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## Journal Pre-proof

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# **Comparison of the new Cl<sub>2</sub>/O<sub>3</sub>/UV process with different ozone- and UV-based AOPs for wastewater treatment at pilot scale: Removal of pharmaceuticals and changes in fluorescing organic matter**

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**ABSTRACT**

This work critically compared the removal of fluorescing PARAFAC components and selected pharmaceuticals (carbamazepine, fluoxetine, gemfibrozil, primidone, sulfamethoxazole, trimethoprim) from a tertiary wastewater effluent by different UV- and ozone-based advanced oxidation processes (AOPs) operated at pilot-scale. Investigated AOPs included UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, and the new Cl<sub>2</sub>/O<sub>3</sub>/UV. AOPs comparison was accomplished using various ozone doses (0 – 9 mg/L), UV fluences (191 – 981 mJ cm<sup>-2</sup>) and radical promoter concentrations of Cl<sub>2</sub> = 0.04 mM and H<sub>2</sub>O<sub>2</sub> = 0.29 mM. Chlorine-based AOPs produced radical species that reacted more selectively with pharmaceuticals than radical species and oxidants generated by other AOPs. Tryptophan-like substances and humic-like fluorescing compounds were the most degraded components by all AOPs, which were better removed than microbial products and fulvic-like fluorescing substances. Removal of UV absorbance at 254 (UV<sub>254</sub>) nm was always low. Overall, chlorine-based AOPs were more effective to reduce fluorescence intensities than similar H<sub>2</sub>O<sub>2</sub>-based AOPs. The Cl<sub>2</sub>/O<sub>3</sub>/UV process was the most effective AOP to degrade all target micro-pollutants except primidone. On the other hand, the oxidation performance of pharmaceuticals by other ozone-based AOPs followed the order H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV > O<sub>3</sub>/UV > O<sub>3</sub>. UV/Cl<sub>2</sub> process outcompeted UV/H<sub>2</sub>O<sub>2</sub> only for the removal of trimethoprim and sulfamethoxazole. Correlations between the removal of pharmaceuticals and spectroscopic indexes (PARAFAC components and UV<sub>254</sub>) had unique regression parameters for each compound, surrogate parameter and oxidation process. Particularly, a diverse PARAFAC component for each investigated AOP resulted to be the most sensitive surrogate parameter able to monitor small changes of pharmaceuticals removal.

**Keywords:** contaminants of emerging concern (CEC); micro-pollutants; ozone/chlorine; UV/chlorine; fluorescence spectroscopy; on-line monitoring

## 1. Introduction

In recent years, contaminants of emerging concern (CEC) such as pharmaceuticals, personal care products, pesticides, and industrial chemicals have been detected and extensively investigated in different water matrices, including wastewater, surface water and drinking water (Benotti et al., 2009; Dickenson et al., 2011; Focazio et al., 2008). Particularly, wastewater treatment plants (WWTPs) have been recognized as significant hotspots for the transfer of CEC into the environment (Michael et al., 2013; Sgroi et al., 2017a, 2017b). Furthermore, extensive studies have shown that some of these contaminants can have drastic effects on aquatic organisms at concentrations typical for wastewater discharges (Draughton and Ternes, 2009; Richardson and Ternes, 2018).

Traditional WWTPs usually utilize only primary and secondary treatments, with the latter often based on conventional activated sludge. These treatments tend to provide poor removal for most CEC in wastewater, and thus advanced/tertiary treatment methods are necessary to achieve an effective removal of these micro-pollutants (Guillossou et al., 2020; Roccaro et al., 2013; 2018; Villarín and Merel, 2020). Advanced oxidation processes (AOPs) are effective technologies for the removal of refractory micro-pollutants, such as pharmaceuticals, via the generation of reactive radicals, such as hydroxyl radical ( $\cdot\text{OH}$ ) (Rizzo et al., 2019; Wang and Zhuan, 2020). There are various different process technologies that have been investigated for use as AOPs. Several AOPs, especially those involving ozonation and UV irradiation (e.g.,  $\text{O}_3$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{H}_2\text{O}_2$ ) are already well established and operated at full-scale in drinking water treatment and water reuse

facilities (Gogate and Pandit, 2004; Liu et al., 2019b; Miklos et al., 2018b). However, studies of numerous emerging AOPs for water treatment (e.g., UV/chlorine, UV/persulfate, UV/CaO<sub>2</sub>) are constantly being reported by various researchers (Mehrjouei et al., 2015; Miklos et al., 2018b; Zheng et al., 2019). The general aim of those studies is the development of oxidation processes that should be highly effective for micro-pollutants degradation and economically sustainable (Gogate and Pandit, 2004; Miklos et al., 2018b). Further aim of researchers is the development of water treatment technologies able to completely mineralize micro-pollutants, and avoid the production of transformation substances with higher toxicity than parent compounds (W. L. Wang et al., 2018). The latter scope is often reached by the use of biofiltration or adsorption after the AOP (Magdeburg et al., 2014).

The UV/chlorine (UV/Cl<sub>2</sub>) process is an emerging and attractive AOP for water and wastewater treatment, which is able to produce different radical species, including  $\cdot\text{OH}$  and reactive chlorine species (RCS) (i.e.,  $\text{Cl}\cdot$ ,  $\text{Cl}^-\cdot_2$ ,  $\text{ClO}\cdot$ ) (Cecilia et al., 2020; Guo et al., 2018, 2017). RCS are very powerful oxidants that are produced with much higher yield than  $\cdot\text{OH}$  during UV irradiation (Guo et al., 2018, 2017). However, RCS are selective oxidants, and preferentially react with electron-rich moieties containing olefins, phenols, anilines, and alkyl-/alkoxybenzenes (Guo et al., 2018, 2017; Lei et al., 2019). On the contrary, electron-withdrawing compounds, such as primidone, ronidazole and ibuprofen, are better removed by hydroxyl radicals, which are nonselective oxidants (Guo et al., 2018, 2017; Miklos et al., 2019). Studies have also reported that UV/Cl<sub>2</sub> process is less affected by the water and wastewater matrices than UV/H<sub>2</sub>O<sub>2</sub>, and that UV/Cl<sub>2</sub> is a more economical process than UV/H<sub>2</sub>O<sub>2</sub> (Guo et al., 2018; Miklos et al., 2018b).

Ozone is a commonly used disinfectant and oxidant in water and wastewater treatment. During conventional ozonation, CEC can be oxidized by O<sub>3</sub> and/or by hydroxyl radicals that are gener-

ated from  $O_3$  decomposition in real water matrices (von Sonntag and von Gunten, 2012).  $O_3$  is a selective oxidant and reacts preferentially with organics that have olefins, activated aromatic systems, or amines (von Sonntag and von Gunten, 2012). Hence, many ozone-resistant CEC that can only be oxidized by  $\cdot OH$  are less efficiently abated during conventional ozonation. Methods to enhance the formation of hydroxyl radicals include the combinations  $O_3/H_2O_2$  (also called peroxone-process),  $O_3/UV$ , and  $H_2O_2/O_3/UV$  (Liu et al., 2019a, 2019b; H. Wang et al., 2018; Yao et al., 2018). However, benefits from the combination of  $O_3/H_2O_2$ , and  $O_3/UV$  have been shown to be limited in wastewater matrices due to the fast reaction of ozone with dissolved organic matter (DOM) moieties, and the high scavenging effect for  $\cdot OH$  radicals (Lado Ribeiro et al., 2019; Miklos et al., 2018b; H. Wang et al., 2018). On the contrary, much higher  $\cdot OH$  yields and micro-pollutants abatement have been observed when combining  $H_2O_2/O_3/UV$  (Liu et al., 2019b, 2019a). Furthermore, the presence of  $H_2O_2$  in ozone-based AOPs reduce the formation of bromate (Von Gunten and Oliveras, 1998). The above summarized results were produced by several studies that investigated and compared oxidant exposures and micro-pollutants removal by different ozone-based and UV-based AOPs. However, those comparative studies have mainly been accomplished at laboratory scale, and similar comparisons at pilot scale are very scarce in the literature, particularly for the chlorine-based AOPs. In this study, we critically discussed the removal of different pharmaceuticals during treatment at pilot scale of a wastewater effluent by various AOPs, which included  $UV/H_2O_2$ ,  $UV/Cl_2$ ,  $O_3$ ,  $O_3/UV$ , and  $H_2O_2/O_3/UV$ . Furthermore, we investigated a new AOP that has never been applied to wastewater treatment previously, and it is the combination of  $Cl_2/O_3/UV$ . Particularly, a recent study has shown that the combination of ozone and chlorine was able to improve the removal of dodecylbenzyltrimethylammonium chloride in deionized (DI) water due to the increased yield of  $\cdot OH$  and the formation of others

reactive oxidants, which can be classified as RCS, compared to conventional ozonation (Huang et al., 2020).

Diverse AOPs can be discriminated by the produced oxidant/radical species (e.g.,  $\cdot\text{OH}$ ,  $\text{Cl}\cdot$ ,  $\text{Cl}_2\cdot^-$ ,  $\text{ClO}\cdot$ ,  $\text{SO}_4\cdot^-$ ), and by the yield of those produced radicals (Guo et al., 2017; von Sonntag and von Gunten, 2012). The oxidants exposure in water/wastewater can be evaluated by monitoring the degradation kinetics of probe compounds, which are generally selected according to their reactivity with the investigated oxidants/radical species (Guo et al., 2018; von Sonntag and von Gunten, 2012). A further approach useful to compare the oxidative potential of different AOPs in natural water/wastewater is the investigation of the reactivity of the produced/used oxidants with different DOM moieties (Cruz-Alcalde et al., 2019; Merel et al., 2015; Miklos et al., 2018a; Varanasi et al., 2018; Wenk et al., 2013; Westerhoff et al., 2007). Fluorescence excitation emission matrix (EEM) is a fast and sensitive technique able to characterize bulk organic matter in natural and engineered aquatic systems (Carstea et al., 2016). EEM of natural water and wastewater tend to have distinct features with maxima located at characteristic combinations of excitation and emission wavelengths, and this spectroscopic technique has been shown to be very useful for discriminating between different source and components of DOM (Carstea et al., 2016; Korshin et al., 2015). Thus, fluorescence spectroscopy is highly attractive to investigate the degradation of DOM during different AOPs (Chen et al., 2017). In addition, fluorescence measurements have been suggested as suitable surrogate parameters to predict the removal of pharmaceuticals during conventional and advanced wastewater treatments (Korshin et al., 2018; Miklos et al., 2019; Sgroi et al., 2017a). Nevertheless, since diverse fluorescence components may have different reactivity with different oxidants, different fluorescence indexes may show dissimilar sensitivity to monitor the removal of pharmaceuticals during AOPs in wastewater.



Hence, aims of this study were: (i) to investigate the removal of pharmaceuticals by a new AOP based on the combination of ozone, chlorine and UV ( $\text{Cl}_2/\text{O}_3/\text{UV}$ ) in wastewater; (ii) to critically compare the removal of different pharmaceuticals by different ozone-based and UV-based AOPs ( $\text{UV}/\text{H}_2\text{O}_2$ ,  $\text{UV}/\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ ,  $\text{Cl}_2/\text{O}_3/\text{UV}$ ) during wastewater treatment at pilot scale; (iii) to investigate the degradation and evolution of different fluorescing components of wastewater organic matter during diverse AOP treatments; (iv) to identify the most sensitive surrogate parameters based on fluorescence measurements suitable for monitoring the removal of pharmaceuticals during different AOPs.

## **2. Materials and methods**

### **2.1. Chemicals and reagents**

All purchased solvents, standards, and reagents were of high purity. The details concerning these materials are reported in the Supplementary material section (Text S1). The selection of six pharmaceuticals (i.e., carbamazepine - CBZ, fluoxetine - FLU, gemfibrozil - GMF, primidone - PRM, sulfamethoxazole - SMZ, trimethoprim - TMP) as target CEC was based on data presented in previous literature that rely on chemical-physical properties, reaction rates with different oxidants, photosensitivity, and availability of robust analytical methods (Anumol and Snyder, 2015; Gerrity et al., 2012; Guo et al., 2018; Lam et al., 2005; Wols et al., 2014; H. W. Yu et al., 2015). Particularly, target compounds were selected in order to investigate micro-pollutants, which show very different reactivity with the oxidants and radical species examined in this study. Detailed information about the selected pharmaceuticals is reported in Table 1.

### **2.2. AOPs pilot plant and experimental conditions**

The container-based AOP pilot-scale plant, which has a capacity to treat a flow rate of 1000 – 6000 L per hour, was designed by Wedeco (Xylem, Germany) and installed on site at a WWTP treating municipal wastewater. The treatment train of the investigated WWTP foresees preliminary treatments followed by a biological nutrient removal oxidation ditch, which operates on an extended aeration, nitrification, and denitrification process within the oxidation ditch by cycling the aeration on and off. The clarified effluent is then sand filtered before its utilization as influent of the AOP pilot plant. Typical water quality parameters of the wastewater influent to the pilot plant are reported in Table 2. Concentrations of target pharmaceuticals in wastewater before AOP treatment are reported in Table 1.

The AOP pilot-scale system consisted of dosing pump for  $\text{H}_2\text{O}_2/\text{Cl}_2$  addition, ozone generator, LP-UV-reactor with an intensity of radiant energy ranging from 65 to 75  $\text{W}/\text{m}^2$ , and final degasser vessel for stripping ozone residual gas from the wastewater effluent. Several sampling points allow collection of the wastewater entering the pilot system: after mixing of  $\text{H}_2\text{O}_2/\text{Cl}_2$  in the main stream, after ozone dosage, and the final effluent of the pilot plant (Figure S1). UV doses for the wastewater treatment were selected by changing the flowrate that passed through the LP-UV-reactor, which had a volume of 21 L. Tested ozone doses were 0.5, 1, 1.5, 3, 4.5, 6, 7.5, 9  $\text{mg O}_3/\text{L}$ . Using these transferred ozone doses, an ozone residual in the range 0 – 1.2  $\text{mg}/\text{L}$  was measured after ozone injection in the wastewater stream. Tested UV doses were 191  $\text{mJ}/\text{cm}^2$  (flow rate of 6000 L/h), 465  $\text{mJ}/\text{cm}^2$  (flow rate of 2500 L/h), and 981  $\text{mJ}/\text{cm}^2$  (flow rate of 1200 L/h). In this work, experiments were accomplished by different ozone and UV doses to evaluate the degradation kinetics of target pharmaceuticals. In addition, selected ozone and UV doses were typical for wastewater treatment (Lee et al., 2016). During AOP treatments,  $\text{H}_2\text{O}_2$  and  $\text{Cl}_2$  were added to the pilot influent at concentrations of 10  $\text{mg}/\text{L}$  (i.e., 0.29 mM), and 3  $\text{mg}/\text{L}$  (i.e.,

0.04 mM), respectively, which are typical doses used for wastewater treatment (Guo et al., 2018; Liu et al., 2019a; Miklos et al., 2019). In the case of chlorine, sodium hypochlorite solution was dosed in order to measure a total chlorine residual of 3 mg/L soon after the mixing with the wastewater stream. Investigated AOPs resulted by the combination of different oxidants and included UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, Cl<sub>2</sub>/O<sub>3</sub>/UV. Experiments designed to compare UV-based AOPs (i.e., UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>) were performed at different UV doses. On the contrary, experiments designed to compare ozone-based AOPs (i.e., O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, Cl<sub>2</sub>/O<sub>3</sub>/UV) were accomplished varying the ozone doses, whereas the flow rate and, thus, the UV fluence was kept constant (i.e., fluence of 465 mJ/cm<sup>2</sup> with a flow rate of 2500 L/h). Lists of all AOP treatment conditions used to investigate fluorescing organic matter oxidation and pharmaceuticals removal are reported in Table S3 and Table S4, respectively. After reaction, which lasts few seconds in plug-flow reactors, residual oxidants (i.e., H<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>, O<sub>3</sub>) were quenched by 10 mg/L of sodium bisulfite, which is an oxidant quenching agent that entails negligible effects on the optical properties of wastewater organic matter (Park and Snyder, 2018). While effluent samples were taken for each setting, different influent samples were taken during the experimentation time. However, no changes in water quality and pharmaceuticals concentrations in the wastewater influent to the pilot system were observed.

All samples were stored at 4 °C with ice packs upon collection and were brought to the laboratory. At the laboratory samples were immediately filtered, doped with the surrogate standards, and stored in fridge at 4 °C following the best preservation practices before pharmaceuticals analysis (Anumol and Snyder, 2015) and spectroscopic measurements (Sgroi et al., 2020a). Samples were stored in fridge one week for pharmaceuticals analysis, and two day for spectroscopic measurements.

### **2.3. Analytical methods**

All pharmaceuticals were analyzed using an automated liquid chromatography online SPE system coupled to an Agilent 6460 triple-quadrupole mass spectrometer (Agilent Technologies, Santa Clara, CA). Further details of the analytical method are available in previously published literature (Anumol and Snyder, 2015), and are also briefly described in Supplementary material section (Text S2, Table S1 – S2). Resulting reporting limits in ultrapure water ranged from 0.1 to 3 ng/L (Table S5). For dissolved organic carbon (DOC) and total dissolved nitrogen (TN) concentrations analysis, samples were filtered through 0.45  $\mu\text{m}$  hydrophilic polypropylene filter (GHP Membrane Acrodisc, Pall Life Sciences) and acidified to  $\text{pH} < 3$  with hydrochloric acid. A Shimadzu TOC-L<sub>CSH</sub> (Kyoto, Japan) total carbon analyzer was used for quantification.

Initial and residual concentrations of  $\text{H}_2\text{O}_2$  were determined on site at the AOP pilot-plant by the Peroxide Vacu-vials Kit (CHEMetrics), using a SAM photometer (V3000 SAM, CHEMetrics). Residual concentrations of free chlorine, total chlorine, and ozone were also determined on site using a portable Hach-Lange spectrophotometer (DR2500, Hach-Lange) and suitable reagent kits.

Absorbance measurements were performed with a Shimadzu UV-1800 spectrophotometer (Kyoto, Japan). Fluorescence data acquired by a Shimadzu RF-5301PC fluorescence spectrophotometer (Kyoto, Japan) were corrected as described in published work (SgROI et al., 2020b) and also reported in Text S3. Fluorescence intensities were produced in Raman unit (RU). Parallel Factor (PARAFAC) analysis was carried out using the drEEM toolbox (Murphy et al., 2013) (details in Text S4).

### **2.4. Calculation of observed degradation rate constants**

Values of observed degradation rate constants ( $k_{obs}$ ) for pharmaceuticals and PARAFAC components were calculated using the pseudo-first order kinetic equation (Chen et al., 2017; Miklos et al., 2018a; von Sonntag and von Gunten, 2012). Particularly, for UV-based AOPs, it was used the equation:

$$\ln\left(\frac{c}{c_0}\right) = -k_{obs} \cdot fluence \quad (1)$$

where  $k_{obs}$  is in [ $\text{cm}^2/\text{mJ}$ ], and fluence in [ $\text{mJ}/\text{cm}^2$ ].

Calculation of  $k_{obs}$  values during ozone-based AOPs was accomplished by:

$$\ln\left(\frac{c}{c_0}\right) = -k_{obs} \cdot ozone \quad (2)$$

where  $k_{obs}$  is in [ $\text{L}/\text{mg}$ ], and the term “*ozone*” represent the transferred ozone dose in [ $\text{mg}/\text{L}$ ].

### 3. Results and discussion

#### 3.1. Removal of fluorescence and UV absorbance by different AOPs

In this study fluorescence spectra coupled with PARAFAC analysis, and UV absorbance measurements at 254 nm ( $\text{UV}_{254}$ ) were used to evaluate the reactivity of different radical species and oxidants with different DOM moieties, and, thus, the oxidation performance of different AOPs in wastewater. The simple visual analysis of fluorescence EEMs can provide a qualitative estimate of treatment efficacy of tested AOPs as shown in Figure 1 and Figure S2. Particularly, in Figure S2 the fluorescence EEM of the wastewater influent to the pilot plant is compared with EEMs of wastewater collected after addition of  $\text{H}_2\text{O}_2$  and chlorine. In this case, no quenching agent was added to evaluate the full effect of  $\text{H}_2\text{O}_2/\text{Cl}_2$  addition on fluorescence measurements. In Figure 1

are reported fluorescence EEMs obtained treating the tested wastewater by diverse AOPs. Different reduction of fluorescence intensities were produced by different AOPs. Particularly, it is easily observable that at same level of UV fluence, UV/Cl<sub>2</sub> process was more effective to degrade fluorescing organic matter than UV/H<sub>2</sub>O<sub>2</sub> process. On the other hand, at same ozone dose and UV fluence, Cl<sub>2</sub>/O<sub>3</sub>/UV was the most effective process to degrade fluorescing organic matter between the ozone-based AOPs investigated in this study. O<sub>3</sub> and O<sub>3</sub>/UV produced similar reduction of fluorescence intensities, which was lower than fluorescence reduction produced by the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV process (Figure 1). Overall, ozone-based AOPs were more effective to diminish fluorescence intensities of DOM than UV-based AOPs. In this study, removal of DOC, which is a further bulk parameter of water, was insignificant for all tested conditions confirming the negligible mineralization of wastewater organic matter upon oxidation processes (von Sonntag and von Gunten, 2012).

A useful tool for EEMs interpretation is PARAFAC analysis. This method, which is a technique of multivariate data analysis, enables the deconvolution of complex EEMs into independent components that represent groups of similarly behaving fluorophores. Such deconvolution helps discriminate and ascertain contributions of different DOM types, and by providing the fluorescence maxima intensity for the identified components it gives a basis for quantitative analysis of change in the composition of fluorescent organic matter during water treatment (Murphy et al., 2013; Sgroi et al., 2018b). In this study, PARAFAC analysis identified 4 independently varying fluorescing components as shown in Table 3, which reports the positions of the excitation and emission maxima for each component and the related fluorescence intensities observed in the wastewater before AOP treatment. The excitation and emission loadings of these fluorescent components, denoted henceforth as C1–C4, are shown in Figure S3. Figure S4 shows the corre-

sponding spectral fingerprints. Based on the position of the excitation and emission peaks, components C1, C2, and C3 were identified as humic- and fulvic-like fluorescence (Table 3 and Figure S2). Specifically, component C3 represents the contribution of a terrestrial fulvic- and humic-like component, and component C2 that of microbial humic-like fluorescence, as has been established in prior PARAFAC studies of surface water and wastewater (Sgroi et al., 2017b; H. Yu et al., 2015). Component C1 corresponds to a group of humic-like fluorescing species found in prior studies in high nutrient and wastewater impacted environments (Table 3). Tryptophan-like and proteinaceous fluorescing compounds are associated with components C4 (Table 3).

Degradation of different moieties of DOM was evaluated by plotting the decline of normalized fluorescing PARAFAC components and  $UV_{254}$  with respect to ozone dose or fluence (Figure 2). Particularly, degradation of DOM was evaluated at different fluence exposures for the UV-based AOPs, whereas degradation of DOM by ozone-based AOPs was assessed at different ozone doses (Figure 2). Observed percentage removal for all tested AOP conditions are reported in Table S3.

Control experiments showed that UV irradiation alone or  $H_2O_2$  addition alone did not change the optical properties of wastewater organic matter, whereas slight removal of  $UV_{254}$  and fluorescing components (10 – 28%) were produced by chlorine addition (Table S3) in agreement with previous studies (Miklos et al., 2019; Sgroi et al., 2020a). During all tested AOP treatments, reduction of  $UV_{254}$  and intensity of PARAFAC components increased with the increase of applied ozone dose/fluence (Figure 2). Particularly, observed removal of  $UV_{254}$  and PARAFAC components was different between different AOPs. Indeed, different fluorescing DOM moieties showed different reactivity with radical species and oxidants produced during different AOPs. For an effective comparison of the oxidation performance among all tested AOPs, the natural logarithm of

the relative residual fluorescence intensity of each PARAFAC component or  $UV_{254}$  value ( $C/C_0$ ) was plotted as a function of UV-fluence or ozone dose (Figure S5). Linear regression lines were determined and the respective slopes, which represent the observed pseudo first-order degradation rate constants ( $k_{obs}$ ), were obtained (Table 4) according to Eq. (1) and Eq. (2) (Chen et al., 2017; Miklos et al., 2019). For such regression analyses, data points related to the plateau of the normalized degradation curves (Figure 2) were excluded to avoid to skew values of the coefficient of determination ( $R^2$ ) and accomplish incorrect comparisons between the calculated  $k_{obs}$  (Figure S5).

Based on the obtained  $k_{obs}$  values (Table 4), the degradation order of  $UV_{254}$  and identified PARAFAC components was  $C4 > C1 > C2 > C3 > UV_{254}$  for the UV-based AOPs (i.e., UV/ $H_2O_2$ , UV/ $Cl_2$ ). On the contrary, the degradation order was  $C1 > C4 > C2 > C3 > UV_{254}$  during the ozone-based AOPs (i.e.,  $O_3$ ,  $O_3/UV$ ,  $Cl_2/O_3/UV$ ), except for the  $H_2O_2/O_3/UV$  process, where the degradation order of  $UV_{254}$  and PARAFAC components was the same of the UV-based AOPs. This is the first study to compare the degradation of different PARAFAC components by different radical species under a broad selection of AOP treatments. Two previous studies performed a similar comparison for the  $O_3$ , UV/ $H_2O_2$  and UV/persulfate processes, but such comparison was performed at bench-scale using synthetic wastewater, which entailed the determination of diverse fluorescing PARAFAC components than those identified in this work (Ahn et al., 2017; Chen et al., 2017).

Oxidants and main radical species that should be produced during the investigated AOPs include ozone,  $\cdot OH$ , and RCS (i.e.,  $Cl\cdot$ ,  $Cl_2\cdot^-$ ,  $ClO\cdot$ ). Ozone is a selective oxidant, which has been suggested to react with aromatic and other electron-rich components of DOM by electron transfer reactions (von Sonntag and von Gunten, 2012). RCS are also selective oxidants, which react



preferentially with electron-rich moieties such as olefins, phenols, anilines, and alkyl-/alkoxybenzenes (Guo et al., 2018, 2017). On the contrary,  $\cdot\text{OH}$  radicals have been classified as non-selective oxidants able to react quickly with structurally very different compounds. Nevertheless,  $\cdot\text{OH}$  radicals are also electrophilic oxidants, and, thus, they tend to react faster with aromatic compounds compared to substances with electron-withdrawing moieties (Lee and Von Gunten, 2016; Westerhoff et al., 1999). All these discussed observations are in agreement with the observed degradation order of PARAFAC components in this work. Indeed, component C4, which is typical of aromatic and proteinaceous substances (Chen et al., 2003), was the most degraded or the second most degraded component in all tested AOPs. Component C1 was the most reduced fluorescence by  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$  and  $\text{Cl}_2/\text{O}_3/\text{UV}$  processes, and it was the second most degraded fluorescing component by all other AOPs. C1 is a humic-like fluorescence component typical of wastewater environments. Humic acids are a wide class of compounds, which include quinones, phenols, and carboxylic acids (De Melo et al., 2016). Hence, humic-like fluorescing substances also contain electron-rich organic compounds able to react rapidly with selective oxidants, such as  $\text{O}_3$  and RCS. Furthermore, C1 was the component with the highest fluorescence intensity in the untreated wastewater (Table 3), and, probably, the most abundant group of independent fluorophores in the tested water if considering that this group of fluorophores is scarcely removed by biological treatments (Cohen et al., 2014; Sgroi et al., 2017a). The supposed high abundance of component C1 may have contributed to the observed degradation rates by various oxidants as well. Previous studies have shown that microbial derived DOM has lower aromaticity and reactivity with ozone than DOM obtained from other sources in natural waters (Westerhoff et al., 1999). This observation is in agreement with the observed lower  $k_{obs}$  values of the microbial component C2 compared to C4 and C1. Component C3 was the group of fluoro-

phores that showed the lowest reactivity with all oxidant species produced in this work. Component C3 is a terrestrial fulvic-like fluorescing component. Fulvic-acids are generally less aromatic and have a lower number of reaction sites than humic-acids (Senesi et al., 1989; Westerhoff et al., 1999). This fact may explain the observed low reactivity for component C3. Finally, previous studies have also hypothesized fluorescence DOM to be lower in molecular weight than UV-absorbing DOM (SgROI et al., 2018a; Shimabuku et al., 2017; Velten et al., 2011). Particularly, studies that investigated the reactivity of different DOM fractions based on molecular weights (MW) and size exclusion chromatography have shown that high MW DOM moieties (e.g., biopolymers) have low reactivity with oxidants (e.g., ozone) (Dong et al., 2010; von Sonntag and von Gunten, 2012). In addition, since fluorescence is ascribed to an extended  $\pi$ -electron system, the reaction of radicals/oxidants with fluorophore groups might reduce fluorescence signals, while chromophore characteristics of the compound may still be present (Lakowicz, 2006). These rationales are in agreement with the observed lower reduction of  $UV_{254}$  compared to fluorescence by AOPs.

When comparing the two UV-based AOPs (i.e., UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>), it is easy to observe that all identified PARAFAC fluorescing components were better degraded during the UV/Cl<sub>2</sub> process. The higher oxidation performance of UV/Cl<sub>2</sub> compared to UV/H<sub>2</sub>O<sub>2</sub> has already been described by previous studies that investigated the removal of micro-pollutants from water and wastewater, and it was related to the higher photolysis rate constants of chlorine compared to H<sub>2</sub>O<sub>2</sub>, which results in a very high yield of RCS (Fang et al., 2014; Guo et al., 2018, 2017; Miklos et al., 2019). Particularly, even though the used chlorine molar concentration (i.e., 0.04 mM) was lower than used H<sub>2</sub>O<sub>2</sub> molar concentration (i.e., 0.29 mM), the chlorine consumption by UV photolysis was significantly higher (average consumed Cl<sub>2</sub> ~ 0.028 mM) than that of hydrogen peroxide (aver-

age consumed  $\text{H}_2\text{O}_2 \sim 0.009 \text{ mM}$ ) during the UV treatments investigated in this work. Furthermore, it has to be highlighted that the investigated wastewater was a fully nitrified tertiary effluent, where measurements of free chlorine concentration and total chlorine concentration were very similar. This fact confirms that the investigated UV/ $\text{Cl}_2$  process worked as an actual UV/free chlorine process, and not as an UV/chloramine process, which has a lower oxidation performance (Wu et al., 2019; Zhang et al., 2019).

$\text{O}_3$  and  $\text{O}_3/\text{UV}$  processes showed very similar oxidation performance (Table 4 and Figure 2) in agreement with previous studies that reported limited increase of  $\cdot\text{OH}$  production when combining ozone and UV in wastewater (Lado Ribeiro et al., 2019; Miklos et al., 2018b; H. Wang et al., 2018). On the contrary,  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  and  $\text{Cl}_2/\text{O}_3/\text{UV}$  had a better oxidation performance, even though the degradation order of PARAFAC components was different for these two AOPs as previously discussed. Except component C4, the  $\text{Cl}_2/\text{O}_3/\text{UV}$  AOP outperformed the  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  process for the degradation of all PARAFAC components. This fact can be probably related to the different radical species and yields of radicals produced in these two AOPs. Particularly, a significant production of  $\cdot\text{OH}$  is expected in  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ , whereas both  $\cdot\text{OH}$  and RCS are formed during the  $\text{Cl}_2/\text{O}_3/\text{UV}$  AOP. During the  $\text{Cl}_2/\text{O}_3/\text{UV}$  process, RCS can be produced by the UV photolysis of chlorine (Guo et al., 2018), and during the reaction of chlorine with ozone (Huang et al., 2020). Although a slow reaction has been reported between hypochlorite and ozone ( $k = 170 \text{ M}^{-1} \text{ s}^{-1}$ ) (Haag and Hoigne, 1983; von Sonntag and von Gunten, 2012), RCS can be generated following the high reaction rate of  $\text{HOCl}/\text{OCl}^-$  with  $\cdot\text{OH}$  ( $k = 2.0 \times 10^9 - 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Fang et al., 2014; Guo et al., 2018). Further water constituents (e.g., bromide, carbonates, DOM components) may lead to the production of secondary radical species

getting complex the chemistry of the process (Cheng et al., 2018; von Sonntag and von Gunten, 2012).

### **3.2. Removal of emerging contaminants by different AOPs**

Photolytic removal of target pharmaceuticals is reported in Table S4, and it aligns well with experimental results obtained in previous studies (Guo et al., 2018; Miklos et al., 2019, 2018a). UV photolysis alone under the investigated conditions (i.e., fluence of 465 mJ/cm<sup>2</sup> and 981 mJ/cm<sup>2</sup>) produced a significant degradation of SMZ (52 – 75%), and a low removal of FLU and GMF (9 – 37%). On the contrary, the effect of UV photolysis was negligible on the removal of other investigated pharmaceuticals (i.e., TMP, PRM and CBZ). Previous studies have also shown that degradation of pharmaceuticals is negligible by H<sub>2</sub>O<sub>2</sub> alone, whereas the removal of some micro-pollutants, such as TMP and SMZ is significant by chlorination (Guo et al., 2018; Miklos et al., 2019). In this work, chlorine removed very effectively SMZ (92%) and TMP (100%) during control experiment, where chlorine was allowed to react in wastewater until depletion (Table S4). The effect of chlorine in the removal of other pharmaceuticals was negligible (Table S4). It is interesting to observe that chlorination alone was more effective to remove SMZ and TMP than many investigated AOPs (i.e., UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV) when operated at low ozone dose/fluence (Table S4).

Figure 3 shows normalized concentration of target pharmaceuticals as function of the employed ozone dose or fluence. Observed percentage removal of pharmaceuticals for all tested AOP conditions are reported in Table S4. Even in this case, for an effective comparison of the oxidation performance of target pharmaceuticals by different AOPs, the natural logarithm of the relative residual concentration ( $C/C_0$ ) of each pharmaceutical was plotted as a function of UV-fluence or

ozone dose (Figure S6). Linear regression lines were determined and the respective slopes, which represent the observed pseudo first-order degradation rate constants ( $k_{obs}$ ), were obtained according to Eq. (1) and Eq. (2) (Table 5). In some cases, calculation of  $k_{obs}$  values was not possible for some pharmaceutical, which were reduced at concentration level below the detection limit by the lowest used oxidant dosages. In Table 5, the contaminant degradation was labelled as “*very fast*” if the compound concentration was below the minimum reporting limit at the lowest oxidant dose, whereas it was labelled as “*fast*” if the compound concentration was below the minimum reporting limit at the second lowest oxidant dose.

By the analysis of Figure 3 and the size of box plots in Table 5, it is observable that radical species produced in the UV/Cl<sub>2</sub> process (i.e., RCS and <sup>•</sup>GH) showed higher selectivity than radicals formed by UV/H<sub>2</sub>O<sub>2</sub> (i.e., <sup>•</sup>OH) for the reaction with pharmaceuticals. Particularly, the higher selectivity of RCS compared to hydroxyl radicals resulted in a higher range of  $k_{obs}$  values (difference between maximum and minimum value, i.e.  $\Delta k_{obs}$ ) in the UV/Cl<sub>2</sub> process than in the UV/H<sub>2</sub>O<sub>2</sub> AOP (see box plots in Table 5). On the contrary, such selectivity of RCS was not evident for the degradation of PAH and AC components (Figure 2 and Table 4) suggesting that most of fluorescing organic matter constituents in wastewater are electron-rich moieties with high propensity to react with RCS. Outcomes of the experiments showed that UV/Cl<sub>2</sub> process out-competed UV/H<sub>2</sub>O<sub>2</sub> for the removal of the antibiotics TMP and SMZ, whereas UV/H<sub>2</sub>O<sub>2</sub> was superior in the degradation of PRM, CBZ and GMF. The two processes showed similar effectiveness to remove FLU.

When comparing the ozone-based AOPs, the effectiveness in the degradation of pharmaceuticals was in the order H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV > O<sub>3</sub>/UV > O<sub>3</sub> if excluding Cl<sub>2</sub>/O<sub>3</sub>/UV (Table 5). As expected, the size of the box plots in Table 5 was similar for these three AOPs, since same radical species (i.e.,

$\cdot\text{OH}$ ) were produced. On the contrary, a very high compound selectivity for the oxidation of pharmaceuticals was observed during the  $\text{Cl}_2/\text{O}_3/\text{UV}$  AOP (Table 5). Particularly,  $\text{Cl}_2/\text{O}_3/\text{UV}$  was the most effective process to degrade SMZ, CBZ and GMF. A similar effectiveness (i.e., slightly lower) to  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  for this new ozone and chlorine-based AOP was observed for the removal of FLU, whereas the removal of PRM was very low, and it was lower than simple ozonation (Table 5 and Table S4). PRM has a low reactivity with ozone and RCS, whereas it can be effectively oxidized by  $\cdot\text{OH}$  (Table 1). Nevertheless, the presence of chlorine (i.e.,  $\text{HOCl}/\text{OCl}^-$ ) in the  $\text{Cl}_2/\text{O}_3/\text{UV}$  process is able to significantly scavenges  $\cdot\text{OH}$  ( $k = 2.0 \times 10^9 - 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Fang et al., 2014; Guo et al., 2018) reducing the capability of this AOP to degrade PRM. Finally, TMP was very quickly removed by all investigated AOPs except  $\text{UV}/\text{H}_2\text{O}_2$ .

To sum up, differences can be observed when comparing different AOPs in terms of change of fluorescing organic matter or pharmaceutical degradation. Overall, chlorine-based AOPs were the most effective processes to degrade fluorescing components in wastewater when compared to similar AOPs that used  $\text{H}_2\text{O}_2$  instead of chlorine. On the contrary, the effectiveness of different AOPs in the removal of pharmaceuticals was compound-specific because of the different selectivity of formed radical species with target pharmaceutical. Finally, it can be highlighted that the new  $\text{Cl}_2/\text{O}_3/\text{UV}$  process was the most effective AOP to degrade fluorescing organic matter and all investigated pharmaceuticals except PRM.

### **3.3. Sensitivity of surrogate parameters for on-line monitoring**

The analysis of pharmaceuticals at trace levels in water is laborious, time-consuming and expensive. In addition, it requires sophisticated analytical equipment and highly trained technicians. Hence, the use of surrogate parameters that can accurately predict the removal of pharmaceuti-

icals in a simple, fast, and cost-effective manner is highly desirable. In the last decade, the use of spectroscopic parameters like UV absorbance and fluorescence has been shown to be a promising approach in predicting the removal of pharmaceuticals during various AOP treatments (Gerrity et al., 2012; Miklos et al., 2019; Park et al., 2017; H. W. Yu et al., 2015). Therefore, the existing literature offers the following conclusions: (1) spectroscopic parameters based on UV and fluorescence measurements are strongly correlated with the elimination of aromatic and non-aromatic pharmaceuticals, (2) each compound has a unique set of regression parameters related to its rate constants for reactions with various oxidants, (3) unit processes with different oxidation mechanisms (e.g., ozone/UV vs. UV/H<sub>2</sub>O<sub>2</sub>) also have unique sets of correlations, and (4) the correlations for specific contaminants and oxidation processes are consistent between different secondary or tertiary effluents (Gerrity et al., 2012; Korshin et al., 2018; Miklos et al., 2019). Furthermore, in this study we observed that different fluorescing organic matter components and UV<sub>254</sub> have different reaction rates with different oxidant/radical species. In Table 6 are reported the calculated regression parameters of linear correlations between the removals of pharmaceuticals and the removal of different spectroscopic indexes, which included UV<sub>254</sub> and PARAFAC components. Particularly, regression parameters shown in Table 6 resulted unique for each compound, surrogate parameter and oxidation process. The calculated coefficients of determination ( $R^2$ ) for those correlations are reported in Table S6.

Surrogate parameters that have high slope of regression line are inconvenient indexes for real-time monitoring of pharmaceuticals. Indeed, these indexes indicate high pharmaceuticals removal per unit % change of their value. On the contrary, the most sensitive surrogate parameter to monitor pharmaceuticals oxidation is the spectroscopic index with the lowest slope in the regression line. In this case, unit % change of the spectroscopic parameter is able to quantify small re-

removal of pharmaceuticals. As an example, in Figure 4 is highlighted the different sensitivity of  $UV_{254}$  and PARAFAC component C4 to monitor the removal of PRM during the UV/H<sub>2</sub>O<sub>2</sub> treatment. In Table 6 are highlighted the most sensitive spectroscopic surrogates to monitor pharmaceuticals upon the investigated AOPs. The most suitable index for monitoring the removal of pharmaceuticals was different for each investigated AOP. Particularly, component C4 resulted the preferable index to monitor UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, and Cl<sub>2</sub>/O<sub>3</sub>/UV AOPs, component C1 was the best surrogate to monitor UV/Cl<sub>2</sub> process, whereas component C3 was the most suitable parameter to monitor H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV treatment. This finding is in agreement with the diversity of radical species that can be produced during different AOPs, and that show different reactivity with diverse organic matter components. Finally, it can be observed that fluorescence indexes were more sensitive measurements than  $UV_{254}$  to monitor pharmaceuticals oxidation by various AOPs.

#### 4. Conclusions

This study investigated the removal of fluorescing organic matter and selected pharmaceuticals (i.e., CBZ, FLU, GMF, PRM, SMZ, TMT) from wastewater by different UV- and ozone-based AOPs (i.e., UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, Cl<sub>2</sub>/O<sub>3</sub>/UV) at pilot-scale. In addition, this study evaluated the sensitivity of different spectroscopic parameters based on UV and fluorescence measurements to predict pharmaceuticals removal. Based on the results of the study, the following conclusions can be obtained:

- Radical species generated during chlorine-based AOPs (i.e., UV/Cl<sub>2</sub>, Cl<sub>2</sub>/O<sub>3</sub>/UV) showed higher selectivity than those generated by H<sub>2</sub>O<sub>2</sub>- and ozone-based AOPs (i.e., UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV) for the reaction with different pharmaceuticals. On



the contrary, such high selectivity of radical species produced by chlorine-based AOPs was not observed during the reaction with fluorescing components of wastewater organic matter;

- Tryptophan-like substances and humic-like fluorescing compounds typical of wastewater environments were the most degraded fluorescing components by all AOPs, whereas microbial products and fulvic-like fluorescing substances resulted less reactive to oxidation. Low removal of UV absorbance at 254 nm were observed by all investigated AOPs. Overall, chlorine-based AOPs were more effective to reduce fluorescence intensities than H<sub>2</sub>O<sub>2</sub>-based AOPs;
- The new proposed Cl<sub>2</sub>/O<sub>3</sub>/UV process was the most effective AOP to degrade all investigated pharmaceuticals except PRM, which had a very low removal. When comparing other ozone-based AOPs, the oxidation performance of pharmaceuticals followed the order H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV > O<sub>3</sub>/UV > O<sub>3</sub>. UV/Cl<sub>2</sub> process (Cl<sub>2</sub> = 3mg/L) showed better removal of TMP and SMZ, similar removal of FLU, and lower removal of PRM, CBZ and GMF than UV/H<sub>2</sub>O<sub>2</sub> AOP (H<sub>2</sub>O<sub>2</sub> = 10 mg/L);
- Correlations between the removal of pharmaceuticals and the removal of spectroscopic indexes (i.e., PARAFAC components and UV<sub>254</sub>) had unique regression parameters for each compound, surrogate parameter and oxidation process. This fact entails a different sensitivity for monitoring pharmaceuticals by different surrogate parameters since the slope of regression line affects the extent of change of pharmaceuticals removal that can be monitored per unit % change of fluorescence intensity. Particularly, component C4 (i.e., tryptophan-like fluorescence) resulted the preferable index to monitor pharmaceuticals removal by UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, and Cl<sub>2</sub>/O<sub>3</sub>/UV AOPs. Component C1

(humic-like fluorescence) was the best surrogate to monitor UV/Cl<sub>2</sub> process, whereas component C3 (fulvic-like fluorescence) was the most suitable parameter to monitor pharmaceuticals oxidation by H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV treatment.

## Supplementary data

Texts S1 – S4, Table S1 – S6, and Figures S1 – S6. This material is available free of charge.

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**Figure 1. Fluorescence EEMs (RU) of the final effluent of the pilot plant after different AOPs treatments. Chlorine ( $Cl_2$ ) was dosed at 3 mg/L, hydrogen peroxide ( $H_2O_2$ ) at 10 mg/L.**

**Figure 2. Decline of normalized fluorescing PARAFAC components and UV absorbance at 254 nm ( $UV_{254}$ ) with respect to fluence exposure or ozone dose for all investigated AOPs. Chlorine ( $Cl_2$ ) was dosed at 3 mg/L, hydrogen peroxide ( $H_2O_2$ ) at 10 mg/L. The UV fluence during the ozone based AOPs was 465 mJ/cm<sup>2</sup>.**

**Figure 3. Decline of normalized concentration of target pharmaceuticals with respect to fluence exposure or ozone dose for all investigated AOPs. Chlorine ( $Cl_2$ ) was dosed at 3 mg/L, hydrogen peroxide ( $H_2O_2$ ) at 10 mg/L. The UV fluence during the ozone based AOPs was 465 mJ/cm<sup>2</sup>.**

**Figure 4. Difference in sensitivity between the PARAFAC component C4 and UV absorbance at 254 nm ( $UV_{254}$ ) for monitoring PRM during the UV/ $H_2O_2$  treatment.**

**Table 1. Summary of target compounds with indication of their concentration before treatment, second-order rate constants with different radical species, quantum yield of photo-degradation at 254 nm ( $\Phi_{254}$ ), and molar absorption coefficient at 254 nm ( $\epsilon_{254}$ ).**

Compound	Concentration before treatment (ng/L)	$k_{O_3}$ ( $M^{-1} s^{-1}$ ), pH = 7	$k_{OH}$ ( $M^{-1} s^{-1}$ )	$k_{ClO\cdot}$ ( $M^{-1} s^{-1}$ )	$\Phi_{254}$ ( $10^{-2}$ , mol/E)	$\epsilon_{254}$ ( $10^3$ , L/M/cm)	Reference
<i>Group I – High reactivity with ozone and RCS. High photosensitivity.</i>							
SMZ	1813	$3 \times 10^6$	$6 \times 10^9$	$< 2.23 \times 10^9$	0.1	13	(Gerrity et al., 2012; Guo et al., 2018; Wols et al., 2014)
<i>Group II – High reactivity with ozone and RCS. Photo-resistant.</i>							
TMP	21	$3 \times 10^5$	$7 \times 10^9$	$4.46 \times 10^{10}$	0.09	16	(Gerrity et al., 2012; Guo et al., 2018; Wols et al., 2014)
<i>Group III – High reactivity with ozone, and moderate/low reactivity with RCS. Photo-resistant.</i>							
CBZ	235	$3 \times 10^5$	$9 \times 10^9$	$2 \times 10^8$	0.33	5.8	(Gerrity et al., 2012; Guo et al., 2018; Wols et al., 2014)
<i>Group IV – Moderate reactivity with ozone, and moderate/low reactivity with RCS. Moderate photosensitivity.</i>							
FLU	36	N.A.	$9 \times 10^9$	N.A.	41	0.79	(Lam et al., 2005; Wols et al., 2014)
GMF	116	$5 \times 10^4$	$1 \times 10^{10}$	$4.16 \times 10^8$	9.2	0.37	(Gerrity et al., 2012; Guo et al., 2018; Wols et al., 2014)
<i>Group V – Low reactivity with ozone, and moderate/low reactivity with RCS. Photo-resistant.</i>							
PRM	384	1	$7 \times 10^9$	$6 \times 10^7$	8.20	0.220	(Gerrity et al., 2012; Guo et

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al., 2018; H. W.

Yu et al., 2015)

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*N.A.: not available*

Journal Pre-proof

**Table 2. Water quality parameters of tested wastewater.**

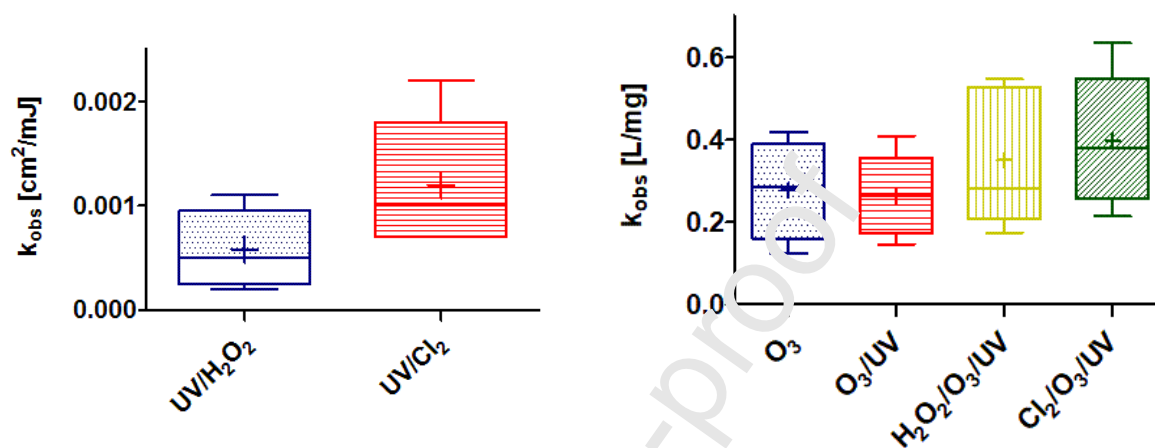
Parameter	Value
DOC (mg/L)	5.4
TN (mg/L)	2.4
UV <sub>254</sub>	0.148
pH	7.5

Journal Pre-proof

**Table 3. Fluorescing components determined in the tested wastewater by PARAFAC modeling and wavelengths corresponding to the positions of their excitation and emission maxima.**

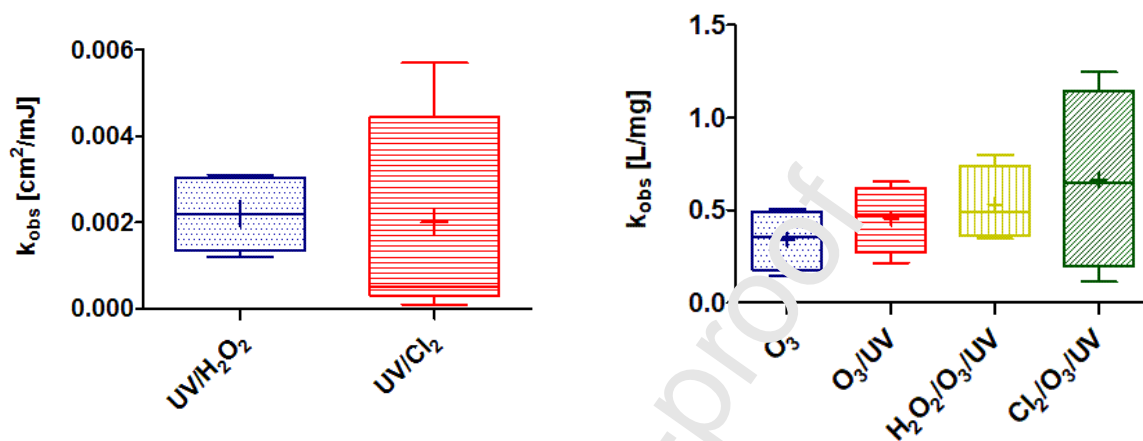
Component	Wavelengths of the maxima (nm)		Description	Intensity before treatment (RU)	Previously reported by
	Excitation	Emission			
<i>C1</i>	<250 & 350	440	Wastewater/nutrient enrichment tracer, humic-like fluorescence	1.758	(Murphy et al., 2011; Sgroi et al., 2018a, 2017b; H. Yu et al., 2015; Yu et al., 2010)
<i>C2</i>	<250 & 315	400	Microbial/humic-like fluorescence	1.047	(Murphy et al., 2011; Sgroi et al., 2018a, 2017b; H. Yu et al., 2015)
<i>C3</i>	<250 & 385	475	Fulvic-like and humic-like fluorescence	0.870	(Murphy et al., 2011; Sgroi et al., 2018a, 2017b; H. Yu et al., 2015)
<i>C4</i>	280	350	Protein, tryptophan-like fluorescence	0.672	(Murphy et al., 2011; Sgroi et al., 2018a, 2017b; H. Yu et al., 2015)

**Table 4. Observed first-order degradation rates ( $k_{obs}$ ) for the investigated spectroscopic surrogates during different AOPs with indication of the coefficient of determination ( $R^2$ ), and their box-plot representation.  $k_{obs}$  are in [ $\text{cm}^2/\text{mJ}$ ] for UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{Cl}_2$  processes, and in [ $\text{L}/\text{mg}$ ] for  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ ,  $\text{Cl}_2/\text{O}_3/\text{UV}$  processes.**



Treatment	C1		C2		C3		C4		UV <sub>254</sub>	
	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$
UV/ $\text{H}_2\text{O}_2$	0.0008	0.987	0.0005	0.991	0.0003	0.975	0.0011	0.994	0.0002	0.752
UV/ $\text{Cl}_2$	0.0014	0.984	0.0010	0.884	0.0007	0.872	0.0022	0.928	0.0007	0.904
$\text{O}_3$	0.4183	0.966	0.2859	0.983	0.1979	0.976	0.3597	0.995	0.1225	0.987
$\text{O}_3/\text{UV}$	0.4093	0.957	0.2522	0.974	0.1993	0.998	0.3041	0.997	0.1463	0.991
$\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$	0.5065	0.912	0.2824	0.925	0.2403	0.948	0.5474	0.959	0.1742	0.870
$\text{Cl}_2/\text{O}_3/\text{UV}$	0.6344	0.822	0.3809	0.838	0.3012	0.912	0.4644	0.952	0.2133	0.884

**Table 5. Observed first-order degradation rates ( $k_{obs}$ ) for the target pharmaceuticals during different AOPs with indication of the coefficient of determination ( $R^2$ ), and their box-plot representation.  $k_{obs}$  are in [ $\text{cm}^2/\text{mJ}$ ] for UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{Cl}_2$  processes, and in [ $\text{L}/\text{mg}$ ] for  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$ ,  $\text{Cl}_2/\text{O}_3/\text{UV}$  processes.**



Treatment	TMP		PRM		SMZ		CBZ		FLU		GMF	
	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$	$k_{obs}$	$R^2$
UV/ $\text{H}_2\text{O}_2$	0.0031	0.995	0.0012	0.999	0.0030	0.994	0.0022	0.999	0.0031	0.999	0.0015	0.987
UV/ $\text{Cl}_2$	very fast		0.0005	0.898	0.0057	0.996	0.0005	0.864	0.0032	0.989	0.0001	0.966
$\text{O}_3$	very fast		0.1455	0.992	0.5079	0.876	fast		0.2664	0.853	0.4487	0.911
$\text{O}_3/\text{UV}$	very fast		0.2157	0.986	0.6520	0.946	fast		0.5187	0.978	0.4338	0.959
$\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$	very fast		0.3407	0.990	0.7985	0.965	fast		0.5705	0.963	0.4050	0.966
$\text{Cl}_2/\text{O}_3/\text{UV}$	very fast		0.1116	0.998	1.2460	0.869	very fast		0.4531	0.949	0.8484	0.940

very fast = 100% removal was observed at the lowest oxidant dose; fast = 100% removal was observed at the second lowest oxidant dose.



**Table 6. Summary of regression parameters for correlations between surrogates removal and pharmaceuticals removal with indication of most suitable index for the on-line monitoring (highlighted in italics and by colors).**

AOP	Index	$\Delta R^*$	TMP		PRM		SMZ		CBZ		FLU		GMF	
		(%)	slope	y-int	slope	y-int	slope	y-int	slope	y-int	slope	y-int	slope	y-int
$H_2O_2/$ UV	C1	39	1.561	16.93	1.188	4.97	1.155	34.29	1.303	17.26	1.464	21.05	1.180	13.92
	C2	31	1.908	35.13	1.479	18.33	1.404	47.94	1.610	32.14	1.793	38.06	1.451	27.53
	C3	20	2.855	42.71	2.248	23.83	2.087	53.65	2.432	38.29	2.686	45.14	2.182	33.18
	C4	47	<i>1.278</i>	15.91	<i>0.972</i>	4.22	<i>0.946</i>	33.52	<i>1.066</i>	16.43	<i>1.198</i>	20.10	<i>0.966</i>	13.16
	UV <sub>254</sub>	6	9.109	-50.75	6.699	-43.38	6.829	-16.97	7.451	27.11	8.513	-42.03	6.817	-36.30
$Cl_2/$ UV	C1	32	-	-	<i>1.156</i>	-30.60	<i>0.816</i>	49.83	<i>0.855</i>	11.65	<i>2.299</i>	-39.89	-	-
	C2	14	-	-	2.677	-76.44	1.908	16.83	1.990	-45.91	5.317	-	-	-
	C3	10	-	-	3.750	-79.79	2.681	14.18	2.792	-48.54	7.440	-	-	-
	C4	21	-	-	1.685	-83.33	1.211	11.09	1.260	-51.49	3.339	-	-	-
	UV <sub>254</sub>	10	-	-	3.429	-77.84	2.472	22.20	2.564	-39.94	6.792	-	-	-
$O_3$	C1	55	-	-	1.854	-100.17	1.404	-21.43	-	-	3.058	-	2.506	-
	C2	56	-	-	1.704	-66.71	1.190	10.45	-	-	2.793	-	2.259	-70.46
	C3	49	-	-	1.713	-49.37	1.126	26.39	-	-	2.756	-84.49	2.340	-49.42
	C4	64	-	-	<i>1.320</i>	-50.67	<i>0.903</i>	23.04	-	-	<i>2.150</i>	-88.41	<i>1.764</i>	-49.62
	UV <sub>254</sub>	37	-	-	2.198	-37.01	1.406	35.95	-	-	3.598	-66.87	2.753	-25.05
$O_3$ /UV	C1	43	-	-	1.797	-90.74	0.710	36.97	-	-	1.185	-8.05	2.172	-95.63
	C2	52	-	-	1.531	-46.23	0.582	55.89	-	-	1.019	20.77	1.782	-37.79
	C3	55	-	-	<i>1.401</i>	-22.61	0.508	66.07	-	-	0.942	36.01	1.554	-6.68
	C4	61	-	-	<i>1.249</i>	-32.49	<i>0.464</i>	61.81	-	-	<i>0.835</i>	29.64	<i>1.419</i>	-19.71
	UV <sub>254</sub>	40	-	-	1.301	-13.33	0.591	64.21	-	-	0.827	44.33	1.805	-12.22
$H_2O_2/$ $O_3$ /UV	C1	19	-	-	1.950	-83.82	0.714	37.70	-	-	1.144	-2.15	1.617	-48.88
	C2	28	-	-	1.311	-9.26	0.456	66.42	-	-	0.740	43.33	1.053	14.96
	C3	33	-	-	<i>1.104</i>	8.62	<i>0.381</i>	72.78	-	-	<i>0.620</i>	53.60	<i>0.883</i>	29.53
	C4	29	-	-	1.278	-35.10	0.464	55.89	-	-	0.745	26.87	<i>1.054</i>	-7.97

	<b>UV<sub>254</sub></b>	20	-	-	1.725	-6.91	0.572	68.46	-	-	0.940	46.15	1.346	18.59
	<b>C1</b>	6	-	-	5.311	-	-	-	-	-	3.626	-	-	-
						419.47						225.44		
<b>Cl<sub>2</sub>/</b>	<b>C2</b>	12	-	-	2.696	-	-	-	-	-	1.836	-43.58	-	-
<b>O<sub>3</sub></b>						153.58								
<b>/UV</b>	<b>C3</b>	19	-	-	1.638	-65.43	-	-	-	-	1.117	16.31	-	-
	<b>C4</b>	23	-	-	1.330	-66.38	-	-	-	-	0.909	15.54	-	-
	<b>UV<sub>254</sub></b>	15	-	-	2.147	-70.28	-	-	-	-	1.464	13.06	-	-

\* $\Delta R$  = width of the observed removal range for the surrogate parameters.

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## CRedit author statement

**Massimiliano Sgroi:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - Original Draft, Writing - Review & Editing, Visualization. **Tarun Anumol:** Formal analysis, Data curation. **Federico G.A. Vagliasindi:** Resources, Funding acquisition. **Shane A. Snyder:** Resources, Funding acquisition, Supervision. **Paolo Roccaro:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing - Review & Editing, Visualization, Supervision, Funding acquisition.

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**Declaration of competing interests**

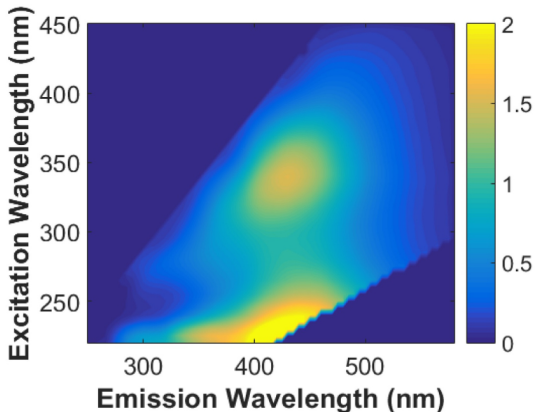
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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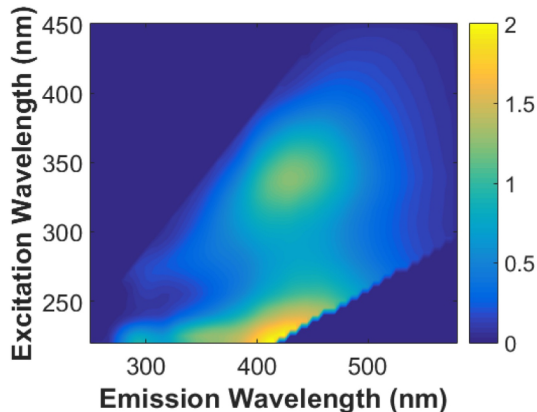
### Highlights

- Comparison of UV/H<sub>2</sub>O<sub>2</sub>, UV/Cl<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, Cl<sub>2</sub>/O<sub>3</sub>/UV at pilot scale
- Cl<sub>2</sub>-based AOPs better degraded fluorescence organic matter than H<sub>2</sub>O<sub>2</sub>-based AOPs
- Cl<sub>2</sub>-based AOPs showed higher selectivity to remove CEC than O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>-based AOPs
- Cl<sub>2</sub>/O<sub>3</sub>/UV was the most effective AOP to degrade target CEC except primidone
- The most sensitive surrogate for on-line monitoring was different for diverse AOPs

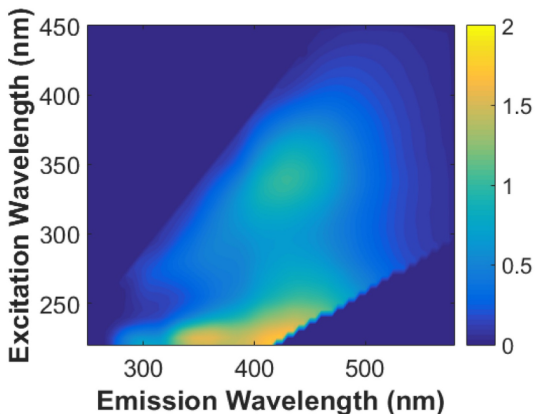
*H<sub>2</sub>O<sub>2</sub> UV 465 mJ/cm<sup>2</sup>*



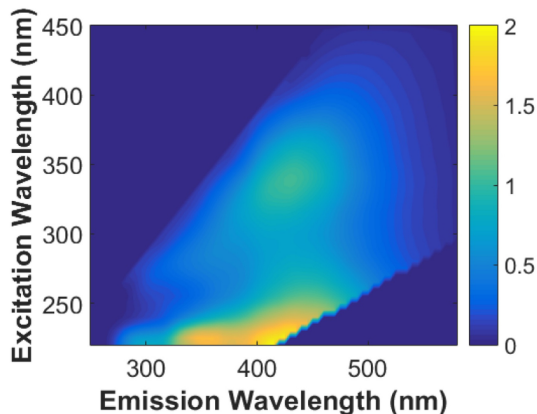
*Cl<sub>2</sub> UV 465 mJ/cm<sup>2</sup>*



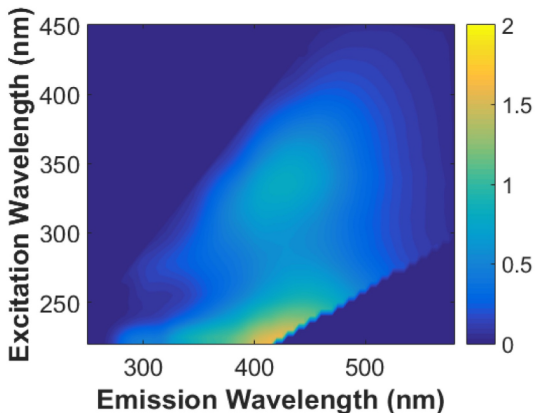
*O<sub>3</sub> 1.5 mg/L*



*O<sub>3</sub> 1.5 mg/L UV 465 mJ/cm<sup>2</sup>*



*H<sub>2</sub>O<sub>2</sub> O<sub>3</sub> 1.5 mg/L UV 465 mJ/cm<sup>2</sup>*



*Cl<sub>2</sub> O<sub>3</sub> 1.5 mg/L UV 465 mJ/cm<sup>2</sup>*

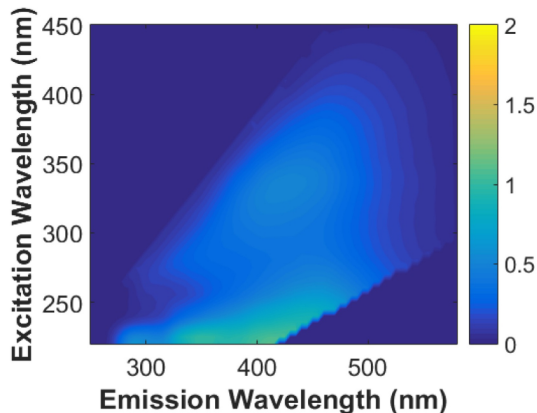


Figure 1

■ C1    ● C2    ▲ C3    ● C4    \* UV254

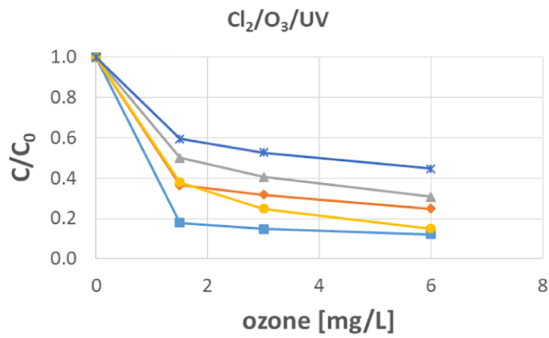
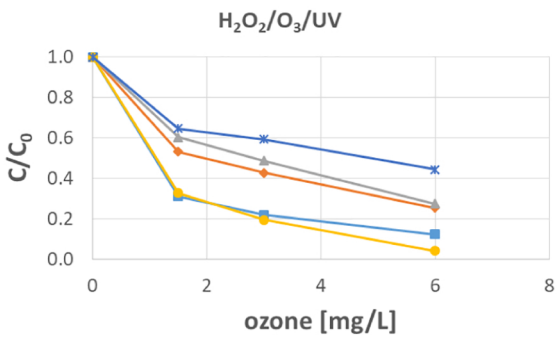
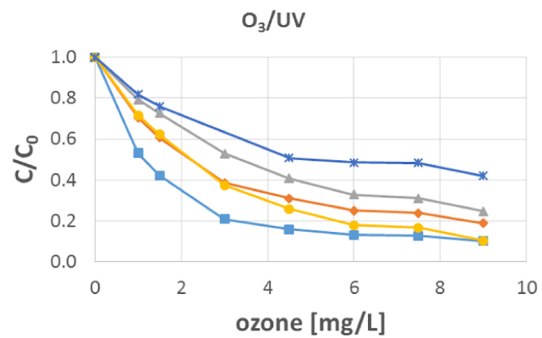
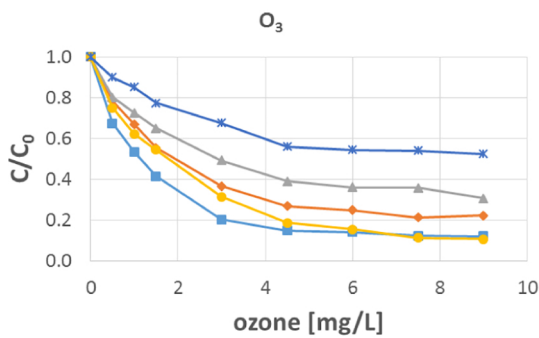
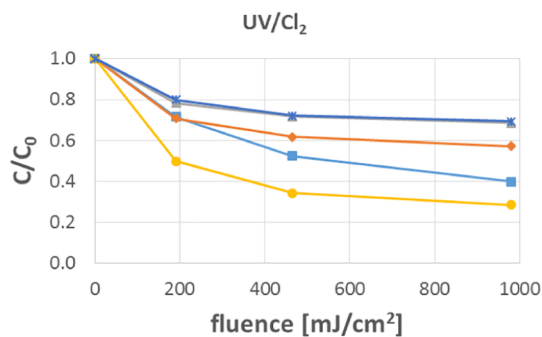
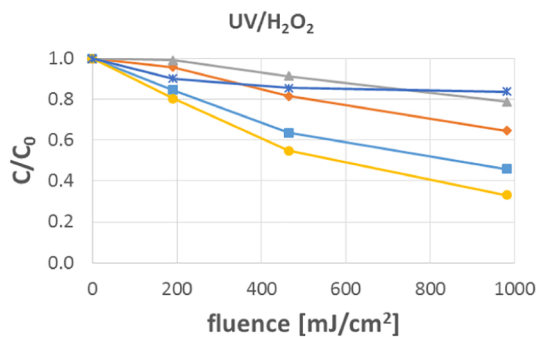


Figure 2

■ TMP   
 ◆ PRM   
 ▲ SMZ   
 ● CBZ   
 — FLU   
 × GMF

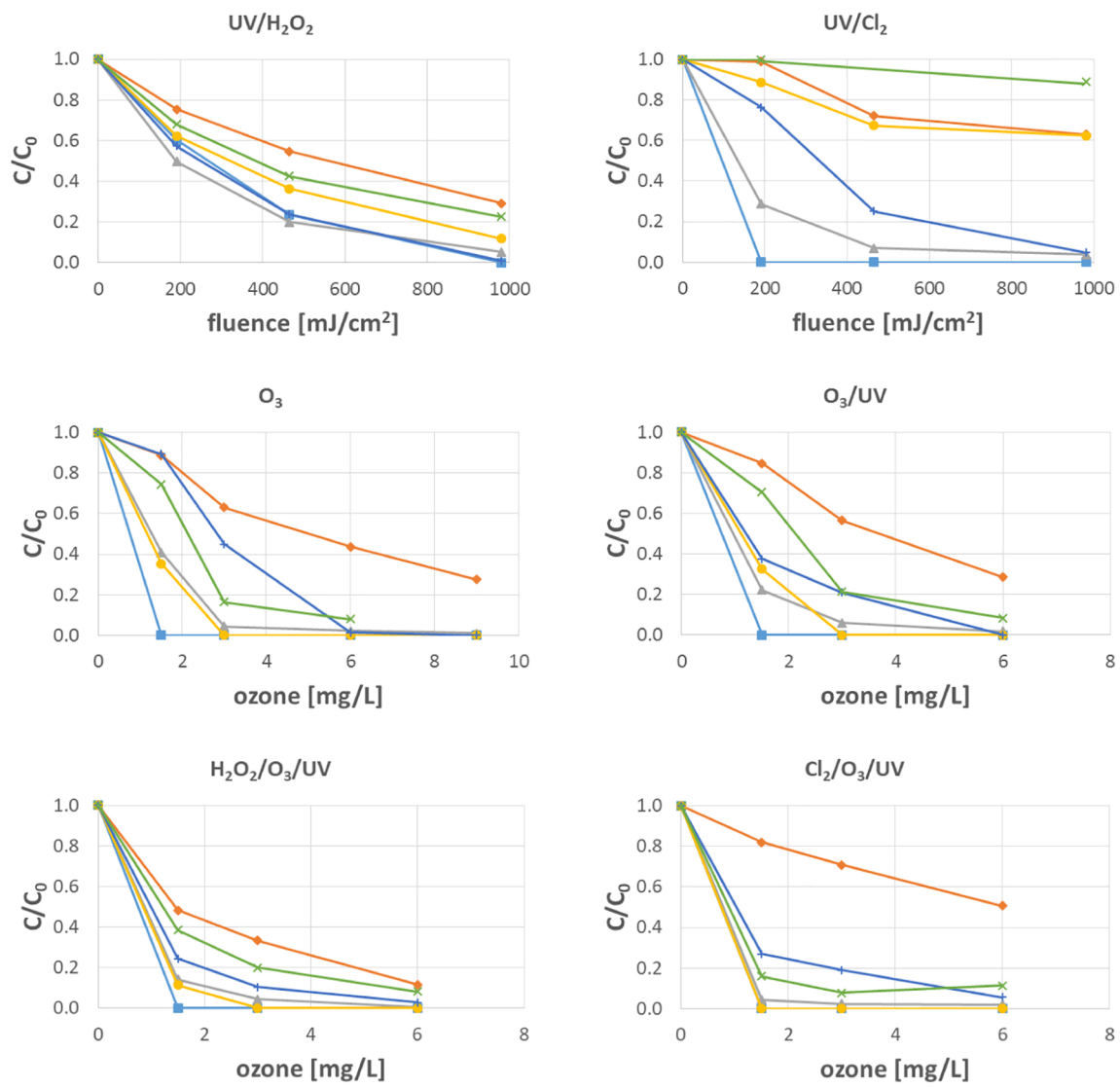


Figure 3



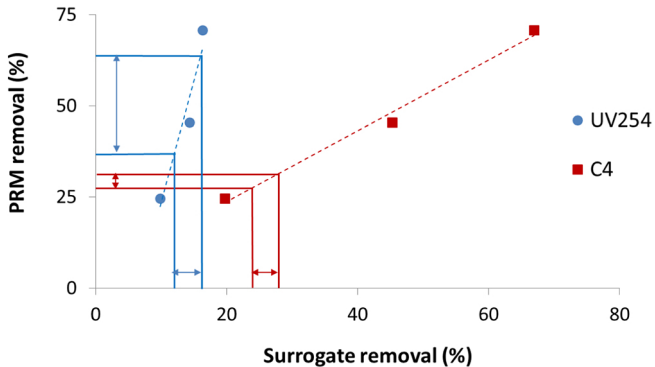


Figure 4