to the ozone dosing strategy, also the chloride content of the treated water plays an important role in the $SO_4^{\bullet-}$ contribution. Although $^{\bullet}OH$ and $SO_4^{\bullet-}$ are the main radicals, other radicals

(e.g. single oxygen and chloride based radicals) might also play a role. As such it would be interesting to further investigate such radicals in the future.

Among the four different ozone strategies investigated – all adding the same total amount of ozone to the reaction solution and thus maintaining a similar cost of ozone dosing – the sequential ozone dosing techniques improved the PMS activation and/or ATZ removal during O_3/PMS in comparison to the single ozone dosing technique. Furthermore, the best results in terms of ATZ removal and PMS activation are observed in a 3-step ozone dosing approach where the first ozone addition is the lowest. Therefore, an optimized sequential ozone dosing and PMS activation has the potential to improve the (cost-)effectiveness of the O_3/PMS process. It also avoids peak ozone concentrations during the process and can control the $^{\bullet}OH$ radical exposure. All this also offers a promising outlook to reduce secondary pollution originating from PMS and/or ozonation by-products like bromate (Hubaux and Schachtler, 2016; Krasner et al., 1993; Soltermann et al., 2017).

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518

519 **Table 1**. Characteristics of the water matrices (secondary effluent: EFF, groundwater: GW, surface water: SW) used in the ATZ

520 degradation and radical exposure experiments.

	ATZ degradation experiments			**Radical exposure experiments**		
	EFF	**GW**	**SW**	**EFF**	**GW**	**SW**
Alkalinity (mg/L as $CaCO_3$) (n = 3)	178 ± 6	166 ± 8	193 ± 1	272 ± 1	153 ± 1	205 ± 1
COD (mg/L)	35	8	8	23	1	6
Chloride (mg Cl^-/L)	67	25	99	152	22	98
Sulphate (mg SO_4^{2-}/L)	40	202	97	96	206	96
Nitrite (mg NO_2^-/L)	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015	< 0.015
IOD (mg O_3/L) (n = 3)	8.6 ± 0.5	1.4 ± 0.2	1.1 ± 1.1	3.2 ± 0.4	0.2 ± 0.6	0.8 ± 0.4
IOD_{PMS} (mg O_3/L) (n = 3)	9.1 ± 0.6	3.0 ± 0.2	3.5 ± 1.1	4.2 ± 0.6	2.9 ± 0.6	2.8 ± 0.9

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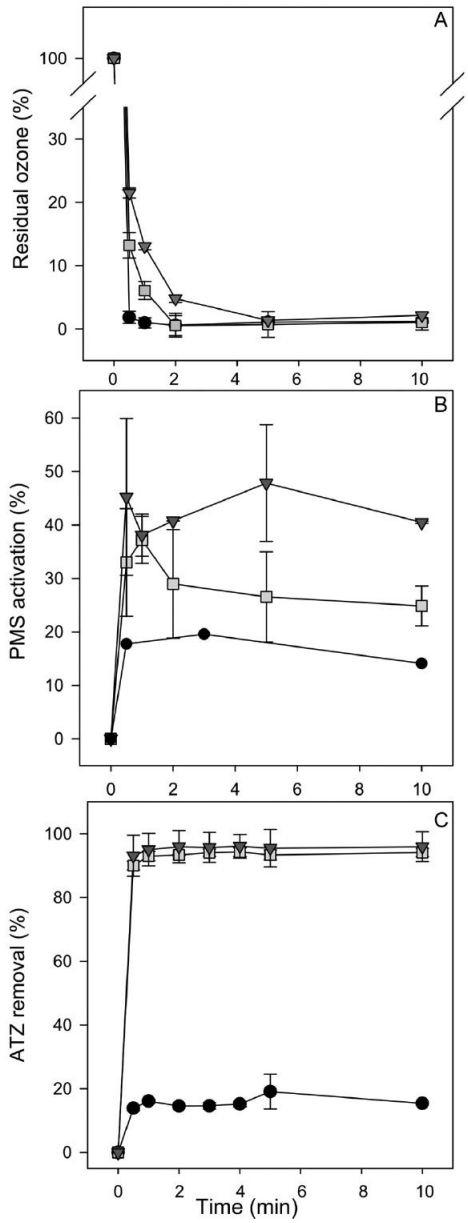

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530 **Figure 1.** Residual ozone concentration (A, %), PMS activation (B, 1-n/n_0, %) and ATZ removal (C, 1-
531 n/n_0, %) as a function of time, when applying the O_3/PMS process in secondary effluent (●), surface
532 water (■) and groundwater (▼). The one-step ozone dosing strategy was applied. Conditions: [ATZ] =
533 5 µM, [O_3] = 16.0 ± 1.9 mg/L, [PMS] = 64 mg/L.

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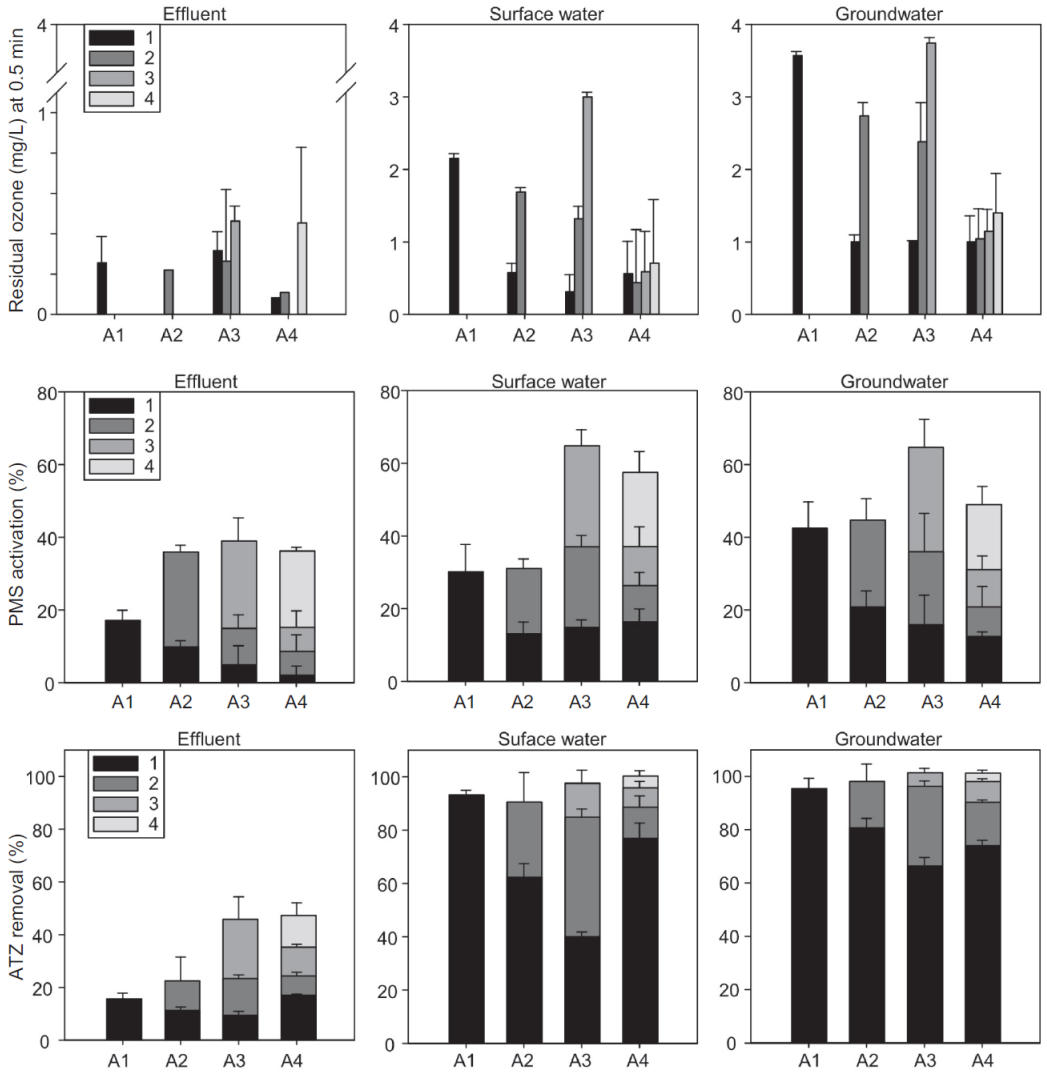
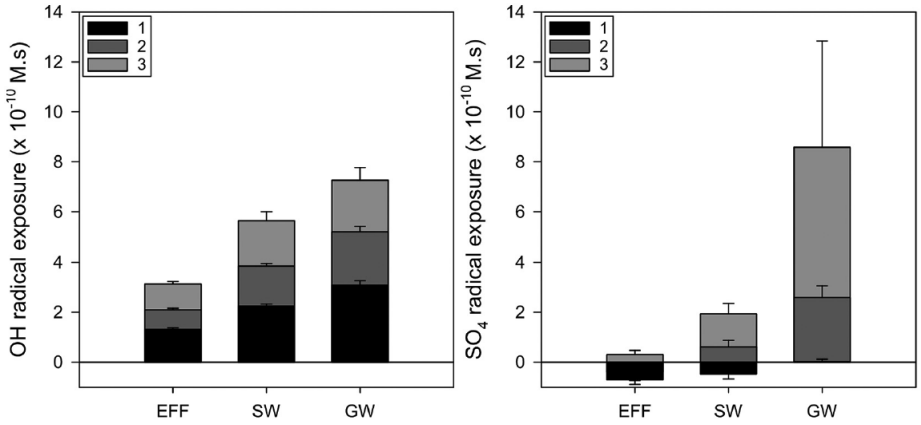


Figure 2. Residual ozone concentration (mg/L), PMS activation (1-n/n_0, %) and ATZ removal (1-n/n_0, %) during the four different ozone dosing strategies: A1, A2, A3 and A4. Results are shown for the experiments in secondary effluent, surface water and groundwater. The numbers in the legend represent the first, second, third or fourth ozone addition. Conditions: [PMS] = 64 mg/L, [ATZ] = 5 µM, $[O_3]_{A1}$ = 16.0 ± 1.9 mg/L, $[O_3]_{A2,first\ addition}$ = 8.2 ± 0.9 mg/L, $[O_3]_{A2,second\ addition}$ = 8.1 ± 1.0 mg/L, $[O_3]_{A3,first\ addition}$ = 5.6 ± 0.5 mg/L, $[O_3]_{A3,second\ addition}$ = 5.5 ± 0.8 mg/L, $[O_3]_{A3,third\ addition}$ = 5.1 ± 0.4 mg/L, $[O_3]_{A4,first\ addition}$ = 8.1 ± 0.7 mg/L, $[O_3]_{A4,second\ addition}$ = 2.5 ± 0.3 mg/L, $[O_3]_{A4,third\ addition}$ = 2.4 ± 0.4 mg/L, $[O_3]_{A4,fourth\ addition}$ = 2.4 ± 0.5 mg/L



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559 **Figure 3.** Hydroxyl and sulfate radical exposure in secondary effluent (EFF), surface water (SW) and
560 groundwater (GW) during the ozone dosing strategy A3. The numbers in the legend represents the
561 first, second or third ozone addition. Conditions: [ATZ] = [pNBA] = 100 µg/L, $[O_3]_{A3,first\ addition}$ = 4.0 ± 0.3
562 mg/L, $[O_3]_{A3,second\ addition}$ = 3.5 ± 0.3 mg/L, $[O_3]_{A3,third\ addition}$ = 3.1 ± 0.2 mg/L, [PMS] = 64 mg/L.

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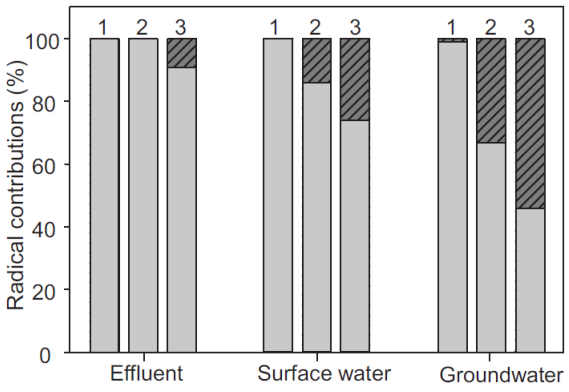

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566 **Figure 4.** Contributions (%) of $^{\bullet}OH$ and $SO_4^{\bullet-}$ (f_{OH} and f_{SO4}) to the removal of ATZ during O_3/PMS in
567 secondary effluent, surface water and groundwater, following the ozone dosing strategy A3. The
568 diagonal striped, dark grey areas in the bars represents f_{SO4}, while the other light grey areas
569 represents f_{OH}. The numbers above the bars represent the first, second or third ozone addition.

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