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1 # Supplementary Information

2

3 **COMBI, continuous ozonation merged with biofiltration to study oxidative and**
4 **microbial transformation of trace organic contaminants**

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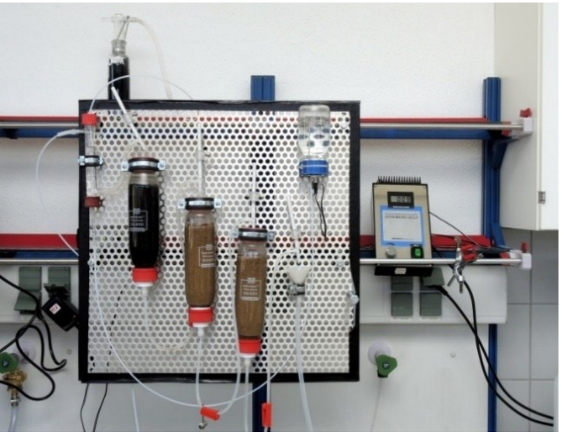
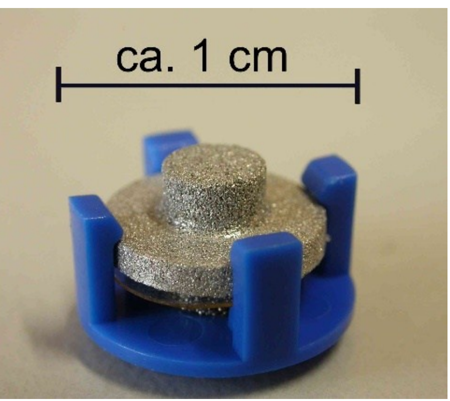
32 ## S1 COMBI system





33 **Figure S1**: Top: Photographs of the COMBI System 1. Bottom: Photographs of the
34 ozone micro cell holder with one electrolysis system (left-hand side), and a close up
35 of the electrolysis unit (right-hand side).

36

37 **Table S1**: Approximate cost of the parts needed to build a COMBI system (2017).

	Cost / €
Pump (e.g. KNF IP54 24V FMM 20 KPDC-P, including house built controller)	215
Ozone micro-cell (including control box and power supply)	265
Glassware (glass tubing with added standard threads, standard thread bottles for System 2 & standard thread bottles, columns for System 1)	90
Tubing	20
Fittings	40
Storage tank	30
Total	**660**

38

39 # S2 Materials and Methods

40

41 ## S2.1 Trace organic contaminants

42 Carbamazepine, diclofenac sodium salt and fluoxetine hydrochloride in solid form
43 (purity ≥98%) were purchased from Sigma-Aldrich. Stock solutions used to spike the
44 synthetic wastewater were regularly prepared in Milli-Q water. Diclofenac sodium
45 analytical standard was purchased from Sigma-Aldrich. Fluoxetine hydrochloride
46 solution (1 mg/mL in methanol) used as a standard, fluoxetine-d_5 solution (1 mg/mL
47 in methanol) used as an internal standard, carbamazepine solution (1 mg/mL in
48 methanol) used as a standard, and carbamazepine-$^{13}C_6$ solution (100 µg/mL in
49 methanol) used as an internal standard, were purchased from Sigma Aldrich.

50 Acesulfame potassium and *N,N*-dimethylsulfamide (DMS) were provided by LGC
51 (formerly Dr. Ehrenstorfer, Wesel, Germany). Acesulfame-d_4 was purchased from
52 Campro Scientific (Berlin, Germany) and DMS-d_6 from Bayer (Leverkusen,
53 Germany). *N*-Nitrosodimethylamine (NDMA) was provided by Supelco (now Sigma-
54 Aldrich, St.Louis, USA) and NDMA-d_6 by CDN Isotopes (Pointe-Claire, Canada).

55 The reference standard of OP168 was produced in the TZW lab as follows: ACE (5 g,
56 25 mmol) was dissolved in 1000 mL distilled water and treated with ozone gas for 3 h.
57 The resulting reaction solution was concentrated at a rotary evaporator. Hereby water
58 and a part of semi-volatile acids (acetic acid and formic acid) can be removed from the
59 mixture. The highly concentrated reaction mixture was neutralized with potassium
60 hydroxide solution to pH 7. Crystal growth of the potassium salt of OP168 took place
61 within a few days. For further purification a re-crystallization from water was
62 performed. The confirmation of the anionic species OP168 (mz = 167.9608) was done
63 by ion exchange chromatography coupled to an accurate time of flight mass
64 spectrometer after electrospray ionization (IC-ESI-TOF). The salt-composition was
65 confirmed by elemental analyses using inductively coupled plasma coupled to mass
66 spectrometry *(*ICP-MS): sulfur (calculated 13.1%, found 14.0%); potassium (calculated
67 31.9%, found 29.9%).

68 Sodium trifluoroacetate, was purchased from Sigma Aldrich (Steinheim, Germany)
69 and the respective isotopically labeled internal standard sodium trifluoroacetate-$^{13}C_2$
70 was obtained from TRC (Toronto, Canada).

71 **Table S2:** Trace organic contaminants and ozonation products investigated in this study.

Parent compounds			Ozonation products		
Compound (Abbreviation)	**[CAS] Molecular formula MW / (g/mol)**	**Structure**	**Compound (Abbreviation)**	**[CAS] Molecular formula MW / (g/mol)**	**Structure**
N,N-Dimethylsulfamide (DMS)	[3984-14-3] $C_2H_8N_2O_2S$ 124.16		*N*-nitrosodimethylamine (NDMA)	[62-75-9] $C_2H_6N_2O$ 74.08	
Acesulfame potassium (ACE)	[55589-62-3] $C_4H_4KNO_4S$ 201.24		ACE OP168	[1403502-37-3] $C_2H_2NO_6S$ 167.96	
Carbamazepine (CBZ)	[298-46-4] $C_{15}H_{12}N_2O$ 236.27		1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM)	[1401112-00-2] $C_{15}H_{10}N_2O_2$ 250.25	
			1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-one (BaQD)	[n/a] $C_{15}H_{10}N_2O_4$ 282.25	
Diclofenac sodium (DF)	[15307-79-6] $C_{14}H_{10}NO_2Cl_2Na$ 318.13		Diclofenac-2,5-iminoquinone (DF-IQ)	[1254576-93-6] $C_{14}H_9NO_3Cl_2$ 310.13	
			5-Hydroxydiclofenac (OH-DF)	[69002-84-2] $C_{14}H_{11}NO_3Cl_2$ 312.15	
Fluoxetine (FX)	[54910-89-3] $C_{17}H_{18}F_3NO$ 309.33		Trifluoroacetic acid (TFA)	[76-05-1] $C_2HF_3O_2$ 114.02	

S2.2 Analysis

Ultra High Performance Liquid Chromatography-Mass Spectrometry (UHPLC-MS) for CBZ, DF and FLX was performed with a Thermo Scientific Dionex UltiMate 3000 system coupled to a Bruker Daltonics maXis HD electrospray ionization quadrupole time-of-flight (ESI-QTOF) mass spectrometer operated in positive-ion mode, equipped with an Acquity UPLC BEH C18-Column (1.7 µm, 130 Å, 2.1 mm × 50 mm). The mobile phase consisted of water with 0.1% formic acid (A), and methanol with 0.1% formic acid (B). The flow rate was 0.4 mL/min, the injection volume was 20 µL and the column compartment temperature was set to 40 °C. Gradient elution was carried out with 1% mobile phase B until 2 min, followed by a linear gradient to 100% B at 5 min, keeping 100% B up until 8 min, thereafter returned to 1% B until 12 min total run time. For MS, the capillary voltage was set to 4500 V, nebulizing gas at 4 bar, drying gas at 12 L/min at 220 °C. The TOF scan range was from 75 to 1000 mass-to-charge ratio (m/z). For effective transmission of ions, the ion energy was set to 6.0 eV with the collision energy for TOF MS acquisition at 7.0 eV. The MS instrument was calibrated using a range of sodium formate clusters introduced by switching valve injection during the first minute of each chromatographic run. The compounds were detected as $[M + H]^+$ ions. Data processing was performed using the Data Analysis software version 4.3 (Bruker Daltonik GmbH, Bremen, Germany).

Samples were spiked with internal standard (final concentration of 100 ng/mL) and adjusted with methanol to 80/20 (v/v) water/methanol composition, as soon as possible after their collection but no longer than 40 min. Fluoxetine-d_5 (1 mg/mL in methanol) was used as an internal standard for the analysis of FLX, and CBZ-$^{13}C_6$ (100 µg/mL in methanol) was used as an internal standard for the analysis of carbamazepine and diclofenac. The spiked samples were filtered with PTFE filters (0.2 µm pore size) and frozen at −20 °C until analysis. Quantitative analysis was performed using the Quant Analysis software version 4.3 (Bruker Daltonik GmbH, Bremen, Germany).

Transformation products of CBZ and DF were identified based on literature data, mass accuracy (less than 10 ppm mass error in all cases), and consistent retention time. MS/MS analysis in MRM (multiple reaction monitoring) mode was performed to further support the identification of CBZ and DF transformation products. The collision energy used was 15 eV to 30 eV. Observed fragmentation patterns are provided in SI, Section S3.3. Semi-quantitative analysis of the transformation products

106 was performed using the same internal standard that was used for the parent
107 compounds.

108 Direct injection was used for the analysis of TFA, ACE and its ozonation product
109 OP168. DMS and NDMA samples were pre-concentrated with solid phase extraction
110 (SPE) prior the analysis. For DMS a sample volume of 50 mL was adjusted to pH 5
111 for SPE. After extraction cartridges were dried under nitrogen and DMS was eluted
112 with a mixture of dichloromethane and methanol (4:1 v/v). The eluate was blown down
113 using nitrogen and reconstituted in 1 mL of a water/methanol mixture (8:2 v/v). For
114 NDMA analysis, samples were pre-concentrated (Lee et al. 2007).

115 Trifluoroacetic acid (TFA) analysis was performed using ion exchange liquid
116 chromatography-electrospray tandem mass spectrometry (LC-ESI-MS/MS) according
117 to a recently developed method (Scheurer et al. 2017). Briefly, chromatographic
118 separation was achieved in an Agilent 1200 LC system (Waldbronn, Germany) with a
119 Dionex IonPac AS17-C column equipped with a Dionex IonPac AG17-C precolumn.
120 The eluents were ultra-pure water containing 50 mmol/L ammonium bicarbonate and
121 methanol.

122 ACE and OP168 were retained using a DIONEX Ion Pac AG 20 (2 mm x 50 mm).
123 Eluents were ultra-pure water + 10% acetonitrile (A) and ultra-pure water + 10%
124 acetonitrile with 50 mmol/L ammonium bicarbonate (B). The gradient program started
125 at 10% (B), was increased within 5 min to 100% and held for 5 min. Starting
126 conditions were reestablished with a ramp of 1 min. Equilibration time of the column
127 was 5 min and the flow rate was 0.25 mL/min. Detection was achieved with an API
128 5500 Q-Trap triplequadrupole mass spectrometer (Applied Biosystems/MDS Sciex
129 Instruments, Concord, ON, Canada) with an electrospray interface operated in
130 negative ionization.

131 DMS was measured with a similar instrumentation. A Luna C18 column
132 (250 mm x 2 mm, 5 µm) from Phenomenex (Aschaffenburg, Germany) was used for
133 retention. Eluents were ultra-pure water (A) and methanol (B) both with 2 mmol/L
134 ammonium acetate. The gradient program started with 10% (B), held for 7 min and
135 then increased within 1 min to 100%, then held for 7 min and decreased to the starting
136 conditions within 1 min. The flow rate was 0.2 mL/min.

137 The analysis of NDMA was performed after solid-phase extraction (SPE) with
138 NDMA-d_6 as internal standard (Lee et al. 2007). GC analysis for NDMA was carried

139 out with a series 6890 gas chromatograph connected to a MSD 5973 inert mass
140 spectrometer (both Agilent, Waldbronn, Germany) in positive chemical ionization. A
141 ZB-WAXplus column (30 m x 0.25 mm from Phenomenex) was used for the
142 separation of the analytes (flow rate 0.8 mL/min). The temperature program started at
143 40 °C and was held for 3 min, ramped 10 °C/min to 150 °C (held for 2 min), and
144 ramped 10 °C/min to 250 °C and held for another 2 min.

145 Quantitative analytical method performance data for ACE, CBZ, DF, DMS, FLX,
146 NDMA and ACE OP168 are provided in SI Table S3. No quantitative analytical
147 method performance data are available for BQM, BaQD, DF-IQ and OH-DF due to
148 the unavailability of analytical standards of these compounds.

149

150 **Table S3.** Analytical method performance data for trace organic contaminants analysed
151 with LC-MS.

Compound	Linearity		Intra-day performance[a]		LOD[b] / (ng/mL)
	Range / (ng/mL)	R^2	Precision / %	Accuracy / %	
Acesulfame (ACE)	0.01 – 6	0.999	1.4	96	0.01
Carbamazepine (CBZ)	5 – 500	0.995	3.9	83	5
Diclofenac (DF)	5 – 500	0.994	2.9	121	1
DMS	0.01 – 1	0.999	0.4	98	0.01
Fluoxetine (FLX)	0.5 – 500	0.996	1.1	82	0.5
N-nitrosodimethylamine (NDMA)	0.001 – 0.2	0.998	0.3	96	0.001
ACE OP168	5 – 200	0.999	*	*	6

152 [a]Precision is represented by the relative standard deviation (RSD) of triplicate
153 measurements. Accuracy is represented by the measured concentration over the known
154 added concentration of analyte.
155 [b]LOD: Limit of Detection
156 *Specifically developed non-routine IC-ESI-MS/MS method that has not been
157 statistically evaluated.
158

159 **S2.3 Determination of ozone dose and concentration**

160

161 System 1

162 Determination of the ozone concentration:

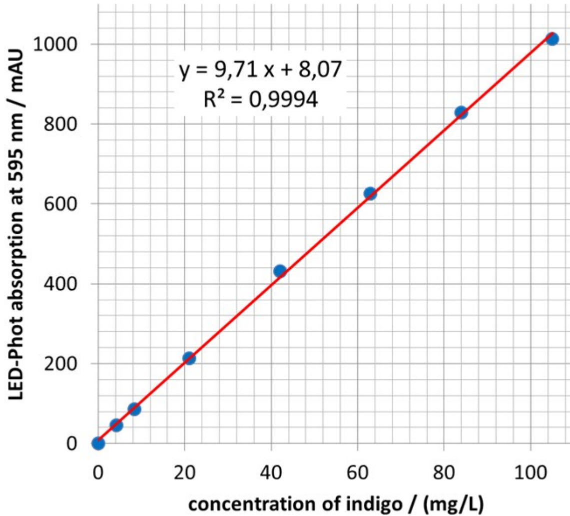
163 The ozone concentration at the outlet of the bubble column was determined according
164 to DIN 38408. The indigo reagent was placed in a volumetric flask and the ozone
165 solution from the bubble column was collected. This process allows the slowly
166 dripping of water to react immediately with the indigo dye.

167

168 Determination of the ozone dose:

169 The determination of the ozone dose by gas input into the water sample in the bubble
170 column was determined by the indigo method. A stock solution (772 mg/L
171 tripotassium indigotrisulfonate (MW 616.7 g/mol) dissolved in ultrapure water with
172 an addition of 1 mL concentrated phosphoric acid) was used in accordance with DIN
173 38408. The DIN standard states that the purity of the indigo dye is typically around
174 80%. Taking this information into account, the stock solution contains a dye
175 concentration of 1 mmol/L. This value is then also in accordance with the calculation
176 formula specified in DIN.

177 This stock solution was diluted with ultrapure water 1 + 9 and pumped through the
178 bubble column as a water sample (0.1 mmol/L, 77.2 mg/L). Bleaching the dye by the
179 reaction with ozone is a stoichiometric reaction. Since one part ozone reacts with one
180 part dye, 0.1 mmol/L ozone (= 4.8 mg/L) can be captured via this solution. The degree
181 of bleaching can be determined by the decrease in extinction by photometry. The
182 maximum extinction of the blue dye is 600 nm. Parallel to a laboratory
183 spectrophotometer, a self-built flow photometer based on light emitting diodes was
184 successfully used. The emission wavelength of 595 nm requires a slightly lower
185 extinction, but nevertheless a linear calibration results in the working range (Figure
186 S2).



187

188 **Figure S2:** Calibration and test of linearity of the home-built online LED-photometer

189 with indigo standards (optical path length = 10 mm).

190

191 A flow-through cuvette with a thickness of 3 mm was used for the test to determine

192 the current-dependent ozone input (Figure S3). The 1:10 diluted indigo stock solution

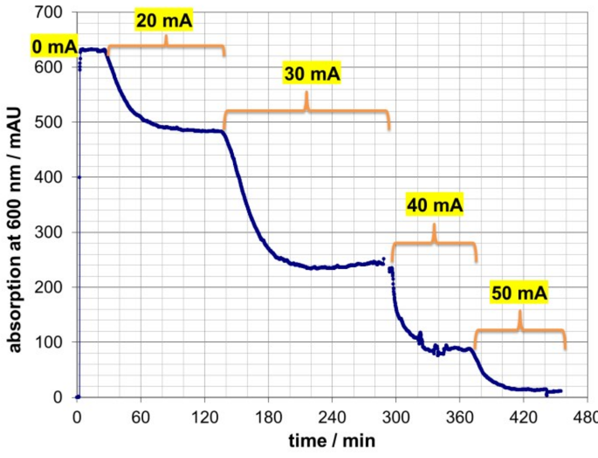
193 has an expected value of approx. 650 mAU (= no ozone entry into the bubble column).

194 After applying current to the ozone-micro-cell, ozone gas is introduced into the bubble

195 column and the dye is partially destroyed. It takes about 1 hour to reach a state of

196 equilibrium. The reasons for this are the complete replacement of the volume in the

197 bubble column and the warming up time of the ozone-micro-cell.



198

199 **Figure S3:** Determination of ozone input depending on the cell current determined

200 online via the reduction rates of the indigo dye (flow rate = 6 mL/min, optical path

201 length = 3 mm)

202 Using the flow rate and relative dye bleaching values, the temporal or volumetric input
203 of ozone can be calculated. In the first step, the relative decrease in extinction in
204 percent is calculated from the photometric measurements.

$$DB = \left(1 - \frac{A_{(Ix)}}{A_{(I0)}}\right) \cdot 100$$

205

206 DB = Dye-Bleaching in %

207 $A_{(IX)}$ = Absorption at I = x mA

208 $A_{(I0)}$ = Absorption at I = 0 mA

209

210 The time-dependent ozone input (OzIn) can then be calculated. This value also gives
211 an impression of the production rate of the ozone-micro-cell.

212 $$OzIn = 0.0048 \cdot FR \cdot DB$$

213 OzIn = Ozone-Intake in mg/min

214 0.0048 = Conversion factor in mg/mL

215 FR = Flow rate in mL/min

216 DB = Dye bleaching in %

217

218 The following equation can be used to determine the ozone dose (OzDo).

$$OzDo = \left(1 - \frac{A_{(Ix)}}{A_{(I0)}}\right) \cdot 4.8$$

219

220

221 OzDo = Ozone dose in mg/L

222 4.8 = Ozone in mg/L (corresponds to the max. turnover of 0.1 mmol/L)

223

224

225 Table S4 contains a comparison of the percentage of dye destruction determined by
226 LED flow photometer and laboratory photometer. The measured values show that both
227 devices provide equivalent data.

228

229

230

231

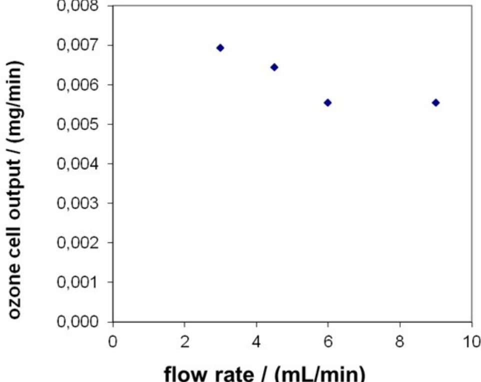
232 **Table S4:** Comparison of the reduction rates depending on the cell current measured
233 by two photometer methods (online and offline)

Cell current / mA	**Indigo reduction measured online by LED-Phot / %**	**Indigo reduction measured offline by EVO300 / %**
0	0.0	0.0
20	23.2	25.6
30	61.4	62.8
40	86.3	86.5
50	98.3	98.1

234

235 If the current in the ozone-micro-cell is kept constant, but the flow rate varies, the same
236 amount of ozone is added to different volumes of indigo solution per time unit. If the
237 flow rate is finally deducted from the measured values, the same production rate should
238 be found for all settings. In a flow range from 2 mL/min to 10 mL/min this is also
239 largely the case (Figure S4).

240

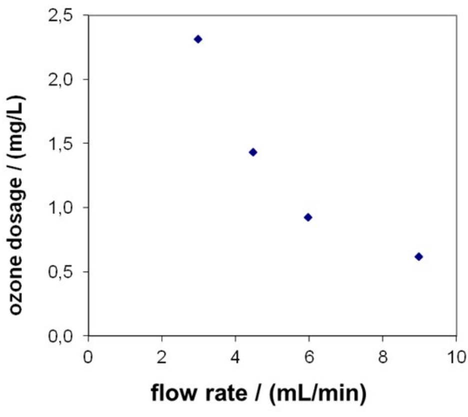


241

242 **Figure S4:** Absolute ozone intake into indigo solution at different flow rates (current
243 = 20 mA)

244

245 The same values can also be used to calculate the flux-dependent ozone dose (Figure
246 S5).



247

248 **Figure S5:** Ozone dosage into indigo solution at different flow rates (current = 20
249 mA).

250

251 System 2

252 The dissolved ozone concentration in the ozonation column was measured in deionized
253 water with the indigo method (Bader and Hoigné 1981). A standard indigo solution
254 was prepared by dissolving 1°mmol/L potassium indigotrisulfonate in deionized water
255 acidified with 20°mM phosphoric acid. In 10 mL volumetric flasks, 1 mL of phosphate
256 buffer of pH°=°2, 100°µL of the indigo standard solution and 1°mL to 5°mL of water
257 sampled directly from the ozonation column were added and the flask was filled with
258 deionized water to the mark. All the reagents were added in quick succession with
259 vigorous stirring. The samples were retrieved from the ozonation column after an
260 equilibration time of approximately 1 hour for each value of the electrical current. The
261 absorption was measured at 600 nm with an Agilent UV/VIS Cary 100
262 spectrophotometer.

263

264

265

266 ## S2.4 Synthetic wastewater

267

268 **Table S5:** Properties of the synthetic wastewater, prepared with tap water or DI

269 water.

	Concentration / (mg/L)
peptone	16
meat extract	11
urea	3
anhydrous dipotassium hydrogen phosphate (K_2HPO_4)	2.8
sodium chloride (NaCl)	0.7
calcium chloride dihydrate ($CaCl_2.2H_2O$)	0.4
magnesium sulphate heptahydrate ($Mg_2SO_4.7H_2O$)	0.2
TOC (freshly prepared)[a,b]	13 ± 1[d]
TOC (after 1 day of storage)	4 ± 1
TOC (after 2 days of storage)	3 ± 1
TN (tap water)[a,c]	10 ± 1
TN (DI water)	5 ± 1
	Value
pH (tap water)[e]	7.4 ± 0.2

270 [a] The concentration of total organic carbon (TOC) as non-purgeable organic carbon and total
271 nitrogen (TN) was determined using a TOC analyzer (TOC-5000A, Shimadzu).

272 [b] The TOC content was similar in tap water and in DI water. Storage was at room temperature,
273 in the influent tank.

274 [c] There was little change of the TN content during 2 days of storage at room temperature.
275 Ammonia, nitrite and nitrate were not measured, but it can be assumed that ammonification
276 and nitrification took place, while N-species remained in the aqueous phase.

277 [d] The ± errors are the standard deviation of samples taken on different days (n=3 to 5).

278 [e] In DI water, some of the buffering capacity was lost but pH was close to 8.

279

280

281 # S3 Results

282

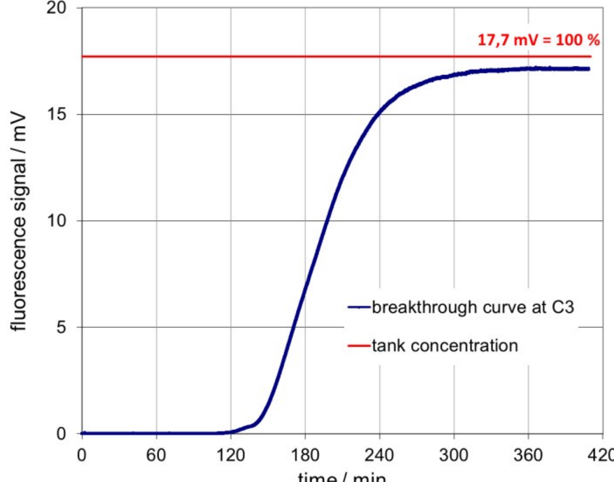
283 ## S3.1 Tracer tests

284

285 System 1

286 For tracer tests, the drinking water pumped through the system was fortified with
287 0.5 mg/L fluorescein. The flow rate was 6 mL/min. At regular intervals, 0.5 mL
288 samples were taken from each of the different sampling points. These were mixed with
289 0.5 mL ammonia buffer. The fluorescein content was determined using a flow-through
290 fluorimeter (821-FP, Jasco, Japan; ex = 491 nm, em = 512 nm). Since the tracer
291 substance fluorescein reacts with ozone, the breakthrough curves would suffer
292 disturbances. Thus, ozonation was switched off during the experiment and a
293 comparable turbulence in the bubble column was achieved by the introduction of
294 nitrogen.

295 The advantage of manual sampling is that all sampling points can be sampled
296 simultaneously. Alternatively, the flow-through fluorimeter can also be connected to
297 the flow system. An additional peristaltic pump actively pumps a certain proportion of
298 the water through the fluorimeter. Figure S7 gives an impression of this online
299 measurement. With this procedure, only one sampling point can be sampled per run.
300 A residence time of approx. 6 hours results over the entire system.

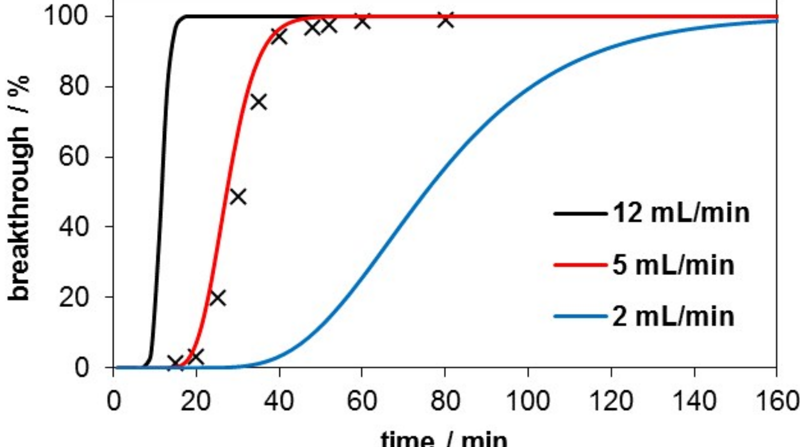


301

302 **Figure S6**: Breakthrough of fluorescein (500 µg/L in tap water) through the complete
303 System 1 (flow rate = 6 mL/min) measured by online fluorescence detection at sample
304 point C3 (ex = 491 nm, em = 512 nm, sample rate = 1 Hz).

305 System 2

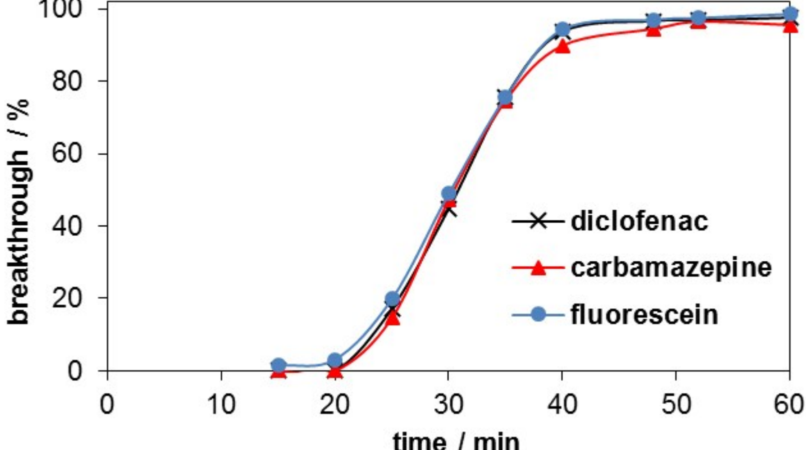
306



307

308 **Figure S7:** Tracer breakthrough in the outlet of a single column for three flow rates
309 modeled with CXTFIT. Crosses represent experimental data upon which the modeling
310 was based (fluorescein breakthrough curve).

311



312

313 **Figure S8:** Breakthrough curve of diclofenac, carbamazepine and fluorescein through
314 a single sand column (not inoculated). Flow rate was 5°mL/min. The compounds were
315 spiked in tap water (initial concentration of diclofenac and carbamazepine approx.
316 1 µmol/L).

317

318

319

320 **S3.2 Formation of ozonation products in System 2**

321

322

323 **Figure S9:** Formation of carbamazepine and diclofenac transformation products
324 during ozonation on four different days. The samples were taken after the ozonation
325 column. The ratio of the area of the target compound over the area of the internal
326 standard is shown. Ozone dose was 1 mg/L to 2 mg/L and ozonation contact time was
327 10 minutes. Error bars refer to the standard deviation of duplicate samples. The internal
328 standard was carbamazepine-$^{13}C_6$ (100 ng/mL).

329

330

331 ## S3.3 MS/MS data for ozonation products in System 2

332

333 **Table S6:** MS/MS data for the studied ozonation products of carbamazepine and
334 diclofenac.

Compound	MS/MS fragments (observed)	Comments	References
BQM	195.0674 223.0869 208.0766 180.0812	two-bond cleavage of the hetero-ring loss of HCN loss of HNCO acridine	Hübner et al. (2014), McDowell et al. (2005)
BaQD	265.0617 222.0559 196.0763	loss of H_2O loss of HNCO and CO_2 loss of HNCO and H_2O	Hübner et al. (2014), Kaiser et al. (2014)
DF-IQ	291.9935 263.9982 229.0280	loss of OH loss of CO_2H loss of CO_2H and Cl	Kosjek *et al.* (2008)
OH-DF	294.0100 266.0143 231.0456	loss of OH loss of CO_2H loss of CO_2H and Cl	Kosjek *et al.* (2008)

335

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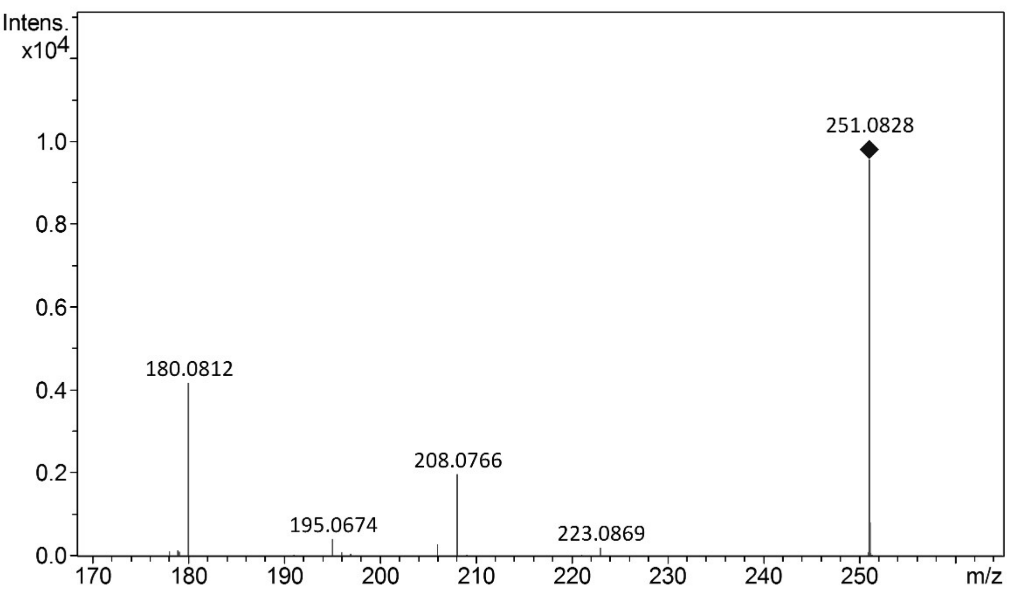
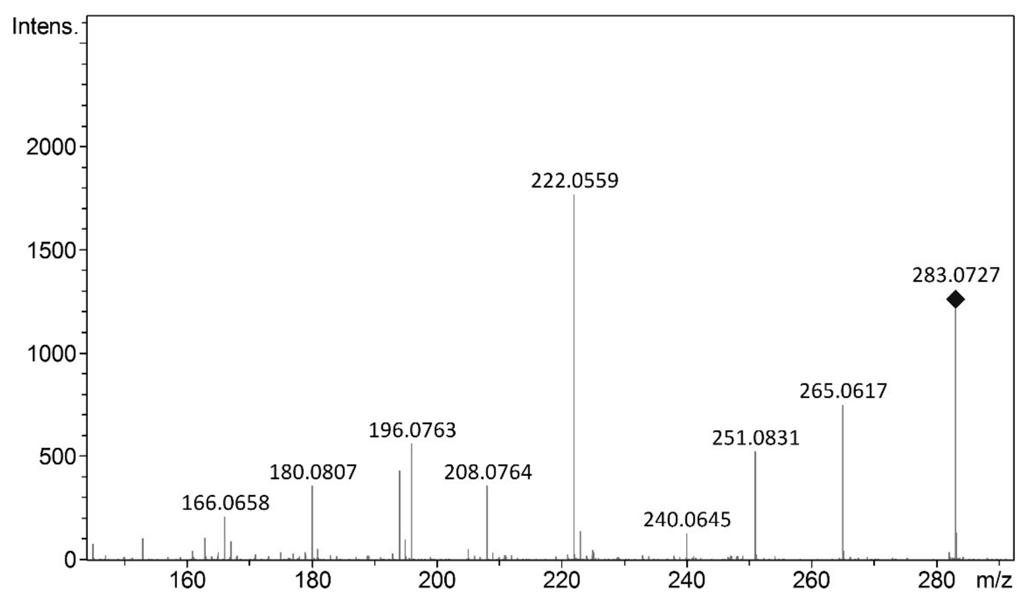


337

338 **Figure S10:** MS/MS MRM spectrum of BQM in a sample taken after C2 (CE =
339 30 eV).

340



341

342 **Figure S11:** MS/MS MRM spectrum of BaQD in a sample taken after C2 (CE =
343 30 eV).

344

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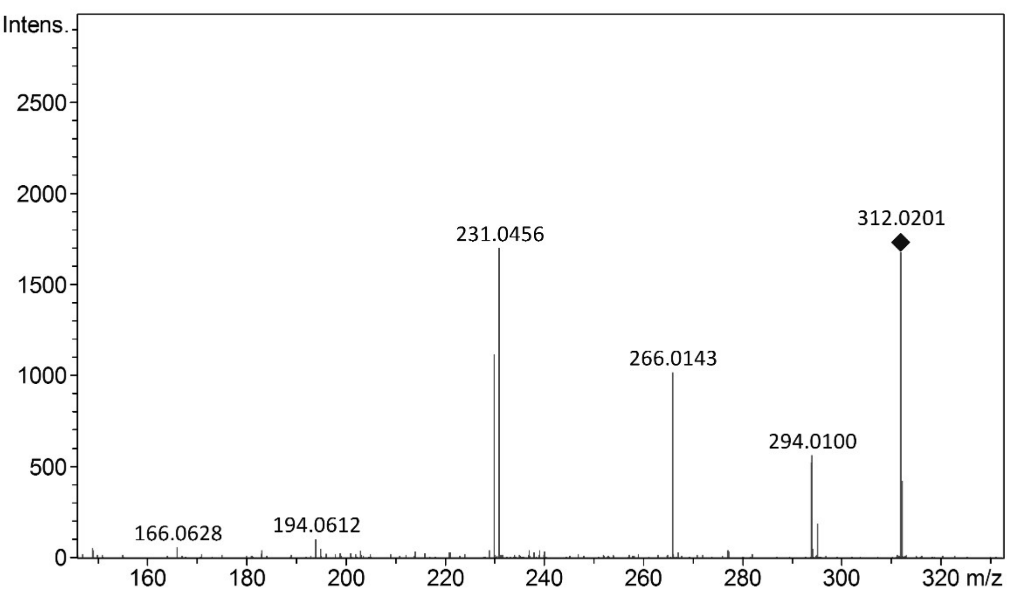
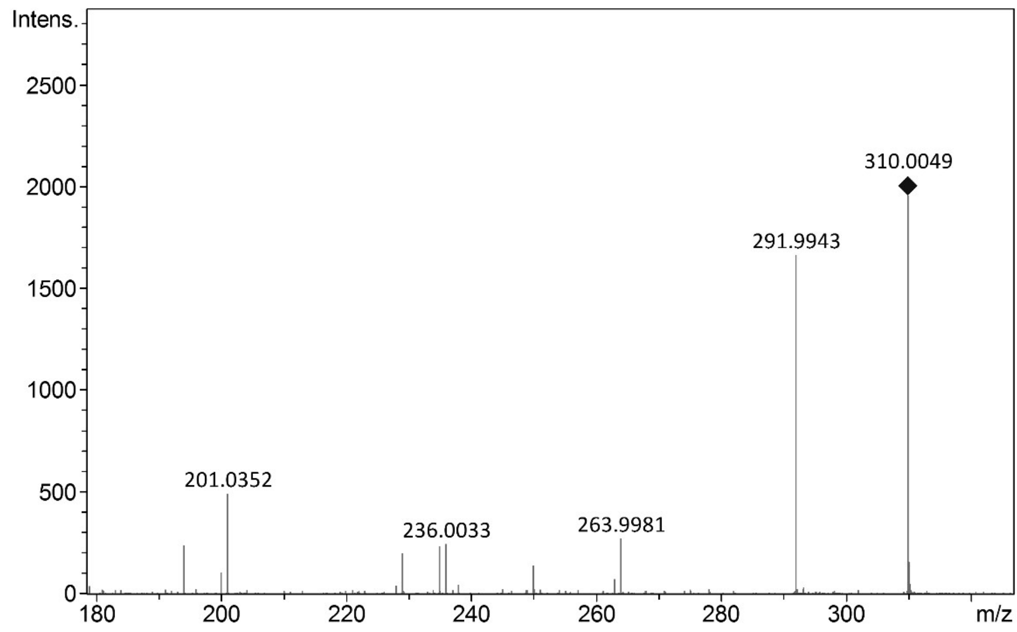


346

347 **Figure S12:** MS/MS MRM spectrum of OH-DF in a sample taken after C2 (CE =
348 30 eV).

349



350

351 **Figure S13:** MS/MS MRM spectrum of DF-IQ in a sample taken after C1 (CE =
352 30 eV).

353

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