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Title: Advanced treatment of urban wastewater by UV-C/free chlorine process: micro-pollutants removal and effect of UV-C radiation on trihalomethanes formation

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Keywords: advanced oxidation processes; contaminants of emerging concern; disinfection by products; pesticides; pharmaceuticals; wastewater reuse

Corresponding Author: Professor Luigi Rizzo, PhD

Corresponding Author's Institution: University of Salerno

First Author: Giusy Cerreta

Order of Authors: Giusy Cerreta; Melina A Roccamante; Patricia Plaza-Bolaños; Isabel Oller; Ana Aguera; Sixto Malato; Luigi Rizzo, PhD

Abstract: The effect of the UV-C/free chlorine (FC) process on the removal of contaminants of emerging concern (CECs) from real urban wastewater as well as the effect of UV-C radiation on the formation of trihalomethanes (THMs) compared to FC process alone was investigated. Unlike of FC process, UV-C/FC was really effective in the degradation of the target CECs (carbamazepine (CBZ), diclofenac, sulfamethoxazole and imidacloprid) in real wastewater (87% degradation of total CECs within 60 minutes, $Q_{UV-C} = 1.33 \text{ kJ L}^{-1}$), being CBZ the most refractory one (49.5 %, after 60 min). The UV-C radiation significantly affected the formation of THMs. THMs concentration (mainly chloroform) was lower in UV-C/FC process after 30 min treatment ($<1 \mu\text{g L}^{-1}$ = limit of quantification (LOQ)) than in FC process in dark ($2.3 \mu\text{g L}^{-1}$). Noteworthy, while in FC treated wastewater chloroform concentration increased after treatment, UV-C/FC process resulted in a significant decrease (residual concentrations below the LOQ), even after 24h and 48h post-treatment incubation. The formation of radicals due to UV-C/FC process can reduce THMs compared to chlorination process, because part of FC reacts with UV-C radiation to form radicals and it is no longer available to form THMs. These results are encouraging in terms of possible use of UV-C/FC process as advanced treatment of urban wastewater even for possible effluent reuse.

Highlights

- UV-C/FC was effective in the degradation of the target CECs (87%, $Q_{UV-C}=1.33 \text{ kJ L}^{-1}$)
- CBZ was the most refractory CEC (49.5 %, after 60 min) to UV-C/FC process
- THMs concentration was lower in UV-C/FC than FC process
- THMs increased after FC treatment (up to 48h), while decreased after UV-C/FC
- FC reacts with UV-C to form radicals and it is only partially available to form THMs

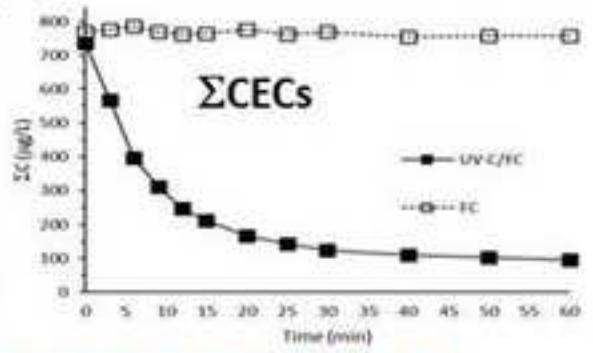
Contaminants of emerging concern (CECs)



- Sulfamethoxazole
- Imidacloprid



- Carbamazepine
- Diclofenac

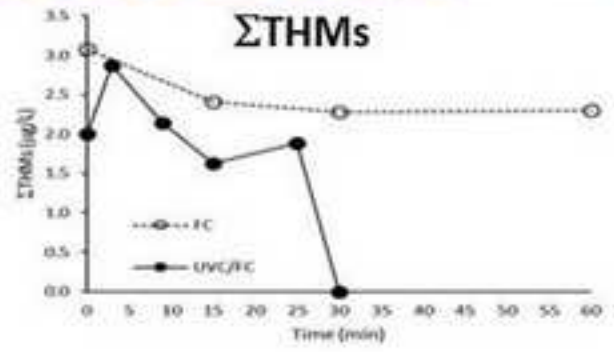


Free chlorine (FC)
Vs
UV-C/FC



CECs?

THMs?



Reuse



Disposal



Declaration of 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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

1 **Advanced treatment of urban wastewater by UV-C/free chlorine process: micro-**
2 **pollutants removal and effect of UV-C radiation on trihalomethanes formation**

3

4 Giusy Cerreta¹, Melina A. Roccamante^{2,3}, Patricia Plaza-Bolaños³, Isabel Oller ^{2,3}, Ana
5 Aguera³, Sixto Malato^{1,2*}, Luigi Rizzo^{1,*}

6 ¹Department of Civil Engineering, University of Salerno, Via Giovanni Paolo II 132,
7 84084 Fisciano (SA), Italy

8 ²Plataforma Solar de Almería-CIEMAT. Ctra. Senés km 4, 04200 Tabernas (Almería),
9 Spain.

10 ³CIESOL, Joint Centre of the University of Almería-CIEMAT, 04120 Almería, Spain.

11 *Corresponding authors:

12 Luigi Rizzo. l.rizzo@unisa.it

13 Sixto Malato. Sixto.malato@psa.es

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20 **Abstract**

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22 emerging concern (CECs) from real urban wastewater as well as the effect of UV-C
23 radiation on the formation of trihalomethanes (THMs) compared to FC process alone was
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26 real wastewater (87% degradation of total CECs within 60 minutes, $Q_{UV-C} = 1.33 \text{ kJ L}^{-1}$),
27 being CBZ the most refractory one (49.5 %, after 60 min). The UV-C radiation
28 significantly affected the formation of THMs. THMs concentration (mainly chloroform)
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30 (LOQ)) than in FC process in dark ($2.3 \mu\text{gL}^{-1}$). Noteworthy, while in FC treated
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32 in a significant decrease (residual concentrations below the LOQ), even after 24h and 48h
33 post-treatment incubation. The formation of radicals due to UV-C/FC process can reduce
34 THMs compared to chlorination process, because part of FC reacts with UV-C radiation to
35 form radicals and it is no longer available to form THMs. These results are encouraging in
36 terms of possible use of UV-C/FC process as advanced treatment of urban wastewater even
37 for possible effluent reuse.

38

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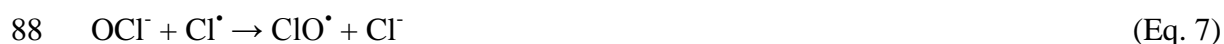
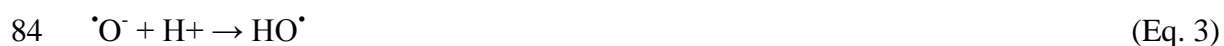
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42 1. Introduction

43 Urban wastewater treatment plants (UWTPs) are hotspots for the release into the
44 environment of organic micro-pollutants, including chemicals (such as pharmaceuticals,
45 personal care products, pesticides, hormones and synthesis products) (Michael et al., 2013;
46 Schröder et al., 2016) and biological elements (such as antibiotic resistant bacteria and
47 genes) (Cacace et al., 2019; Rizzo et al., 2013), also known as contaminants of emerging
48 concern (CECs). Although chemical CECs are released into surface water at concentrations
49 in the range of ngL^{-1} - μgL^{-1} , they can accumulate into the aquatic environment resulting in
50 unpredictable chronic toxic effects to humans and ecosystems (Brooks et al., 2009).
51 Furthermore, higher concern is related to the use of treated wastewater for crop irrigation
52 because plants can uptake such contaminants (Christou et al., 2019; Ferro et al., 2015) thus
53 resulting in increasing risk for human health (Kohl et al., 2019; Malchi et al., 2014).
54 Conventional UWTPs are not designed to remove CECs (Krzeminski et al., 2019) and the
55 lack of specific regulation, still under discussion at EU level (Rizzo et al., 2018), refrains
56 managers to upgrade UWTPs. However, some countries such as Switzerland (due to the
57 implementation of a new Water Protection Act in 2016) and Germany have taken this
58 problem seriously and are upgrading UWTPs with advanced treatments methods, including
59 ozonation (O_3) and activated carbon adsorption (AC), and specifically designed to remove
60 CECs (Rizzo et al., 2019b). Although recognized among the best available technologies,
61 such consolidated methods present some disadvantages including formation of oxidation
62 by products (O_3) and poor disinfection efficiency (AC), respectively, and can require for an
63 additional post treatment step which will increase the cost (Rizzo et al., 2019b). Other
64 conventional tertiary treatment methods such as chlorination (Hua et al., 2019), peracetic
65 acid and UV-C radiation (Rizzo et al., 2019a) are poorly effective in the removal of CECs
66 and additionally chlorination results in the formation of toxic by-products such as
67 trihalomethanes (THMs) (Richardson et al., 2007).

68 Advanced Oxidation Processes (AOPs) produce radicals species (among which hydroxyl
69 radicals, HO[•]) that can effectively remove a wide range of CECs and inactivate pathogens,
70 so they represent a possible alternative to O₃ and AC as tertiary treatment method of urban
71 wastewater. Among AOPs, homogeneous photo driven processes (such as UV/H₂O₂, and
72 photo Fenton) are a perspective attractive option (Fiorentino et al., in press; Miralles-
73 Cuevas et al., 2017). However, taking into account that photo Fenton efficiency is affected
74 by pH and chelating agents may be necessary to operate at neutral pH conditions (De Luca
75 et al., 2014; Fiorentino et al., 2018), and UV/H₂O₂ may be not sufficiently effective in the
76 removal of some CECs (Ferro et al., 2015), the investigation of new photo driven AOPs,
77 such as UV/free chlorine (FC) process, is attracting increasing interest. In addition to HO[•]
78 radicals, UV/FC process can produce chlorine radical ([•]Cl) (Eq. 1 - 3) (D. Wang et al.,
79 2012) and secondary radical species such as ClO[•] (Eq. 4 - 7) (Guo et al., 2018; Hua et al.,
80 2019):

81



89 Radicals formation makes UV-C/FC process more effective than FC in the inactivation of
90 microorganisms in water systems (Rattanakul and Oguma, 2017; Li et al., 2018; Liu et al.,
91 2019).

92 However, the effect of the UV-C/FC process on the removal of CECs from real wastewater
93 has been poorly investigated so far as well as possible effects of UV-C radiation on the
94 formation of THMs. This issue is of additional interest taking into account that (i) the
95 chlorination process is increasingly replaced by alternative disinfection processes in
96 UWTPs (e.g., peracetic acid and UV-C radiation, respectively) (Antonelli et al., 2013; Di
97 Cesare et al., 2016; Formisano et al., 2016) because of its toxicity and (ii) THMs are
98 regulated in treated wastewater to be reused (Italy).

99 Accordingly, in this study, four CECs (carbamazepine (CBZ), diclofenac (DCF),
100 sulfamethoxazole (SMX) and imidacloprid (IMD)), were selected as model pollutants to
101 evaluate the efficiency of UV-C/FC process as tertiary treatment of urban wastewater. The
102 target micro-contaminants were selected because they are representative of different
103 groups of CECs (anticonvulsant, analgesic, antibiotic and insecticide, respectively) as well
104 as because typically detected in water and wastewater (Klavarioti et al., 2009; Petrie et al.,
105 2014). Moreover, the effect of UV-C radiation on the formation of THMs during and after
106 the treatment (incubation at 24 and 48h) through the comparison between FC and UV-
107 C/FC processes was evaluated. Possible reactions that can take place in real urban
108 wastewater treated by UV-C/FC process are also proposed.

109

110 2. Material and methods

111 2.1 Chemicals

112 CBZ, DCF and SMX of high purity grade (>99%) were purchased from Sigma-Aldrich,
113 while IMD (purity 97.9%) was supplied by Bayer Hispania S.A. (Barcelona, Spain). CECs
114 aqueous solutions were prepared by simultaneously dissolving CBZ, SMX and DCF in
115 deionized water at 8 mgL⁻¹ each while IMD solution was prepared separately (16 mgL⁻¹).
116 Finally, the respective solutions were added to the target water matrix in proper volumes to
117 obtain an initial concentration of 200 µg L⁻¹. Sodium hypochlorite solution (NaOCl,
118 Honeywell, 10% w/w) was used as a chlorine source for FC and UV-C/FC tests. Total and
119 free chlorine reagent powder pillows were purchased from HACH, while sodium
120 thiosulfate pentahydrate was purchased from MERK. A commercial mix solution
121 (CRM47904) containing bromodichloromethane, bromoform, chloroform and
122 dibromochloromethane (purity >97.1%) at a concentration of 100 µg mL⁻¹ in methanol
123 (MeOH) was obtained from Supelco (Bellefonte, PA, USA). A stock solution (4 µg mL⁻¹)
124 was then prepared from dilution of the commercial mix with MeOH (Chromasolv
125 Honeywell-Riedel-de Haën, Seelze, Germany) and stored in 4-mL amber bottles at -20 °C;
126 special attention was put to minimize the headspace to avoid evaporation losses. Once
127 open, the stock solution aliquots were used for a maximum of 2 weeks and discarded after
128 this time. A working solution was prepared daily from the stock solution at 1 µg mL⁻¹ in
129 LC-MS water (Chromasolv, Fluka, Steinheim, Germany). Other reagents and materials
130 needed for sample extraction were methyl-tert-butyl ether (MTBE, Suprasolv, Merck,
131 Darmstadt, Germany), acetone (Fluka), anhydrous Na₂SO₄ (J.T. Baker, Deventer, The
132 Netherlands), 0.35-mL glass insert shells (Supelco) and 40-mL clear vials with screw top
133 caps and PTFE/silicone septa (all from Supelco).

134

135 **2.2 Water matrices**

136 Tests were performed using the effluent of the secondary treatment from an UWTP (WW)
137 and 1/1 diluted wastewater (DWW). Physical-chemical characteristics of the investigated
138 WW sample are given in the Table SI1 (in supplementary information file). Samples were
139 collected in amber glass bottles and stored at 4 °C for a maximum of two days.

140

141 **2.3 UV-C/free chlorine and control experiments**

142 2.3.1 Dark control tests at lab scale

143 Possible chlorine effects on the degradation of the target CECs were preliminary evaluated
144 through 60 minute tests under dark conditions. Accordingly, five litre bottles were filled in
145 with the target water matrix and spiked with the CECs aqueous solutions to achieve the
146 desired initial concentration ($200 \mu\text{gL}^{-1}$ for each contaminant). The aqueous matrix was
147 stirred for a few minutes, and a control sample was taken to measure the initial
148 concentration of the contaminants, just before the proper volume of chlorine solution was
149 added to achieve 10 mg L^{-1} of initial FC dose. This concentration (i) was selected
150 according to previous experiments (Cerreta et al., 2019), (ii) it is consistent with chlorine
151 doses used in UWTPs and (iii) it allows to keep a detectable residual FC at the end of the
152 process.

153

154 2.3.2 UV-C and UV-C/free chlorine tests

155 UV-C and photo driven AOP tests were performed in recirculation mode in a reactor
156 equipped with a medium pressure UV-C lamp (peak wavelength at 254 nm and 230 W
157 power) inside a quartz tube (O.D. = 3.70 cm), axially located in a stainless steel cylindrical

158 photoreactor (I.D. = 8.89 cm, 6.21 L illuminated volume). The reactor was filled in with
159 the water sample and the mixture of the four CECs was added at the initial concentration of
160 $200 \mu\text{gL}^{-1}$ each. The aqueous solution was stirred for 15 minute under dark conditions, the
161 first water sample was taken and the chlorine solution (10 mg L^{-1} of FC) was spiked in the
162 reactor. The experiment started after one minute of recirculation, required to warm up the
163 lamp, and the system was operated at a water flow rate of 46 L min^{-1} , measured by a fixed
164 controller (ProMinent) located on the back of the reactor. The UV irradiation was
165 measured (fixed controller by Prominent) in the outer wall of the photoreactor (average
166 value of 87.7 W m^{-2}) during blank experiments. This intensity was used for all the tests.
167 The cumulative energy was calculated according to Eq.8:

$$168 \quad Q_{\text{UVC}} (\text{kJ L}^{-1}) = \text{Dose} (\text{Jm}^{-2}) \cdot A_i / V_T (\text{m}^2 \text{L}^{-1}) (\text{kJ} (1000 \text{ J})^{-1}) \quad (\text{Eq. 8})$$

169

170 where Q_{UVC} is the accumulated UV-C energy per L, Dose is the UV-C ultraviolet
171 irradiation (Wm^{-2}) emitted by the lamp multiplied by the illumination time, A_i (0.338 m^2)
172 is the irradiated surface, V_T (80 L) is the total volume of the water into the pilot plant.

173

174 **2.4 Analytical measurements**

175 2.4.1 Chemical-physical measurements

176 Temperature and pH (which was observed to vary in the range 6.9-7.6) were measured
177 using a multi parametric sensor GLP22 CRISON. Residual chlorine concentration (free
178 ($\text{HOCl} + \text{OCl}^-$) and total (free + combined), respectively) was measured by a
179 spectrophotometer (Model T60U PG Instruments Ltd) through absorbance measurements
180 at 530 nm, according to HACH procedure (equivalent to USEPA and Standard Method
181 4500-Cl G for drinking water and wastewater). Depending on the measurement, a total or

182 free chlorine powder pillow (HACH) was added to 25 mL of water sample and swirled for
183 20 seconds.

184

185 2.4.2 Measurements of contaminants of emerging concern

186 CECs concentrations were measured by an ultra-performance liquid chromatography
187 (UPLC) instrument (Agilent Technologies, series 1260) equipped with a with DAD (Diode
188 Array Detector) and a ZORBAX Eclipse XDB C18 analytical column. The samples (9 mL)
189 were filtered through a 0.22- μm PTFE filter, which was subsequently washed with 1 mL of
190 ACN mixed with the filtered water sample to remove possible adsorbed compounds. 100
191 μL of the filtered samples were injected in the UPLC. The measurements were performed
192 using the following conditions: (i) 90% of 25 mM formic acid solution and 10% of ACN
193 and a linear gradient till to 100% of ACN in 12 min; (ii) 2 min re-equilibration time with a
194 flow rate of 1 mLmin^{-1} to get the initial condition (90:10 v/v). Retention time, limit of
195 quantification (LOQ), limit of detection (LOD) and maximum absorption for the CECs are
196 shown in Table SI2 (in supplementary information file).

197

198 2.4.3 Measurement of trihalomethanes

199 1 mL of sodium thiosulfate pentahydrate (20 mgL^{-1}) was added to 125 mL samples, just
200 after sampling to quench residual chlorine. An Agilent GC system 7890B (Agilent
201 Technologies, Palo Alto, CA, USA) was interfaced to an Agilent quadrupole analyzer
202 5977A. Samples were injected (2 μL) with a 10- μL syringe through an autosampler MPS
203 from Gerstel (Mülheim an der Ruhr, Germany). An HP-5MS UI capillary column (30 m \times
204 0.25 mm i.d \times 0.25 μm film thickness) was used for the chromatographic separation. The
205 carrier gas was helium (99.9999%) at 1 mL min^{-1} (constant flow). The GC separation was

206 based on previously reported conditions (Nikolaou et al., 2005, 2002): the injector
207 temperature was fixed at 175 °C (constant); the split ratio was set at 10:1; a septum purge
208 flow of 3 mL min⁻¹ was applied. The following column oven program was used: 39 °C
209 (hold 6 min) → 54 °C (3 °C min⁻¹) → 300 °C (100 °C min⁻¹, hold 4 min). The Q analyzer
210 operated in electron ionization at 70 eV and using the selected ion monitoring mode (SIM).
211 The temperatures of the transfer line and ionization source were 300 °C and 280 °C,
212 respectively. A 2-min solvent delay was applied. The total acquisition time was divided
213 into 4 acquisition segments; the MS parameters of each analyte are specified in Table SI3.
214 The total running time was 17.46 min. The GC-MS system was controlled, and data was
215 collected using Mass Hunter GC/MS acquisition software.

216 The extraction procedure was based on the official EPA Method 551.1 (Hodgeson et al.,
217 1995) and the validated method reported by Nikolaou et al. (2005). Briefly, 35 mL of water
218 were put into a 40-mL glass vial which was immediately closed. 2 g of Na₂SO₄ was added
219 to the vial and gently stirred, avoiding the formation of bubbles. After this, 2 mL of MTBE
220 were put into the vial and it was shaken vigorously and consistently by hand for 1 min. The
221 vials were left for 2 min to allow the separation of the water and MTBE phases. Then,
222 approximately 200 µL were transferred with a Pasteur pipette into a glass insert placed in a
223 2-mL glass vial which was closed immediately.

224 A calibration set was prepared in 40-ml vials considering a final volume of 35 mL (equal
225 to the real sample volume), using LC-MS water. The concentration of the standards was
226 0.6, 1, 2.5, 5, 10 and 25 µg L⁻¹ of each analyte. Tap water as control sample and a reagent
227 blank were used for daily quality control. As acceptability criterion for routine analysis,
228 linearity was considered adequate when the determination coefficients (R²) were ≥ 0.9800.
229 LOQs were set at 1 µg L⁻¹ (in sample) for all the target THMs. All glassware was
230 previously washed with water and detergent, rinsed with tap water, LC-MS water and

231 acetone and put into an oven at 70 °C for 1 h. Open and clean glassware was capped with
232 aluminum foil.

233

234 **3. Results and discussion**

235 3.1 Free chlorine Vs UV-C/free chlorine process: effect on free chlorine consumption

236 The effect of FC and UV-C/FC processes on FC consumption was observed in WW using
237 10 mgL⁻¹ of chlorine (Figure 1). After 60 minutes of treatment, residual FC was 5.8 mgL⁻¹
238 and 1.7 mgL⁻¹ using chlorination alone and UV-C/FC processes, respectively ($Q_{UV-C} = 1.33$
239 kJ L⁻¹).

240

241 **Figure 1**

242

243 As chlorine is added to natural water or wastewater, the reactions occurring between
244 chlorine and water constituents can be described by the following general relationship:

245 Chlorine demand = chlorine dose – residual chlorine

246 where *chlorine dose* is the chlorine added to the aqueous matrix, *residual chlorine* is the
247 chlorine concentration measured after a given contact time and *chlorine demand* is the
248 result of the reactions in which the *chlorine dose* is consumed by organic (TOC) and
249 inorganic compounds occurring in the aqueous matrix. Those with metals (e.g., iron and
250 manganese) and nitrogen compounds (namely NO₂⁻ and NH₃) are relevant among the
251 reactions involving chlorine and inorganic species (Snoeyink and Jenkins, 1980). In
252 particular, the reaction between HOCl and NH₃ results in the formation of chloramines

253 (combined residual chlorine). The higher FC consumption during UV-C/FC process could
254 be attributed to the generation of radicals from chlorine photolysis, according to Eq.1-7
255 (Fang et al., 2014; Guo et al., 2018; Hua et al., 2019; D. Wang et al., 2012; R. Yin et al.,
256 2018). Faster chlorine decay with the UV-C/FC process was observed in a recent study
257 (Hua et al., 2019) (Wang et al., 2019) at an initial chlorine concentration lower than 10
258 mgL^{-1} and low UV dose, which is consistent with previous studies (Wang et al., 2015;
259 Watts and Linden, 2007).

260

261 3.2 Free chlorine Vs UV-C/ Free chlorine process: effect of UV-C radiation on the removal
262 of contaminants of emerging concern

263 The effect of UV-C/FC process on CECs degradation was evaluated using 10 mgL^{-1} of FC
264 in WW. CECs concentration was quite stable under dark conditions (residual FC= 5.8 mgL^{-1})
265 ¹) (Figure 2a), while 87% of CECs degradation was reached after 60 minutes of UV-C/FC
266 treatment ($Q_{\text{UVC}} = 1.33 \text{ kJ L}^{-1}$; residual FC= 1.7 mgL^{-1}).

267

268

Figure 2

269

270 UV-C/FC process resulted in 90% degradation of DCF, SMX and IMD after 12, 25 and 30
271 minutes treatment (Figure SI1-Figure SI4) ($Q_{\text{UVC}} = 0.27; 0.56; 0.67 \text{ kJ L}^{-1}$, respectively)
272 (Figure 2b). A lower degradation was observed for CBZ (49.5 %, after 60 min and 1.33 kJ
273 L^{-1}). Control tests using UV-C radiation as standalone process were performed in our
274 previous work in natural water, during 120 minutes (Cerreta et al., 2019). UV-C radiation
275 significantly affected CECs removal (77% degradation with a Q_{UVC} of 2.67 kJ L^{-1}). In

276 particular IMD and SMX were completely degraded after 30 minutes, while 45 minutes
277 needed for DCF; on the opposite, CBZ was poorly degraded (only 14% of removal after
278 120 min).

279 The effect of chlorination process on CECs has been investigated in previous studies. CBZ
280 was poorly degraded (5.5%) within 5 min, using similar chlorine dosages (Wang et al.,
281 2016). This result is consistent with that one observed in a previous work (6 mg L⁻¹ of
282 chlorine, 15 min treatment in tap water spiked with 100 mg L⁻¹ of citric acid to enrich
283 DOC), where DCF (30%) and SMX (100%) degradations were also investigated (Sichel et
284 al., 2011). IMD also showed a low reactivity in WW with 20 mgL⁻¹ of chlorine (Chen et
285 al., 2018).

286 The UV-C/FC process has been investigated and found to be effective in the degradation of
287 CECs (Feng et al., 2007; Jin et al., 2011; Sichel et al., 2011; Watts and Linden, 2007) and
288 HO• and reactive chlorine species (RCS) have been found to contribute to their
289 degradation (Fang et al., 2014; Wang et al., 2016; Wu et al., 2016). More specifically, CBZ
290 was efficiently degraded by UV-C/FC in wastewater, but the occurrence of competing
291 organic (e.g., NOM) and inorganic substances decreased CBZ degradation rates compared
292 to deionized water matrix (Wang et al., 2016). NOM can absorb UV light, thus reducing
293 the rate of •OH and •Cl production, but it can also act as radicals scavenger (Fang et al.,
294 2014; Zhou et al., 2016). An enhanced degradation of IMD by UV-C/FC process (20 mg L⁻¹
295 of chlorine and LP Hg lamps) compared to UV-C process alone was also observed in a
296 previous study (Chen et al., 2018).

297

298 3.2.1 Effect of water matrix

299 When WW sample was diluted in 1:1 ratio with deionized water, no particular water
300 matrix effect was observed on CECs removal when chlorination process (10 mg L^{-1} , 60
301 min treatment) was tested (Figure 3). However, when UV-C/FC process was investigated
302 in DWW, a difference in the degradation rates of the target CECs compared to WW matrix
303 was observed (Figure SI1-SI4), in particular for CBZ (71% degradation in DWW Vs
304 49.5% in WW after 60 minutes of treatment, $Q_{\text{UVC}} = 1.33$, Figure 3). CECs degradation by
305 UV-C/FC process was slower in WW compared to DWW, possibly because of a lower
306 formation of radicals in WW matrix due to both (i) the faster FC consumption because of
307 the higher oxidant demand and (ii) the less effective UV-C light penetration compared to
308 DWW matrix.

309

310

Figure 3

311

312 When the effect of UV-C/FC process on CECs was investigated in WW and deionized
313 aqueous solutions in previous works, a water matrix effect was observed. Consistently with
314 our results, UV-C/FC process could efficiently degrade CBZ in WW, although the
315 degradation was reduced by about 30% compared with that in deionized water (Wang et
316 al., 2016). SMX and DCF were also effectively degraded by UV-C/FC process in different
317 water matrices with increased organic load and similar FC doses (Sichel et al., 2011).
318 Differently, but consistently with our results, a worsening of IMD removal by UV-C/FC
319 process using complex water matrices (20 mgL^{-1} of chlorine), was observed in a previous
320 study (K. Yin et al., 2018).

321

322 3.3 Free chlorine Vs UV-C/ Free chlorine process: effect of UV-C radiation on
323 trihalomethanes

324 THMs are potential carcinogenic organohalogenated compounds (the respective cancer
325 descriptors according to United States Environmental protection Agency (EPA, 2018) are
326 given in Table SI4) resulting from the reaction among FC, bromide and natural organic
327 matter (NOM), which have been detected the first time in chlorinated water in the early
328 '70s (Bellar et al., 1974; Rook, 1974). The THMs include chloroform (CLF),
329 dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and bromoform
330 (BRF).

331 The effect of UV-C radiation on the formation of chloroform can be observed from figure
332 4. In chlorinated WW under dark conditions, a CLF concentration of $2.3 \mu\text{gL}^{-1}$ was
333 measured after 60 minutes, while 90% degradation was observed after 30 minutes of UV-
334 C/FC treatment ($Q_{\text{UVC}} = 0.66 \text{ kJ L}^{-1}$). Only CLF and DCBM (below the LOQ and just for
335 FC tests) were detected, the concentration of the other two THMs being zero in all samples
336 (Table SI5). The formation of THMs in chlorinated WW has received far less attention
337 (Matamoros et al., 2007; Sun et al., 2009) than chlorination of drinking water (Gallard and
338 Von Gunten, 2002; Gao et al., 2019; Hua and Reckhow, 2007; Reckhow et al., 1990;
339 Richardson et al., 2007) and the effect UV-C radiation on the formation of THMs during
340 the removal of CECs from real wastewater by UV-C/FC process has not yet been
341 investigated to our knowledge.

342

343

Figure 4

344

345 The possible reactions occurring in UV-C/FC treated real WW are summarized in the
346 scheme proposed in figure 5. According to the discussion in the previous paragraphs, the
347 reaction between FC, organic matter (TOC) and bromide (Br-) results in the formation of
348 THMs (1). However, the formation of radicals due to UV-C/FC process (2) can decrease
349 THMs presence (3) compared to chlorination process alone because part of FC reacts with
350 UV-C radiation to form radicals and it is no longer available to form THMs, and radicals
351 can also degrade THMs. Moreover, THMs can also be reduced by volatilization (mainly
352 chloroform) (Table SI4) (4). Radicals degrade the target CECs (5) but are also scavenged
353 by TOC and other substances (including carbonates and salts) (6). FC is also consumed by
354 the oxidation of metals and nitrogen compounds (7). Finally TOC can absorb UV-C
355 radiation (8).

356

357 **Figure 5**

358

359 3.3.1 Post-treatment incubation: effect on trihalomethanes formation

360 Typically, in WW reuse practice, treated effluent is stored for some hours/days in a tank to
361 be used for crop irrigation as necessary. However, residual FC will keep reacting with
362 substances in WW during storing and THMs are expected to form as well. Therefore, in
363 order to investigate possible formation of THMs during treated WW storage, THMs were
364 measured even after incubation for 24h and 48h, respectively (Figure 6).

365

366 **Figure 6**

367

368 The formation of THMs were close to the detection limit but for chloroform, which
369 concentration was finally plotted in figure 6 (the concentrations of the THMs measured in
370 WW tests are given in Table SI5). After 60 minutes of FC treatment, 1.69 and 1.86 μgL^{-1}
371 of CLF were formed in DWW and WW, respectively. Furthermore, after the incubation at
372 24 and 48 h, CLF concentration increased. More specifically, 3.73 and 6.24 μgL^{-1} CLF
373 concentrations were observed after 24h in DWW and WW respectively, while after 48 h
374 CLF concentration was 4.84 μgL^{-1} in DWW and 8.52 μgL^{-1} in WW. The initial
375 concentration of CLF just after UV-C/FC process (60 minutes treatment), was significantly
376 lower (below LOQ for both DWW and WW) than FC process, and it remained below the
377 LOQ even after 24 and 48 h of incubation, in both (DWW and WW) samples. It is worthy
378 to note that, while the other THMs were not detected in UV-C/FC treated WW samples,
379 even after 24 and 48 h of incubation, they were detected in FC tests (Table SI5). In
380 particular, DCBM, which was under the LOQ after 60 minute FC treatment, increased up
381 to 1.7 and 2.82 μgL^{-1} after 24 and 48 h, respectively. DBCM was not detected during FC
382 tests, but 1.07 μgL^{-1} were measured after 48 h incubation. Finally, BRF was also detected
383 after 48 h, even if at a concentration below the LOQ.

384 In a previous work, the synergistic effect of the sequential use of UV irradiation and
385 chlorine to disinfect reclaimed water was investigated in terms of bacteria inactivation and
386 formation of THMs (X. Wang et al., 2012). The authors observed results consistent with
387 those achieved in our work. As matter of fact, the concentration of THMs in pre-
388 chlorinated wastewater was 16.0 $\mu\text{g L}^{-1}$ and decreased to 14.9 $\mu\text{g L}^{-1}$ after UV-C
389 irradiation (11 W low-pressure lamp, 15 mJ cm^{-2}). In another study the authors also
390 observed an increase in the THMs concentration during chlorination as the contact time
391 increased from 30 min to 210 min (El-Dib and Ali, 1995), and THMs formation continued
392 even in the post- treatment, consistently with our results.

393

394 **4. Conclusions**

395 Unlike of FC process, UV-C/FC was really effective in the degradation of the target CECs
396 in WW. High degradation (90%) of DCF, SMX and IMD after 12, 25 and 30 minutes
397 treatment, respectively (Q_{UVC} 0.44, 0.56 and 0.67 kJ L⁻¹, respectively) where achieved,
398 while a lower degradation rate was observed for CBZ (49.5%, after 60 min and 1.33 kJ L⁻¹).
399 ¹).

400 As THMs formation is of concern, their concentration (mainly chloroform) remained
401 below the limit set by Italian regulation for wastewater reuse for both treatments (FC and
402 UV-C/FC processes) even after 24h and 48h of post-treatment incubation. Most important,
403 while in FC treated WW (and DWW) chloroform concentration increased after treatment,
404 UV-C/FC process resulted in a significant decrease (residual concentrations below the
405 LOQ) even after 24h and 48h compared to FC. These results are encouraging in terms of
406 possible use of UV-C/FC process as advanced treatment of urban wastewater even for
407 possible effluent reuse.

408

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416

417 **5. References**

418 Antonelli, M., Turolla, A., Mezzanotte, V., Nurizzo, C., 2013. Peracetic acid for secondary
419 effluent disinfection: A comprehensive performance assessment. *Water Sci. Technol.*
420 <https://doi.org/10.2166/wst.2013.542>

421 Bellar, T.A., Lichtenberg, J.J., Kroner, R.C., 1974. OCCURRENCE OF
422 ORGANOHALIDES IN CHLORINATED DRINKING WATERS. *J. / Am. Water*
423 *Work. Assoc.*

424 Brooks, B.W., Huggett, D.B., Boxall, A.B.A., 2009. Pharmaceuticals and Personal Care
425 Products: Research Needs for the Next Decade. *Environ. Toxicol. Chem.* 28, 2469.
426 <https://doi.org/10.1897/09-325.1>

427 Cacace, D., Fatta-Kassinos, D., Manaia, C.M., Cytryn, E., Kreuzinger, N., Rizzo, L.,
428 Karaolia, P., Schwartz, T., Alexander, J., Merlin, C., Garelick, H., Schmitt, H., de
429 Vries, D., Schwermer, C.U., Meric, S., Ozkal, C.B., Pons, M.-N., Kneis, D.,
430 Berendonk, T.U., 2019. Antibiotic resistance genes in treated wastewater and in the
431 receiving water bodies: A pan-European survey of urban settings. *Water Res.*
432 <https://doi.org/10.1016/j.watres.2019.06.039>

433 Cerreta, G., Roccamante, M.A., Oller, I., Malato, S., Rizzo, L., 2019. Contaminants of
434 emerging concern removal from real wastewater by UV/free chlorine process: A
435 comparison with solar/free chlorine and UV/H₂O₂ at pilot scale. *Chemosphere*,
436 124354, <https://doi.org/10.1016/j.chemosphere.2019.124354>

437 Chen, S., Liu, T., Luo, S., Yin, K., Wei, Y., Liu, C., He, Q., Deng, Y., 2018. Kinetics,
438 pathways and toxicity evaluation of neonicotinoid insecticides degradation via

439 UV/chlorine process. Chem. Eng. J. 346, 298–306.
440 <https://doi.org/10.1016/j.cej.2018.03.168>

441 Christou, A., Papadavid, G., Dalias, P., Fotopoulos, V., Michael, C., Bayona, J.M., Piña,
442 B., Fatta-Kassinos, D., 2019. Ranking of crop plants according to their potential to
443 uptake and accumulate contaminants of emerging concern. Environ. Res.
444 <https://doi.org/10.1016/j.envres.2018.12.048>

445 De Luca, A., Dantas, R.F., Esplugas, S., 2014. Assessment of iron chelates efficiency
446 for photo-Fenton at neutral pH. Water Res.
447 <https://doi.org/10.1016/j.watres.2014.05.033>

448 Di Cesare, A., Eckert, E.M., D'Urso, S., Bertoni, R., Gillan, D.C., Wattiez, R., Corno, G.,
449 2016. Co-occurrence of integrase 1, antibiotic and heavy metal resistance genes in
450 municipal wastewater treatment plants. Water Res.
451 <https://doi.org/10.1016/j.watres.2016.02.049>

452 El-Dib, M.A., Ali, R.K., 1995. THMs formation during chlorination of raw Nile River
453 water. Water Res. [https://doi.org/10.1016/0043-1354\(94\)00157-3](https://doi.org/10.1016/0043-1354(94)00157-3)

454 EPA, 2018. 2018 Edition of the Drinking Water Standards and Health Advisories, United
455 States Environmental Protection Agency. [https://doi.org/EPA 822-S-12-001](https://doi.org/EPA%20822-S-12-001)

456 Fang, J., Fu, Y., Shang, C., 2014. The roles of reactive species in micropollutant
457 degradation in the UV/free chlorine system. Environ. Sci. Technol. 48, 1859–1868.
458 <https://doi.org/10.1021/es4036094>

459 Feng, Y., Smith, D.W., Bolton, J.R., 2007. Photolysis of aqueous free chlorine species
460 (HOCl and OCl⁻) with 254 nm ultraviolet light. J. Environ. Eng. Sci.
461 <https://doi.org/10.1139/s06-052>

462 Ferro, G., Polo-López, M.I., Martínez-Piernas, A.B., Fernández-Ibáñez, P., Agüera, A.,
463 Rizzo, L., 2015. Cross-Contamination of Residual Emerging Contaminants and
464 Antibiotic Resistant Bacteria in Lettuce Crops and Soil Irrigated with Wastewater
465 Treated by Sunlight/H₂O₂. Environ. Sci. Technol.
466 <https://doi.org/10.1021/acs.est.5b02613>

467 Fiorentino, A., Cucciniello, R., Di Cesare, A., Fontaneto, D., Prete, P., Rizzo, L., Corno,
468 G., Proto, A., 2018. Disinfection of urban wastewater by a new photo-Fenton like
469 process using Cu-iminodisuccinic acid complex as catalyst at neutral pH. Water Res.
470 <https://doi.org/10.1016/j.watres.2018.08.024>

471 Fiorentino, A., Esteban, B., Garrido-Cardenas, J.A., Kowalska, K., Rizzo, L., Agüera, A.,
472 Pérez, J.A.S., 2019. Effect of solar photo-Fenton process in raceway pond reactors at
473 neutral pH on antibiotic resistance determinants in secondary treated urban
474 wastewater. J. Hazard. Mater. <https://doi.org/10.1016/j.jhazmat.2019.06.014>

475 Formisano, F., Fiorentino, A., Rizzo, L., Carotenuto, M., Pucci, L., Giugni, M., Lofrano,
476 G., 2016. Inactivation of Escherichia coli and Enterococci in urban wastewater by
477 sunlight/PAA and sunlight/H₂O₂ processes. Process Saf. Environ. Prot.
478 <https://doi.org/10.1016/j.psep.2016.09.003>

479 Gallard, H., Von Gunten, U., 2002. Chlorination of natural organic matter: Kinetics of
480 chlorination and of THM formation. Water Res. [https://doi.org/10.1016/S0043-](https://doi.org/10.1016/S0043-1354(01)00187-7)
481 [1354\(01\)00187-7](https://doi.org/10.1016/S0043-1354(01)00187-7)

482 Gao, Z., Lin, Y., Xu, B., Xia, Y., Hu, C., Zhang, T., Cao, T., Chu, W., Gao, N., 2019.
483 Effect of UV wavelength on humic acid degradation and disinfection by-product
484 formation during the UV / chlorine process. Water Res. 154, 199–209.
485 <https://doi.org/10.1016/j.watres.2019.02.004>

- 486 Guo, K., Wu, Z., Yan, S., Yao, B., Song, W., Hua, Z., Zhang, X., Kong, X., Li, X., Fang,
487 J., 2018. Comparison of the UV/chlorine and UV/H₂O₂ processes in the degradation
488 of PPCPs in simulated drinking water and wastewater: Kinetics, radical mechanism
489 and energy requirements. *Water Res.* 147, 184–194.
490 <https://doi.org/10.1016/j.watres.2018.08.048>
- 491 Hodgeson, J.W., Cohen, A.L., Munch, D., Hautman, D., 1995. Method 551.1:
492 Determination of chlorination disinfection byproducts, chlorinated solvents , and
493 halogenated pesticides/ herbicides in drinking water by liquid-liquid extraction and
494 gas chromatography with electron-capture detection. U.S. Environ. Prot. Agency,
495 Cincinnati, Ohio 1–61.
- 496 Hua, G., Reckhow, D.A., 2007. Comparison of disinfection byproduct formation from
497 chlorine and alternative disinfectants. *Water Res.*
498 <https://doi.org/10.1016/j.watres.2007.01.032>
- 499 Hua, Z., Guo, K., Kong, X., Lin, S., Wu, Z., Wang, L., Huang, H., Fang, J., 2019. PPCP
500 degradation and DBP formation in the solar/free chlorine system: Effects of pH and
501 dissolved oxygen. *Water Res.* 150, 77–85.
502 <https://doi.org/10.1016/j.watres.2018.11.041>
- 503 Jin, J., El-Din, M.G., Bolton, J.R., 2011. Assessment of the UV/Chlorine process as an
504 advanced oxidation process. *Water Res.* 45, 1890–1896.
505 <https://doi.org/10.1016/j.watres.2010.12.008>
- 506 Klavarioti, M., Mantzavinos, D., Kassinos, D., 2009. Removal of residual pharmaceuticals
507 from aqueous systems by advanced oxidation processes. *Environ. Int.* 35, 402–417.
508 <https://doi.org/10.1016/j.envint.2008.07.009>
- 509 Kohl, A., Golan, N., Cinnamon, Y., Genin, O., Chefetz, B., Sela-Donenfeld, D., 2019. A

510 proof of concept study demonstrating that environmental levels of carbamazepine
511 impair early stages of chick embryonic development. *Environ. Int.*
512 <https://doi.org/10.1016/j.envint.2019.03.064>

513 Krzeminski, P., Tomei, M.C., Karaolia, P., Langenhoff, A., Almeida, C.M.R., Felis, E.,
514 Gritten, F., Andersen, H.R., Fernandes, T., Manaia, C.M., Rizzo, L., Fatta-Kassinos,
515 D., 2019. Performance of secondary wastewater treatment methods for the removal of
516 contaminants of emerging concern implicated in crop uptake and antibiotic resistance
517 spread: A review. *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2018.08.130>

518 Li, G.-Q., Huo, Z.-Y., Wu, Q.-Y., Lu, Y., Hu, H.-Y., 2018. Synergistic effect of combined
519 UV-LED and chlorine treatment on *Bacillus subtilis* spore inactivation. *Sci. Total*
520 *Environ.* 639, 1233-1240. <https://doi.org/10.1016/j.scitotenv.2018.05.240>.

521 Liu, L., Xing, X., Hu, C., Wang, H., Lyu, L., 2019. Effect of sequential UV/free chlorine
522 disinfection on opportunistic pathogens and microbial community structure in
523 simulated drinking water distribution systems. *Chemosphere* 219, 971-980.
524 <https://doi.org/10.1016/j.chemosphere.2018.12.067>

525 Malchi, T., Maor, Y., Tadmor, G., Shenker, M., Chefetz, B., 2014. Irrigation of root
526 vegetables with treated wastewater: Evaluating uptake of pharmaceuticals and the
527 associated human health risks. *Environ. Sci. Technol.*
528 <https://doi.org/10.1021/es5017894>

529 Matamoros, V., Mujeriego, R., Bayona, J.M., 2007. Trihalomethane occurrence in
530 chlorinated reclaimed water at full-scale wastewater treatment plants in NE Spain.
531 *Water Res.* <https://doi.org/10.1016/j.watres.2007.04.021>

532 Michael, I., Rizzo, L., McArdell, C.S., Manaia, C.M., Merlin, C., Schwartz, T., Dagot, C.,
533 Fatta-Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for the

534 release of antibiotics in the environment: A review. *Water Res.* 47, 956–957.
535 <https://doi.org/10.1016/j.watres.2012.11.027>

536 Miralles-Cuevas, S., Darowna, D., Wanag, A., Mozia, S., Malato, S., Oller, I., 2017.
537 Comparison of UV/H₂O₂, UV/S₂O₈²⁻, solar/Fe(II)/H₂O₂ and solar/Fe(II)/S₂
538 O₈²⁻ at pilot plant scale for the elimination of micro-contaminants in natural water:
539 An economic assessment. *Chem. Eng. J.* <https://doi.org/10.1016/j.cej.2016.06.121>

540 Nikolaou, A., Golfinopoulos, S., Rizzo, L., Lofrano, G., Lekkas, T., Belgiomo, V., 2005.
541 Optimization of analytical methods for the determination of DBPs: Application to
542 drinking waters from Greece and Italy. *Desalination* 176, 25–36.
543 <https://doi.org/10.1016/j.desal.2004.10.028>

544 Nikolaou, A.D., Lekkas, T.D., Golfinopoulos, S.K., Kostopoulou, M.N., 2002. Application
545 of different analytical methods for determination of volatile chlorination by-products
546 in drinking water. *Talanta* 56, 717–726. [https://doi.org/10.1016/S0039-](https://doi.org/10.1016/S0039-9140(01)00613-0)
547 [9140\(01\)00613-0](https://doi.org/10.1016/S0039-9140(01)00613-0)

548 Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2014. A review on emerging contaminants in
549 wastewaters and the environment: Current knowledge, understudied areas and
550 recommendations for future monitoring. *Water Res.* 72, 3–27.
551 <https://doi.org/10.1016/j.watres.2014.08.053>

552 Rattanakul S., Oguma K., 2017. Analysis of Hydroxyl Radicals and Inactivation
553 Mechanisms of Bacteriophage MS2 in Response to a Simultaneous Application of
554 UV and Chlorine. *Environ. Sci. Technol.* 51, 455-462.
555 <https://doi.org/10.1021/acs.est.6b03394>

556 Reckhow, D.A., Singer, P.C., Malcolm, R.L., 1990. Chlorination of Humic Materials:
557 Byproduct Formation and Chemical Interpretations. *Environ. Sci. Technol.*

558 <https://doi.org/10.1021/es00081a005>

559 Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007.
560 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection
561 by-products in drinking water: A review and roadmap for research. *Mutat. Res. - Rev.*
562 *Mutat. Res.* <https://doi.org/10.1016/j.mrrev.2007.09.001>

563 Rizzo, L., Agovino, T., Nahim-Granados, S., Castro-Alfárez, M., Fernández-Ibáñez, P.,
564 Polo-López, M.I., 2019a. Tertiary treatment of urban wastewater by solar and UV-C
565 driven advanced oxidation with peracetic acid: Effect on contaminants of emerging
566 concern and antibiotic resistance. *Water Res.* 149, 272–281.
567 <https://doi.org/10.1016/j.watres.2018.11.031>

568 Rizzo, L., Krätke, R., Linders, J., Scott, M., Vighi, M., de Voogt, P., 2018. Proposed EU
569 minimum quality requirements for water reuse in agricultural irrigation and aquifer
570 recharge: SCHEER scientific advice. *Curr. Opin. Environ. Sci. Heal.*

571 Rizzo, L., Malato, S., Antakyali, D., Beretsou, V.G., Đolić, M.B., Gernjak, W., Heath, E.,
572 Ivancev-Tumbas, I., Karaolia, P., Lado Ribeiro, A.R., Mascolo, G., McArdell, C.S.,
573 Schaar, H., Silva, A.M.T., Fatta-Kassinos, D., 2019b. Consolidated vs new advanced
574 treatment methods for the removal of contaminants of emerging concern from urban
575 wastewater. *Sci. Total Environ.* 655, 986–1008.
576 <https://doi.org/10.1016/j.scitotenv.2018.11.265>

577 Rizzo, L., Manaia, C., Merlin, C., Schwartz, T., Dagot, C., Ploy, M.C., Michael, I., Fatta-
578 Kassinos, D., 2013. Urban wastewater treatment plants as hotspots for antibiotic
579 resistant bacteria and genes spread into the environment: A review. *Sci. Total*
580 *Environ.* 447, 345–360. <https://doi.org/10.1016/j.scitotenv.2013.01.032>

581 Rook, J.J., 1974. Formation of haloforms during chlorination of natural waters. *Water*

582 Treat. Exam. 23, 234–243.

583 Schröder, P., Helmreich, B., Škrbić, B., Carballa, M., Papa, M., Pastore, C., Emre, Z.,
584 Oehmen, A., Langenhoff, A., Molinos, M., Dvarioniene, J., Huber, C., Tsagarakis,
585 K.P., Martinez-Lopez, E., Pagano, S.M., Vogelsang, C., Mascolo, G., 2016. Status of
586 hormones and painkillers in wastewater effluents across several European states—
587 considerations for the EU watch list concerning estradiols and diclofenac. Environ.
588 Sci. Pollut. Res. <https://doi.org/10.1007/s11356-016-6503-x>

589 Sichel, C., Garcia, C., Andre, K., 2011. Feasibility studies: UV/chlorine advanced
590 oxidation treatment for the removal of emerging contaminants. Water Res. 45, 6371–
591 6380. <https://doi.org/10.1016/j.watres.2011.09.025>

592 Snoeyink, V.L., Jenkins, D., 1980. Water chemistry.

593 Sun, Y.X., Wu, Q.Y., Hu, H.Y., Tian, J., 2009. Effects of operating conditions on THMs
594 and HAAs formation during wastewater chlorination. J. Hazard. Mater.
595 <https://doi.org/10.1016/j.jhazmat.2009.03.013>

596 Wang, C., Moore, N., Bircher, K., Andrews, S., Hofmann, R., 2019. Full-scale comparison
597 of UV/H₂O₂ and UV/Cl₂ advanced oxidation: The degradation of micropollutant
598 surrogates and the formation of disinfection byproducts. Water Res.
599 <https://doi.org/10.1016/j.watres.2019.06.033>

600 Wang, D., Bolton, J.R., Andrews, S.A., Hofmann, R., 2015. UV/chlorine control of
601 drinking water taste and odour at pilot and full-scale. Chemosphere.
602 <https://doi.org/10.1016/j.chemosphere.2015.05.049>

603 Wang, D., Bolton, J.R., Hofmann, R., 2012. Medium pressure UV combined with chlorine
604 advanced oxidation for trichloroethylene destruction in a model water. Water Res.

605 <https://doi.org/10.1016/j.watres.2012.06.007>

606 Wang, W.L., Wu, Q.Y., Huang, N., Wang, T., Hu, H.Y., 2016. Synergistic effect between
607 UV and chlorine (UV/chlorine) on the degradation of carbamazepine: Influence
608 factors and radical species. *Water Res.* 98, 190–198.
609 <https://doi.org/10.1016/j.watres.2016.04.015>

610 Wang, X., Hu, X., Wang, H., Hu, C., 2012. Synergistic effect of the sequential use of UV
611 irradiation and chlorine to disinfect reclaimed water. *Water Res.*
612 <https://doi.org/10.1016/j.watres.2011.12.027>

613 Watts, M.J., Linden, K.G., 2007. Chlorine photolysis and subsequent OH radical
614 production during UV treatment of chlorinated water. *Water Res.*
615 <https://doi.org/10.1016/j.watres.2007.03.032>

616 Wu, Z., Fang, J., Xiang, Y., Shang, C., Li, X., Meng, F., Yang, X., 2016. Roles of reactive
617 chlorine species in trimethoprim degradation in the UV/chlorine process: Kinetics and
618 transformation pathways. *Water Res.* 104, 272–282.
619 <https://doi.org/10.1016/j.watres.2016.08.011>

620 Yin, K., Deng, Y., Liu, C., He, Q., Wei, Y., Chen, S., Liu, T., Luo, S., 2018. Kinetics,
621 pathways and toxicity evaluation of neonicotinoid insecticides degradation via
622 UV/chlorine process. *Chem. Eng. J.* <https://doi.org/10.1016/j.cej.2018.03.168>

623 Yin, R., Ling, L., Shang, C., 2018. Wavelength-dependent chlorine photolysis and
624 subsequent radical production using UV-LEDs as light sources. *Water Res.*
625 <https://doi.org/10.1016/j.watres.2018.06.018>

626 Zhou, S., Xia, Y., Li, T., Yao, T., Shi, Z., Zhu, S., Gao, N., 2016. Degradation of
627 carbamazepine by UV/chlorine advanced oxidation process and formation of

628 disinfection by-products. *Environ. Sci. Pollut. Res.* 23, 16448–16455.

629 <https://doi.org/10.1007/s11356-016-6823-x>

630

Figure1

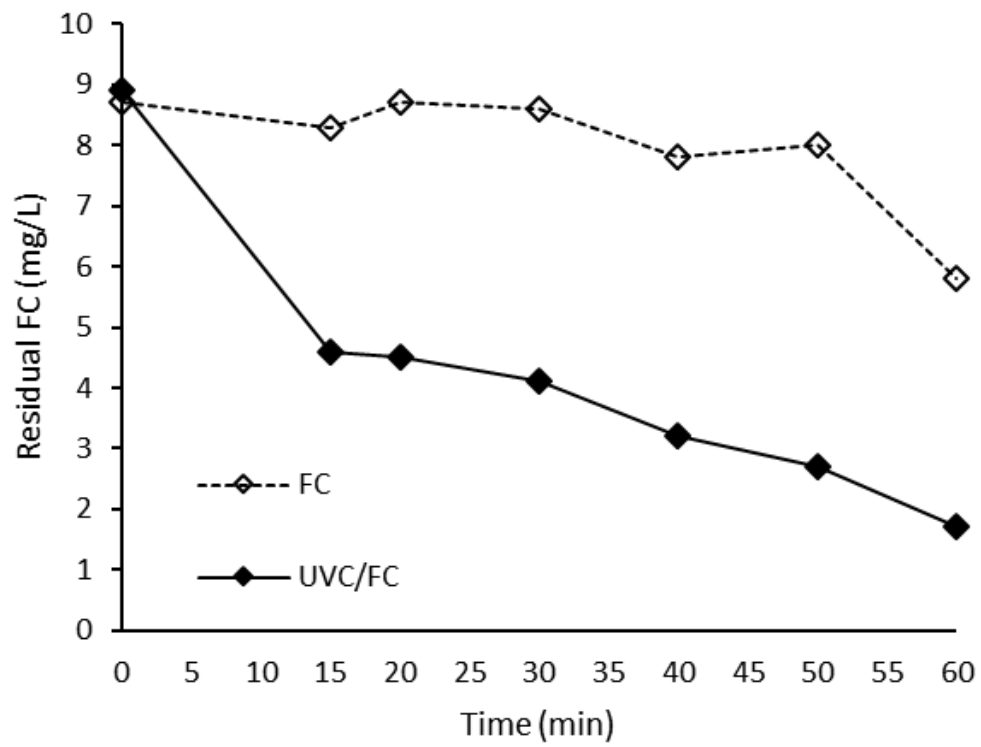


Figure 1: FC consumption in WW during FC and UV-C/FC process with an initial FC dose of 10 mgL^{-1} .

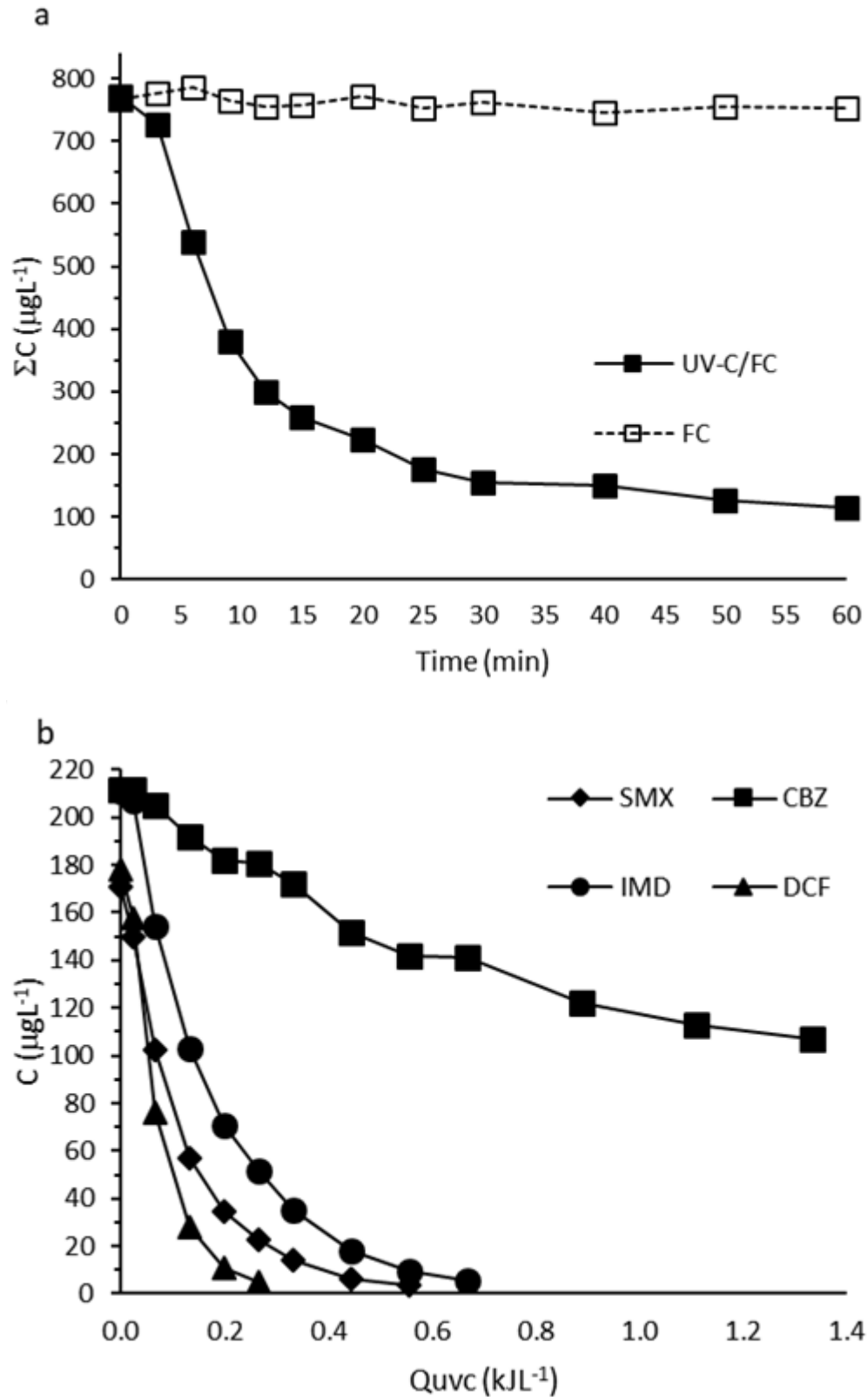


Figure 2: Effect of UV-C and UV-C/FC (10 mgL⁻¹ of FC) processes on the removal of total CECs (a) and effect of UV-C/FC process on the removal of each CEC (b).

Figure3

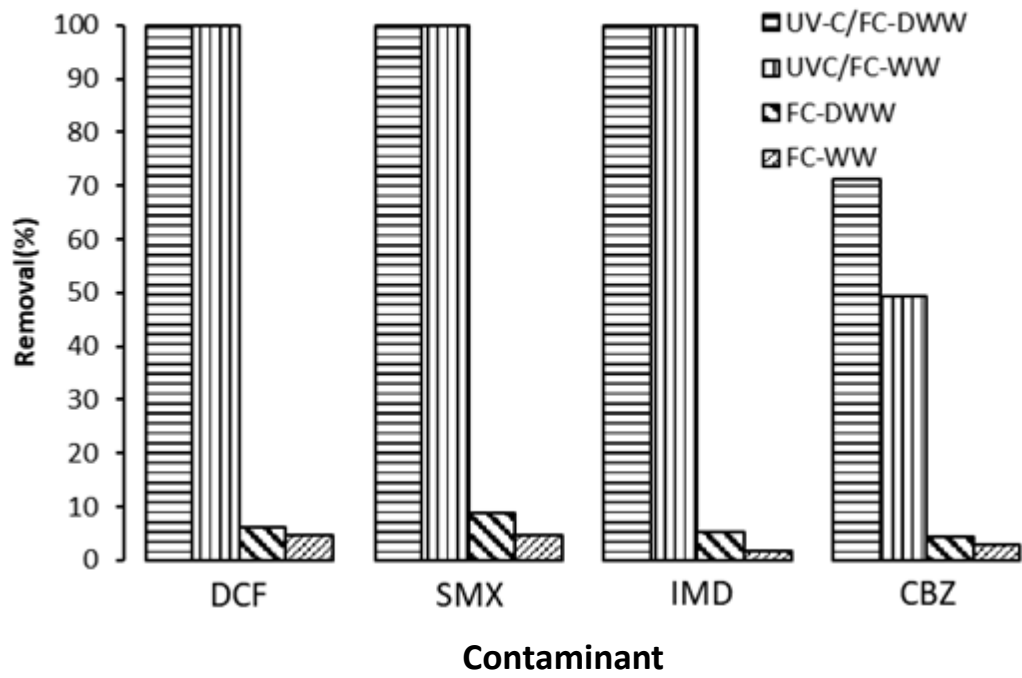


Figure 3: Effect of water matrix (DWW Vs. WW) on CECs degradation after 60 minutes treatment by FC and UV-C/FC processes with 10 mgL^{-1} of FC.

Figure4

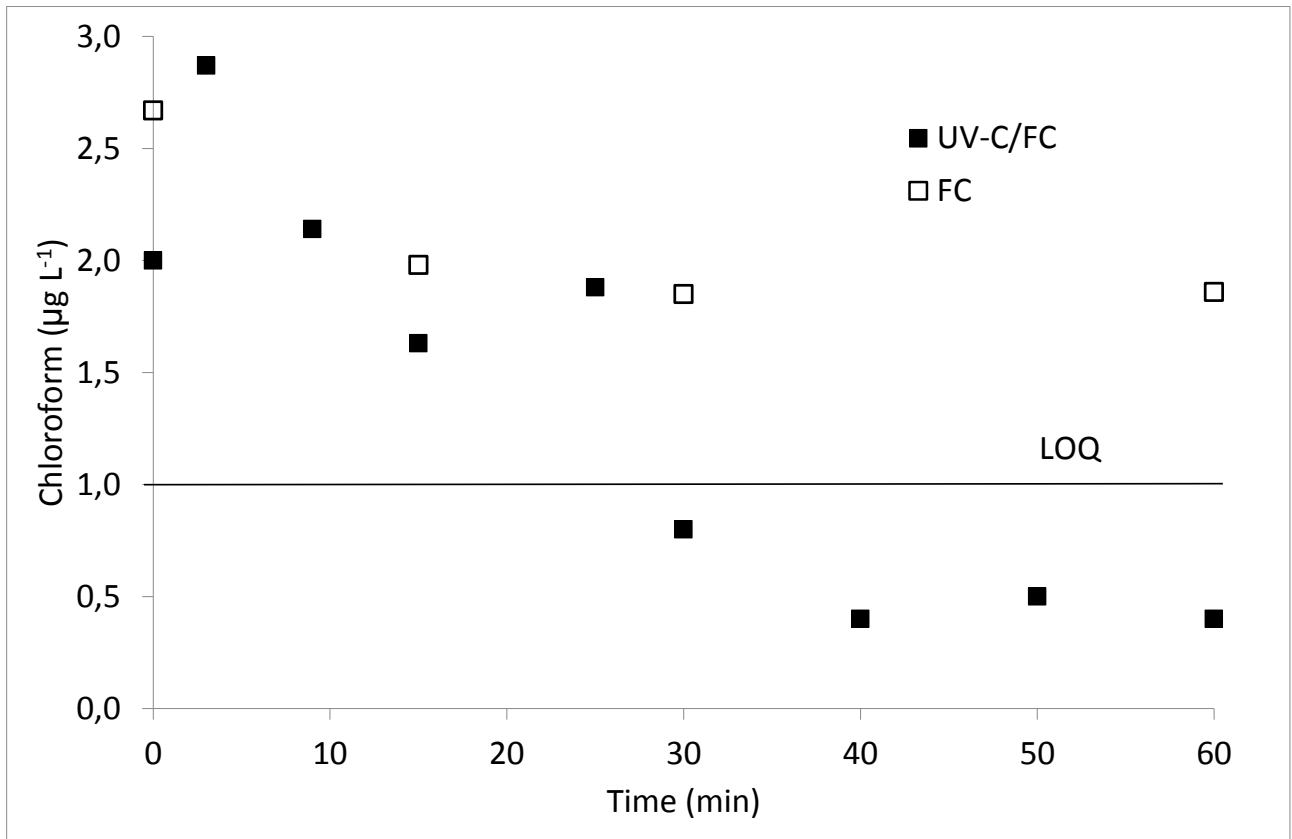


Figure 4: Effect of UV-C radiation on chloroform in WW during UV-C/FC process (10 mgL⁻¹ of FC).

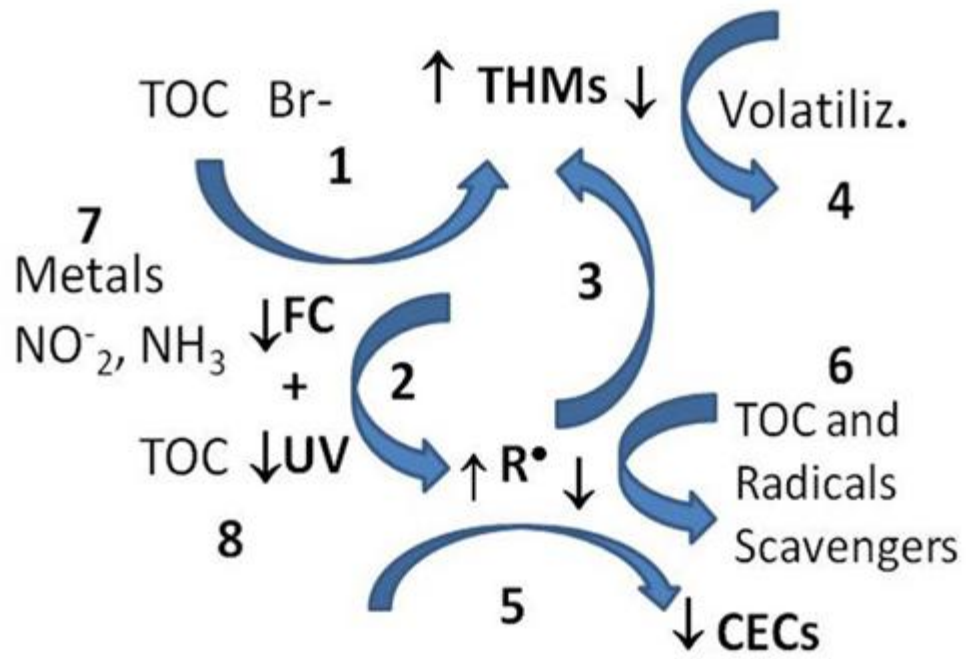


Figure 5: possible reactions can take place in real urban wastewater treated by UV-C/FC process.

Figure6

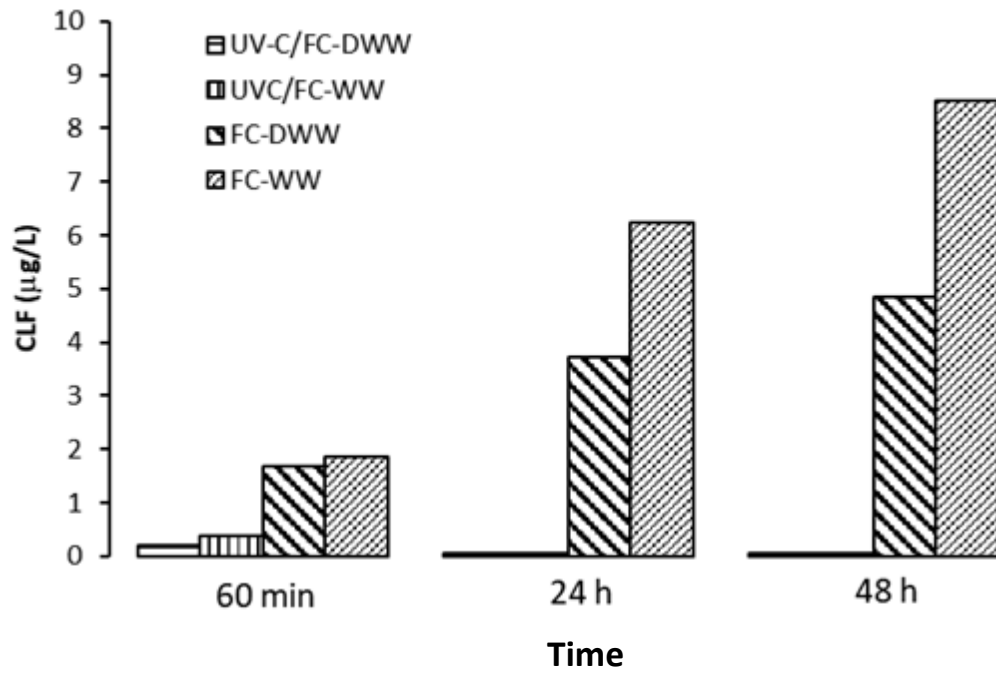


Figure 6: chloroform formation after FC and UV-C/FC treatment, respectively: comparison between the end of the treatment (60 min) and 24h and 48h post-treatment incubation.

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