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Ozone as oxidizing agent for the total oxidizable precursor (TOP) assay and as a preceding step for activated carbon treatments concerning per- and polyfluoroalkyl substance removal

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Funding

This research is solely based on in-house and personal contributions and did not receive any specific grant.

Conflicts of interest

The authors declare that they have no conflict of interest.

27 **Abstract**

28 Several thousands of highly persistent per- and polyfluoroalkyl substances (PFAS)
29 exist and it is therefore challenging to analytically determine a larger spectrum of
30 these compounds simultaneously in one sample. It is even more difficult to efficiently
31 remove mobile PFAS in wastewater treatment plants (WWTPs) to protect the
32 receiving waters. The total oxidizable precursor (TOP) assay is an approach that
33 enables the detection of the total PFAS content in a sample via oxidation of
34 precursors, followed by subsequent analysis of the perfluoroalkyl acid (PFAA)
35 concentration before and after oxidative processes. Activated carbon combined with
36 a preceding ozonation step is considered a promising tool for the removal of
37 micropollutants but considering PFAS removal efficiencies in effluents for this
38 process combination more information is required.

39 The focus of the study was to implement and assess the TOP assay with ozone as
40 oxidizing agent to estimate the total PFAS content in a WWTP effluent. Additionally,
41 granular activated carbon (GAC) and powdered activated carbon (PAC) with a
42 preceding ozonation step was tested for the removal efficiencies for 22 PFAS. For
43 the TOP assay the obtained accordance in molarity using spiked tap water as quality
44 control was 95.2% (15 mg O₃/L) and 99.1% (6 mg O₃/L). Applying the TOP assay, an
45 estimated total PFAS content of 840 ng/L was determined in the respective effluent,
46 which was 91.1% higher than obtained by target PFAS analysis, implying the
47 presence of unknown precursors not included in common monitoring. While all
48 treatment techniques that included ozone or a preceding ozonation step solely
49 transformed precursors and long-chain perfluoroalkyl acids (PFAA, i.e., >C₉) to

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50 shorter congeners, PAC was the only tested water treatment application that was
51 able to remove 19.3% of the total PFAS molarity.

52

53 **Keywords:** TOP assay, ozone, per- and polyfluoroalkyl substances, wastewater
54 treatment, activated carbon

55

56 **Abbreviations**

57

58 6:2 Cl-PFESA 6:2 chlorinated polyfluorinated ether sulfonate (or F-53B)

59 AC activated carbon

60 DONA dodecafluoro-3H-4,8-dioxanonoate

61 BTA Benzotriazole

62 CBZ Carbamazepine

63 diPAP polyfluoroalkyl phosphate diester

64 DW deionized water

65 EFSA European Food Safety Authority

66 ESI electrospray ionization

67 EtFOSA N-ethyl-perfluoro-1-octane sulfonamide

68 EtFOSAA N-ethyl-perfluoro-1-octane sulfonamido acetic acid

69 EtFOSE N-ethyl-perfluoro-1-octane sulfonamido ethanol

70 FOSA perfluoro-1-octane sulfonamide

71 FTSA fluorotelomer sulfonate

72 GAC granular activated carbon

73 HFPO-DA hexafluoropropylene oxide-dimer acid (or GenX)

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Journal of Environmental Management, 300 (2021) 113692, which has been published in final form at <https://doi.org/10.1016/j.jenvman.2021.113692>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

74	HPLC-MS/MS	high-performance liquid chromatography tandem-mass spectrometry
75		
76	LOD	limit of detection
77	LOQ	limit of quantification
78	MPs	micropollutants
79	O ₃	ozone
80	PAC	powdered activated carbon
81	PAPs	polyfluoroalkyl phosphate esters
82	PFAAs	perfluoroalkyl acids
83	PFBA	perfluoro-n-butanoate (perfluoro-n-butanoic acid)
84	PFBS	perfluoro-n-butane sulfonate
85	PFCA	perfluoroalkyl carboxylate (perfluoroalkyl carboxylic acid)
86	PFDA	perfluoro-n-decanoate (perfluoro-n-decanoic acid)
87	PFDoDA	perfluoro-n-dodecane carboxylate (perfluoro-n-decanoic acid)
88	PFDS	perfluoro-n-decane sulfonate
89	PFEAs	per- and polyfluoroalkyl ether acids
90	PFESA	perfluoroether sulfonate (perfluoroether sulfonic acid)
91	PFHpA	perfluoro-n-heptane carboxylate (perfluoro-n-heptanoic acid)
92	PFHpS	perfluoro-n-heptane sulfonate
93	PFHxA	perfluoro-n-hexane carboxylate (perfluoro-n-hexanoic acid)
94	PFHxS	perfluoro-n-hexane sulfonate
95	PFNA	perfluoro-n-nonane carboxylate (perfluoro-n-nonanoic acid)
96	PFNS	perfluoro-n-nonane sulfonate

97	PFOA	perfluorooctanoate (perfluoro-n-octanoic acid)
98	PFOS	perfluorooctane sulfonate
99	PFPeA	perfluoro-n-pentane carboxylate (perfluoro-n-pentanoic acid)
100	PFPeS	perfluoro-n-pentane sulfonate
101	PFSA	perfluoroalkane sulfonate (perfluoroalkane sulfonic acid)
102	PFTeDA	perfluoro-n-tetradecane carboxylate (perfluoro-n-tetradecanoic acid)
103	PFTrDA	perfluoro-n-tridecane carboxylate (perfluoro-n-tridecanoic acid)
104	PFUnDA	perfluoro-n-undecane carboxylate (perfluoro-n-undecanoic acid)
105	POPs	persistent organic pollutants
106	SPE	solid phase extraction
107	TMP	Trimethoprim
108	TOP	total oxidizable precursor
109	US EPA	United States Environmental Protection Agency
110	WWTP	wastewater treatment plant
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112		

113 **1. Introduction**

114 Per- and polyfluoroalkyl substances (PFAS) are of anthropogenic origin with the
115 characteristic of being chemically extremely persistent, and many are showing
116 hydrophobic and lipophobic properties (Buck et al., 2011). PFAS surround us
117 everywhere and every day, substances are used in fire-fighting foams, chrome
118 plating, photographic surface layers, electronic devices, semiconductors, in the
119 energy sector, F-gases, lubricants, construction products, cosmetics and personal
120 care products, textiles, leather, ski waxes, food contact materials and paper and
121 board and waste (Glüge et al., 2020). Currently around 4730 PFAS are registered on
122 the global market (OECD, 2018), and the United States Environmental Protection
123 Agency (US EPA) even reports more than 9200 chemical structures (US EPA, 2020).
124 A myriad of published papers are available today describing their worldwide detection
125 in various environmental media, natural waters, wildlife animals and humans, as well
126 as their ecological and human health risks (Lau, 2015; Nakayama et al., 2019; Wang
127 et al., 2017). Several adverse effects on fish and aquatic organisms (e.g. neurotoxic
128 effects, endocrine effects and developmental delays) had been reported and
129 reviewed by Lee et al. (2020). Recently, effects on the immune system were
130 considered critical for human health and the European Food Safety Authority (EFSA)
131 derived a considerably low tolerable weekly intake value (TWI) of 4.4 ng/kg body
132 weight based on the sum of 4 PFAS: perfluorooctanoic acid (PFOA), perfluorooctane
133 sulfonate (PFOS), perfluorononanoic acid (PFNA), and perfluorohexane sulfonate
134 (PFHxS) (EFSA, 2020). A good water quality for surface waters is achieved if the
135 annual average concentration in surface water does not exceed a value of 0.65 ng/L

136 PFOS (European Commission, EQS Dossier (2011)). An environmental quality
137 standard is only available for surface waters and biota (9.1 µg PFOS/kg ww) but not
138 for groundwater or any other PFAS, although other PFAS can be detected in Austrian
139 WWTP effluents (BMLFUW, 2017), surface waters (Clara et al., 2009) and
140 groundwaters (Brielmann et al., 2018). Recently, the European Commission
141 introduced a limit value for drinking water of 0.1 µg/L for the sum of 20 individual
142 PFAS and 0.5 µg/L for the total PFAS concentration; however, the limit value for the
143 total PFAS concentration will only be applied once an applicable method is available
144 (European Commission, 2020). From an analytical perspective, the large number of
145 PFAS poses a challenge to detect the total amount of PFAS simultaneously in one
146 sample. The total oxidizable precursor (TOP) assay, a method first published by
147 Houtz and Sedlak (2012), was developed to address this challenging task.
148 Briefly explained, precursors are oxidized to (mostly) perfluoroalkyl acids (PFAAs) via
149 hydroxyl radicals generated by thermolysis of persulfate ($S_2O_8^{2-}$) under alkaline pH
150 (≥ 12) conditions and the total PFAS content is estimated by the determination of the
151 total PFAAs content before and after the oxidation (Houtz and Sedlak, 2012). A
152 similar approach was investigated in the present study by assessing the applicability
153 of the TOP assay with ozone as oxidizing agent. PFOA and PFOS are listed as
154 persistent organic pollutants (POPs) (Stockholm Convention, 2020) which are not
155 degraded during conventional biological wastewater treatment (Zareitalabad et al.,
156 2013) even though Austrian wastewater treatment plants (WWTPs) are operated
157 according to the best available technologies (i.e., carbon, nitrogen, and phosphorous
158 removal).

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159 Although, it is well known that even at high doses and long contact times ozone
160 alone is not capable to remove PFAS from water (Eschauzier et al., 2012; Sun et al.,
161 2018; Yang et al., 2014) and that granular activated carbon filters are less efficient for
162 short-chain PFAS (i.e., $\leq C5$) (Dai et al., 2019; Franke et al., 2019), it was suggested
163 that a preceding ozonation step may improve the removal efficiencies of activated
164 carbon filters (or treatments) by the oxidization of otherwise competitive organic
165 compounds (Sun et al., 2018). While nanofiltration (NF) and reverse osmosis (RO)
166 can effectively remove PFAS from water, they have a high energy consumption and
167 produce a high PFAS-enriched liquid concentrate (Dai et al., 2019; Rahman et al.,
168 2014); therefore according to Merino et al. (2016) combining several treatment
169 techniques besides NF and RO such as advanced oxidation processes (AOP) and
170 activated carbon treatment may be more promising and cost-efficient. While different
171 AOP exist using different chemicals or methods to generate specific free highly
172 reactive radicals (e.g., mostly hydroxyl radicals) (Trojanowicz et al., 2018), ozonation
173 of an effluent can somehow already be considered an AOP since a higher hydroxyl
174 radical exposure can be achieved with increasing organic matter (Buffle et al., 2006;
175 von Sonntag and von Gunten, 2012).

176 The following five advanced wastewater treatment processes and combinations were
177 evaluated for their PFAS abatement: ozonation (O_3), granular activated carbon
178 treatment (GAC), powdered activated carbon treatment (PAC), GAC with preceding
179 O_3 , and PAC with preceding O_3 . Therefore, one municipal WWTP effluent was spiked
180 with a standard mixture comprising several PFAS to investigate the treatment
181 performance. A specific ozone dose of 0.6 mg O_3 per mg dissolved organic carbon

182 (DOC) was applied, which is within the recommended dose range for micropollutant
183 removal in WWTPs (Rizzo et al., 2019). The aims of the present study were (i) to
184 implement and evaluate the TOP assay with ozone as oxidizing agent using spiked
185 tap water samples, (ii) to apply the adapted TOP assay to estimate the total PFAS
186 content in a real effluent sample of a municipal WWTP, and (iii) to evaluate the PFAS
187 removal efficiencies for five advanced wastewater treatment methods including
188 ozonation, GAC, PAC, GAC with preceding O₃, and PAC with preceding O₃.

189

190 **2. Materials and Methods**

191 **2.1 Instruments and material**

192 The ozone generator was an OZ500/5 (Fischer Technology) with a production
193 capacity of 5 g O₃/h using oxygen (O₂) as feed gas. The ozone stock solution (O₃-
194 stock solution) was produced by transferring gaseous ozone to a 2000 mL glass
195 bottle filled with cooled deionized water (DW). The ozone concentration was
196 determined photometrically via indigo according to the DIN 38408-3 (2011) with slight
197 modifications suggested by Zappatini and Götz (2015) using a UV/VIS-spectrometer
198 Dr. Lange – Cadas 100.

199 All PFAS were simultaneously determined by high-performance liquid
200 chromatography tandem-mass spectrometry (HPLC-MS/MS) for which an Agilent
201 Technologies 1290 Infinity Series (Agilent Technologies, Santa Clara, CA, USA)
202 HPLC system with a Luna 5 µm C18(2), 100 x 2 mm (Phenomenex, California, USA)
203 analytical column and a SCIEX 4000 QTRAP mass spectrometer (AB Sciex
204 Technologies, Framingham, MA, USA) in electrospray ionization (ESI) negative mode

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205 were used. Analytical eluents and settings were LC-MS-grade water containing 10
206 mM ammonium acetate (eluent-A) and LC-MS-grade methanol (eluent-B), an
207 analyzing time of 23 min, a flow rate of 0.3 mL/min, an injection volume of 10 µL and
208 a column temperature of 40 °C. Other micropollutants (MPs, i.e., Benzotriazole
209 (BTA), Carbamazepine (CBZ) and Trimethoprim (TMP)) were determined by HPLC-
210 MS/MS with a HPLC system from Agilent Technologies 1260 Infinity II Series using a
211 Poroshell 120 EC C18, 4 µm, 4.6 x 100 mm column (Agilent Technologies, Santa
212 Clara, CA, USA); the used triple quadrupole mass spectrometer was a SCIEX 6500+
213 QTRAP in ESI positive mode. Analytical eluents and settings for the MPs were water
214 containing 0.1% acetic acid (eluent-A) and LC-MS-grade acetonitrile with 0.1% acetic
215 acid (eluent-B), an analyzing time of 40 min, a flow rate of 0.8 mL/min, an injection
216 volume of 50 µL and a column temperature of 40 °C. For the solid-phase extraction
217 (SPE) Oasis® WAX-columns (6 mL, 150 mg, Waters Corporation, Milford, MA, USA)
218 and Chromabond® HR-XAW-columns (6mL, 150 mg, Macherey-Nagel GmbH & Co.
219 KG, Düren, Germany) were used. PFAS-free water was prepared by filtering tap
220 water either with Oasis® HLB-columns (6 mL, 500 mg, Waters Corporation, Milford,
221 MA, USA) or Oasis® WAX-columns (6 mL, 500 mg, Waters Corporation, Milford, MA,
222 USA).

223

224 **2.2 Chemicals**

225 The PFAS-standard mixture contained eighteen perfluoroalkyl acids (PFAAs, C4-C14
226 perfluorocarboxylic acids (PFCAs) and C4-C10 perfluoroalkane sulfonic acids
227 (PFASs)), four perfluoro sulfonamides (perfluorooctane sulfonamide (FOSA), N-

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228 ethylperfluorooctane sulfonamide (EtFOSA), N-ethylperfluorooctane sulfonamido
229 acidic acid (EtFOSAA) and N-ethylperfluorooctane sulfonamido ethanol (EtFOSE)),
230 three fluorotelomer sulfonates (FTSA, 4:2, 6:2 and 8:2), three polyfluoroalkyl
231 phosphoric acid diesters (diPAPs, 6:2, 8:2 and 6:2/8:2), and three per- and
232 polyfluoroalkyl ether acids (PFEAs, hexafluoropropylene oxide-dimer acid (HPFD-DA
233 or GenX), 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFESA or F-53B),
234 and dodecafluoro-3H-4,8-dioxanonanoate (DONA). The isotopes from PFCA (C4, C6
235 and C8-C12), PFSA (C6 and C8), EtFOSA, EtFOSAA, EtFOSE, 6:2 FTSA and 8:2
236 diPAP were used as internal standards.

237

238 All native and internal PFAS standards were purchased from Wellington Laboratories
239 (Ontario, Canada). The MPs standards (i.e., BTA, CBZ) and TMP), LC-MS-grade
240 acetonitrile, water, acetic acid >99,8% and ammonium acetate for mass spectrometry
241 were purchased from Sigma-Aldrich® (St. Louis, USA). LC-MS-grade methanol and
242 formic acid (98-100%) were purchased from Merck (Darmstadt, Germany), and the
243 ammonia solution (25%) from Fisher Scientific (Loughborough, UK).

244

245 **2.3 TOP assay**

246 Five tap water samples, two WWTP effluents and one blank were investigated in a
247 TOP assay using ozone as an oxidizing agent (at pH 7). All tap water samples were
248 spiked with a PFAS-standard mixture with 31 PFAS containing 5 ng of each
249 compound. Three samples were treated with 15 mg O₃/L and one with 6 mg O₃/L.
250 The fifth tap water sample was used as a reference without ozone treatment. One

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251 effluent sample was treated with 15 mg O₃/L and the other one was used as
252 reference (without ozone). The blank was neither spiked with the PFAS-standard
253 mixture nor treated with ozone.

254

255 **2.4 O₃, GAC and PAC**

256 A total effluent volume of 3360 mL was spiked with a PFAS-standard mixture with 31
257 PFAS containing 60 ng of each compound (effluent-S). After manually mixing for 1
258 min, twelve 250 mL polyethylene (PE) bottles were filled with 275 mL of effluent-S. In
259 addition to the 12 samples (1 x 275 mL effluent-S untreated, 1 x 275 mL effluent-S
260 treated with GAC, 1 x 275 mL effluent-S treated with PAC, 3 x 275 effluent-S treated
261 with O₃, 3 x 275 effluent-S treated with O₃ and GAC, and 3 x 275 effluent-S treated
262 with O₃ and PAC (see Table S6)), four blanks were prepared: 2 x 275 mL DW, 1 x
263 275 mL unspiked effluent, and 1 x 300 mL O₃-stock solution. All bottles were either
264 filled up to 310 mL with 35 mL of DW or O₃-stock solution. After a reaction time of 1
265 hour each sample was transferred to a 500 mL PE bottle which was either empty or
266 contained 2 mg GAC or 2 mg PAC. The bottles were horizontally placed on a shaker
267 to enable a maximum of interaction between the target compounds and the activated
268 carbon for 18 hours at 120 rpm. All samples, except for one blank, were filtered
269 through a 1 µm glass fibre filter using a stainless-steel funnel and transferred back to
270 their original 250 mL PE bottle. Finally, all samples were adjusted to 300 mL.

271

272 **2.5 Sample extraction**

273 The analytes were extracted using the ISO 21675 (2019) SPE-method with slight
274 adjustments. The samples were adjusted to a pH value of 3 with formic acid, and
275 ultrasonicated for 15 min. The SPE-method was applied by performing the following
276 four steps: 1) condition with methanol containing 0.1% ammonia, 2) load sample, 3)
277 wash with methanol and PFAS-free water (pH 3), and 4) elution with methanol and
278 0.1% ammonia/methanol. The eluent was combined in one polypropylene (PP) tube
279 and the volume was reduced to 1 mL under a nitrogen flow at 35 °C before the
280 injection to the HPLC-MS/MS.

281

282 **2.6 Quality control**

283 The PFAS concentrations in ng/mL were transformed to their respective molarity to
284 enable an interindividual substance evaluation comparing the total molarity from
285 treated samples with the untreated reference. PFAS were included in the evaluation
286 of the TOP assay if the decrease or increase of the individual substance was $\geq 20\%$
287 (to avoid false interpretations regarding the measurement error).

288 Samples were spiked with isotope labeled standards after the ozonation step and
289 before the extraction procedure to allow to correct for recovery losses during the
290 sample preparation. PFAS were only included in the individual evaluations if the
291 method recovery was at least $\geq 30\%$. Several blanks were used to check for potential
292 contaminations (e.g., pure unfiltered DW, pure filtered DW, pure effluent, and O₃-
293 stock solution). A 10-point calibration curve was used, and the limits of quantification
294 (LOQ) were calculated in accordance with the DIN 32645. Three micropollutants (i.e.,

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295 BTA, CBZ and TMP) frequently detected in Austrian WWTP effluents were used as
296 reference chemicals to validate the experimental approach since their removal
297 patterns are well described in literature for O₃, GAC and PAC treatments. The DOC
298 concentration of the effluent was 6.4 mg/L; a specific ozone dose of 0.6 mg O₃ per
299 mg DOC was applied which is typically used for micropollutant removal as suggested
300 by Rizzo et al. (2019). Additionally, a DOC-specific PAC dose of 1.19 mg PAC/mg
301 DOC was applied suggested by Altmann et al. (2014) to ensure a removal efficiency
302 of >80%; the same quantities of GAC were used to be able to investigate
303 performance differences of both activated carbons (AC).
304 More detailed information on material, instruments, chemicals, ozone treatment,
305 experimental procedure, and quality control can be found in the Supplementary
306 Information (SI).

307

308 **3. Results and Discussion**

309 **3.1 Total oxidizable precursor (TOP) assay with ozone as oxidizing agent**

310 *Recovery*

311 The mean recovery of 14 internal isotope labeled PFAS standards was 90.4% (± 18)
312 in all 6 water samples (i.e., $n = 14 \times (4 \times \text{tap water and } 2 \times \text{effluent})$), and the mean
313 recovery of all 31 native PFAS standards in the tap water reference (i.e., $n = 1 \times 31$)
314 was 78.2% (± 14). No significant recovery differences were observed between tap
315 water and effluent (see Table S3). Omitting the washing step with acetate buffer
316 recommended by the ISO 21675 (2019) showed a positive effect on the recoveries
317 determined for all investigated substances, especially for long chain PFCAs (Kaiser,

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318 2020), which is in line with recoveries reported by Montes et al. (2020). In contrast,
319 Coggan et al. (2019) used the washing step with acetate buffer and reported equally
320 good recoveries including long chain PFCAs.

321

322 *Tap water samples*

323 After ozonation the PFOS molarity in the tap water samples strongly increased (82-
324 140%), and the PFOS increase was larger when the sample was treated with a
325 higher ozone dose, as shown in Table 1. Branched PFOS were only detected in the
326 tap water samples after ozonation and the branched PFOS content was higher when
327 treated with a higher ozone dose. Further molarity increases were observed for
328 PFDA (39% at 6 mg O₃/L), PFUnDA (25% at 6 mg O₃/L), and 6:2 Cl-PFESA (F-53B,
329 22% at 15 mg O₃/L). However, it is unclear and difficult to explain why the PFDS
330 concentration increased to a higher content at lower ozone dosages (+78% at 6 mg
331 O₃/L) compared to a higher ozone treatment level (+35% at 15 mg O₃/L). A decrease
332 was observed for EtFOSE (44-62%) and EtFOSA (28-48%) when treated with 6 mg
333 O₃/L and 15 mg O₃/L, respectively (see Table 1). Other compounds that decreased to
334 a lower degree after ozonation were PFDoDA, FOSA, diPAPs and HFPO-DA (GenX).
335 The molarity of the reference compared to the mean molarity of the ozonated tap
336 water samples (15 mg O₃/L) showed an accordance of 95.2%. The tap water sample
337 which was treated with 6 mg O₃/L showed an accordance of 99.1% compared to the
338 reference. This good accordance of the compared molarities demonstrates that the
339 TOP assay with ozone as oxidizing agent can be considered a useful approach to
340 estimate the total PFAS content in a sample. However, the presented TOP assay

15

341 needs to be optimized (e.g. using basic conditions and providing better mixing), since
342 the investigated precursors were not completely oxidized which lead to
343 underreporting total PFAS levels when applied to real samples.

344

345 *Effluent samples*

346 The application of the TOP assay on the effluent sample showed a PFAS molarity
347 increase of 91.1%, i.e. <10% of the total estimated PFAS molarity in the effluent
348 could be identified within the 31 target PFAS. The total determined PFAS
349 concentration in the untreated effluent was 74.7 ng PFAS/L, and the estimated total
350 PFAS concentration after the ozone treatment was 840 ng PFAS/L. Compared to the
351 tap water samples, an increase of PFCAs with a decreasing carbon-chain length was
352 observed; additionally, perfluorobutane sulfonic acid (PFBS) and 6:2 FTSA increased
353 in the effluent after the treatment as well (see Table 1). Considering the statement of
354 Houtz et al. (2018) that approximately 65% to 75% of PFCAs are generated by the
355 oxidation of precursors it is assumed that the PFCAs increase has its origin in
356 unidentified precursor compounds. Although a molarity increase of 91.1% seems
357 quite high, the total PFAS concentration in the effluent might be even higher.
358 According to Houtz et al. (2018) the TOP assay tends to underreport the total PFAS
359 concentration since it is not able to cover the losses of the organofluorine which
360 converts to inorganic fluorine. Moreover, our results demonstrated that not all target
361 precursors were completely transformed to PFAAs.

362 In contrast to the effluent sample and to Martin et al. (2006) who suggested
363 that perfluoroalkyl sulfonamides (FS) degrade mostly to PFCAs under (atmospheric)

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364 oxidative conditions, the present results for tap water showed that they were
365 frequently transformed to PFOS by ozonation. These results were confirmed by Xiao
366 et al., (2018) who reported that FS in surface water can be quickly transformed to
367 both PFOS and PFOA during conventional ozonation. However, FS have not been
368 detected in the effluent and the effluent showed no increase in PFOA or PFOS after
369 the ozonation. The increase of short chain (<C6) PFAAs after ozonation though is in
370 line with previous studies (Glover et al., 2018; Huang et al., 2016; Pisarenko et al.,
371 2015; Wu et al., 2018).

372 In this study, besides the increase of short chain (<C6) PFCAs and PFBS, 6:2 FTSA
373 showed the highest concentration increase. Even though Glover et al. (2018)
374 reported that 6:2 FTSA could not be removed by ozonation in wastewater (specific
375 ozone dose 0.8 O₃ mg / total organic carbon (TOC)) it was quite surprising that the
376 6:2 FTSA concentration increased to such an extent in our study (+3528%). In
377 contrast to the present study and Glover et al. (2018), other studies reported that 6:2
378 FTSA can degrade under oxidative conditions to PFCAs using persulfate S₂O₈²⁻ at pH
379 ≥12 (Dombrowski et al., 2018; Houtz and Sedlak, 2012; Martin et al., 2019).
380 However, the 6:2 FTSA increase in our study probably was caused due to a higher
381 ozone dosage increasing the interaction between (unknown) precursors and
382 oxidants; but it is unclear if this increase might have had happened under alkaline
383 conditions using ozone as well.

384 These differences indicate that degradation and transformation products can
385 vary and are probably dependent on the oxidants available, the pH value, and the
386 matrix. Compound specific degradation and transformation efficiencies are also

387 dependent on the individual PFAS reaction rate constants (e.g. with ozone (k_{O_3}) or
388 hydroxyl radicals (k_{OH})). Very sparse information though is today available
389 concerning k_{O_3} or k_{OH} values for individual PFAS except for PFOA and PFOS
390 (Trojanowicz et al., 2018). However, water parameters such as the DOC or TOC as
391 well as the pH at which the oxidation occurs should be considered while comparing
392 TOP assay outcomes for different matrices. For example in our study the DOC for the
393 effluent was 6.4 mg/L while for the tap water it was <1.0 mg/L which had an effect on
394 the outcome of the TOP assay. Additionally, the type of oxidant used can influence
395 the outcome. For both TOP assay methods (heat-activation of persulfate and
396 ozonation) different radicals are generated and the radical generation between
397 matrixes could vary as well influencing the oxidation process. Therefore, exact and
398 similar oxidation outcome profiles for both methods are rather unlikely. However,
399 additional experiments are necessary to evaluate the outcome and potential
400 differences of both methods at alkaline conditions for the same matrixes. Concerning
401 the per- and polyfluoroalkyl ethers (PFEAs) Yi et al. (2018) and Zhang et al. (2019)
402 reported that monoether and multiether PFEAs were quite stable in the TOP assay
403 under sulfate reducing conditions. Zhang et al. (2019) observed that only DONA was
404 converted into another PFEAs, probably due to its accessibility via the hydrogen
405 atom in the O-CFH-bond. A study conducted by Hatton et al. (2018) indicated that
406 GenX is neither oxidized in systems containing sulfate radicals nor hydroxyl radicals.
407 In contrast to previous studies, our experiment showed a slight increase of F-53B
408 (22%) and a slight decrease of GenX (20%) but no significant changes of DONA. It
409 might not seem very plausible that fluorotelomers, fluorosulfonamides or PFAAs are

410 transformed into PFEAs but the potential occurrence of such a process cannot be
411 completely excluded. However, considering the very small sample size it is very
412 difficult to explain the results for the three investigated PFEAs. In any case PFEAs
413 seem to be very persistent under oxidative conditions and therefore we share the
414 recommendation by Zhang et al. (2019) that PFEAs should also be included in the
415 TOP assay instead of restricting to PFAAs .

416 Comparing the two TOP assays, the original presented by Houtz and Sedlak
417 (2012) with the present alternative with ozone as oxidizing agent, the results showed
418 that different outcomes might occur and this should be further investigated. A direct
419 comparison of the conventional TOP assay and the new presented version at equal
420 alkaline conditions using the same matrix would be beneficial to evaluate the
421 outcomes of both approaches accurately. However, the TOP assay using ozone as
422 oxidizing agent was up to our best knowledge used for the first time and
423 modifications stated herein are necessary. For example, the adjustment of a higher
424 pH value could modify the performance, since it is known that PFAS can be better
425 transformed by ozone at alkaline conditions ($\text{pH} \geq 11$), while they hardly react at
426 lower pH values ($\text{pH} \leq 5$) (Lin et al., 2012). Lin et al. (2012) hypothesized that alkaline
427 conditions are more favorable for the formation of superoxide radicals ($\cdot\text{O}_2^-$), which
428 achieve a better degradation of PFAS.

429

430 **Table 1:** Observed increase (+) and decrease (-) of PFAS concentrations in % after ozonation in tap
 431 water and one effluent sample in comparison to their reference; for blanks (i.e., empty cells) no
 432 changes after ozonation were observed.

Compound	Tap water		Effluent
	6 mg O ₃ /L (n=1)	15 mg O ₃ /L (n=3)	15 mg O ₃ /L (n=1)
PFBA			+ 321%
PFPeA			+ 130%
PFHxA			+ 59%
PFHpA			+ 53%
PFDA	+ 39%		
PFUnDA	+ 25%		
PFDoDA	- 21%		
PFBS			+ 189%
PFOS	+ 82%	+ 140%	
PFDS	+ 78%	+ 36%	
FOSA		- 22%	
EtFOSA	- 48%	- 62%	
EtFOSE	- 28%	- 44%	
6:2 FTSA			+ 3528%
6:2 diPAP	- 43%		
8:2 diPAP	- 23%	- 21%	
HFPO-DA (GenX)	- 20%		
6:2 Cl-PFESA (F-53B)		+ 22%	

433
 434 Finally, the present results showed that ozone alone is not capable to remove PFAS
 435 in water samples, which is in line with previous results (Eschauzier et al., 2012;
 436 Schröder and Meesters, 2005; Sun et al., 2018; Yang et al., 2014).
 437 Trojanowicz et al. (2018) reviewed different advanced oxidation processes and
 438 concluded that almost all tested methods lead to the formation of shorter chain PFAS
 439 as the product of decomposition. However, remediation options for PFAS include

440 stabilization and immobilization of individual PFAS but activated carbon does not
441 destroy or degrade PFAS. Nevertheless to clean up water, a combination of a GAC
442 with a preceding ozonation step might improve the removal efficiencies, considering
443 that a preceding ozonation step could eliminate highly reactive compounds and
444 disburden the GAC (Sun et al., 2018). In this context an additional experiment was
445 conducted as shown in the next chapter.

446

447 **3.2 Evaluation of five advanced wastewater treatment techniques for the** 448 **abatement of PFAS**

449 Five wastewater treatment methods (i.e., O₃, GAC, PAC, and the combined
450 processes O₃/GAC, and O₃/PAC) were tested to evaluate the abatement of 22 PFAS
451 (8 PFCAs (C4-C11), 6 PFSAAs (C4-C9), 5 PFAA precursors (FOSA, EtFOSAA, 4:2,
452 6:2 and 8:2 FTSA), and 3 per- and polyfluoroalkyl ethers acids (DONA, HFPO-DA
453 and 6:2 Cl-PFESA)). The treatment efficiency tests were conducted with an effluent
454 of a municipal WWTP spiked with a PFAS standard mixture. The mean method
455 recovery for the investigated isotope labeled PFAS (n=11) was >68% (± 26, n=175).
456 The relative standard deviation (RDS) for all individual method triplicates (i.e., O₃,
457 O₃/GAC, and O₃/PAC) was ≤10% (except for 6:2 FTSA: O₃ (17.5%) and O₃/GAC
458 (43.8%); PFBA and EtFOSAA: O₃ (12.7% and 15%)).

459

460 The PFAS concentrations in the unspiked effluent and the PFAA concentrations in
461 the O₃-stock solution are provided in Table 2. While no PFAS could be detected (all
462 values <LOD) in the unfiltered and filtered (1 µm glass fiber) deionized water, five

21

463 PFCA (C4-C8) were detected in concentrations ranging from 0.40 to 3.42 ng/L in the
 464 O₃-stock solution. The contamination of the O₃-stock solution derived from the tubing
 465 and isolations, which were used for the O₃ generation. In the effluent in total 7 PFCAs
 466 (C4-C10), 3 PFSA, DONA and HFPO-DA (GenX) were detected above the LOQ
 467 (see Table 2). PFBA, PFHxA, PFOA and GenX were the compounds with the highest
 468 concentrations making up >69% of the total PFAS concentration in the effluent.

469
 470 **Table 2:** PFAS detected in the unspiked effluent (n=1) and the O₃-stock solution (n=1). The deionized
 471 water which was used for the O₃-stock solution and the blanks was PFAS free (i.e., all values <LOD)
 472 and the contamination can be attributed to the polytetrafluoroethylene (PTFE, or Teflon) tubes used to
 473 transfer gaseous ozone from the O₃-generator to the glass bottle (i.e., O₃-stock solution). Besides
 474 PFAS, Benzotriazole (BTA), Carbamazepine (CBZ) and Trimethoprim (TMP) were detected
 475 additionally in the effluent.

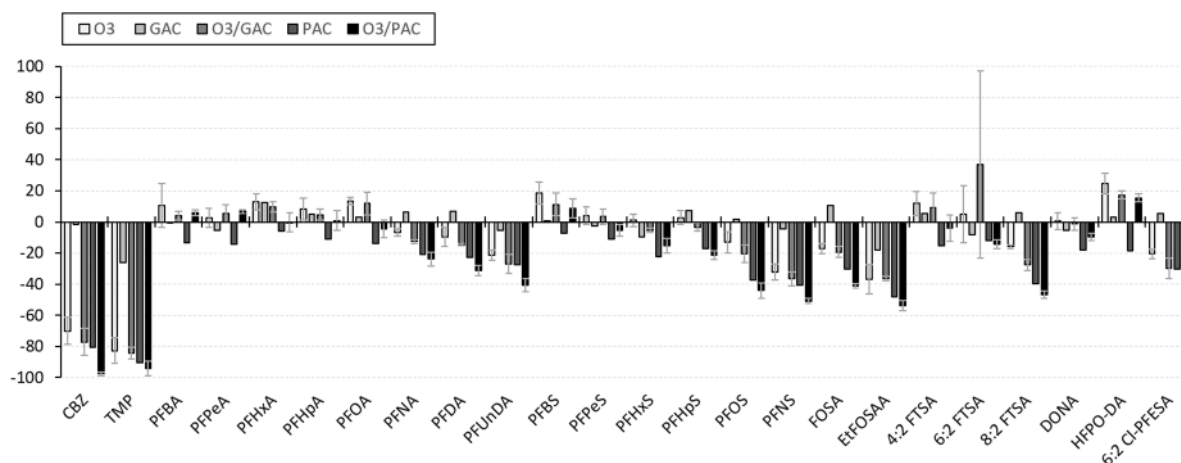
Sample	Compound concentrations (ng/L)							
	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA
Effluent	11.01	3.91	6.83	1.54	12.71	0.70	0.57	<LOD
O ₃ -stock	3.42	2.93	0.75	0.40	0.89	<LOQ	<LOD	<LOD
	PFBS	PFHxS	PFOS	DONA	GenX	BTA	CBZ	TMP
Effluent	2.16	1.14	2.77	2.62	4.45	1311.3	114.5	38.2
O ₃ -stock	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

476
 477
 478 *Ozone (O₃)*

479 Fig. 1 shows the PFAS concentration changes in percent for the five tested treatment
480 applications. Ozone alone showed small varying increases for PFCAs from C4 to C8,
481 with almost analogical increases for PFBA (+10.7%), PFHxA (+13.0%) and PFOA
482 (+13.4%). The elimination efficiency for PFCAs improved with an increasing carbon
483 chain length starting from C9. While the PFBS concentration increased by +18.5%,
484 PFOS and PFNS were removed by 12.9% and 32.1%, indicating improved
485 elimination efficiency trends for long chain (\geq C8) PFASs in analogy to PFCAs.
486 EtFOSAA was the PFAA precursor that was removed most efficiently with 36.9%
487 followed by FOSA (17.3%) and 8:2 FTSA (16.0%). In contrast, 4:2 FTSA showed
488 higher concentrations after the ozone treatment. DONA showed no concentration
489 differences at all, while the HFPO-DA concentration increased by almost 25%, and
490 6:2 CI-PFESA was removed by 20.6%.

491 The total molarity of the spiked untreated effluent matched 101.4% to the total
492 average molarity of the spiked effluent treated with ozone. This indicates that ozone
493 is not removing any PFAS but is rather transforming long-chain PFAAs (\geq C8),
494 precursors and some PFEAs to other (mostly) short chain PFAS.

495



496
 497 **Fig. 1:** PFAS transformation in % for effluent treatments with ozone (O₃, n=3), granular activated
 498 carbon (GAC, n=1), ozonation with a following GAC treatment (O₃/GAC, n=3), powdered activated
 499 carbon (PAC, n=1), and ozonation with a following PAC treatment (O₃/PAC, n=3). Treatments were
 500 compared to an untreated effluent (n=1) and the figure presents the average values of tested
 501 triplicates except for GAC and PAC. Carbamazepine (CBZ) and Trimethoprim (TMP) are highly
 502 reactive with ozone and were therefore used as quality controls/positive controls, respectively.

503
 504 *Granular activated carbon (GAC) and O₃/GAC*

505 No eliminations (i.e., ≥10%) were observed for GAC alone, merely EtFOSAA was
 506 reduced by 18.1%. The PFHxA and PFBA concentrations slightly increased by 12.4%
 507 and 10.5% which is probably rather a cause of the measurement uncertainty than a
 508 real concentration increase. CBZ and TMP, which were used as quality controls,
 509 were sparsely removed by GAC as well, indicating that the experimental set-up for
 510 GAC was not well suited. However, GAC with a preceding ozonation was able to
 511 remove 8 PFAS (PFNA, PFDA, PFUnDA, PFOS, PFNS, FOSA, 8:2 FTSA and 6:2 Cl-
 512 PFESA) slightly better (average -23.4%) than ozone alone (average -17.1%),
 513 whereas the removal for EtFOSAA was equal with or without ozone pre-treatment. O₃

514 reacts with organic and inorganic materials in the effluent and can reduce the
515 competition for GAC adsorption spots between PFAS and other micropollutants (Sun
516 et al., 2018). Though slight removal improvements were observed for some
517 compounds, the general PFAS removal efficiency of O₃/GAC was still very low
518 (average ≤25%). More than half of the observed PFAS were not removed by O₃/GAC
519 at all. Moreover, the concentrations of PFOA, PFBS, 6:2 FTSA, and HFPO-DA
520 increased by >11%. While O₃/GAC showed slightly lower concentration increases for
521 the last four mentioned PFAS, the treatment was not able to compensate or improve
522 the concentration increases for those compounds caused by O₃. The higher
523 concentration increase of 6:2 FTSA using O₃/GAC compared to O₃ alone is not easy
524 to explain, but it could be that more O₃ or hydroxyl radical (OH·) molecules had been
525 able to interact with compounds which could generate 6:2 FTSA (in one sample);
526 Table 1 shows that high ozone doses are able to generate 6:2 FTSA in an effluent,
527 and therefore it is plausible that in one sample more O₃ or OH· molecules were able
528 to interact with 6:2 FTSA related compounds. While the total molarity of the spiked
529 effluent treated with GAC matched 100.7% to the total molarity of the spiked
530 untreated effluent, the total molarity between the spiked untreated effluent matched
531 98.7% to the spiked effluent treated with O₃ before GAC, indicating no removal of
532 PFAS at all. However, as mentioned the experimental set-up for the GAC treatment
533 was suboptimal, and the application of more powdered free granular or a GAC filter
534 could improve the removal efficiencies as demonstrated by Glover et al. (2018).

535

536 *Powdered activated carbon (PAC) and O₃/PAC*

537 PAC alone showed the best overall performance compared to the four other
538 methods, with an average elimination of 21.7% for all 22 observed PFAS. The two
539 micropollutants CBZ and TMP were efficiently removed by >80% as well. PAC with
540 an ozone pre-treatment in comparison removed on average 18.9% of PFAS, and on
541 average >95% of both CBZ and TMP. While O₃/PAC showed the best performance
542 for some compounds (i.e., PFUnDA, FOSA, EtFOSAA, 8:2 FTSA and 6:2 Cl-PFESA),
543 the pre-ozonation step also caused an increase of PFAAs (mostly PFBA, PFOA and
544 PFBS) and HFPO-DA. The PAC was not able to compensate the increased PFAS
545 concentration caused by ozonation. Although compared to all other tested methods
546 PAC showed the best performance in PFAS removal, it cannot be considered as a
547 promising treatment tool for PFAS since an average abatement of ≤25% still has to
548 be considered a low removal potential. The spiked effluent treated with PAC showed
549 a total PFAS molarity removal of 19.3%, and with an ozone pre-treatment PAC was
550 able to remove 12.7% of the total PFAS molarity.

551

552 *Summary*

553 Although, 7 compounds (PFUnDA, PFOS, PFNS, FOSA, EtFOSAA, 8:2 FTSA and
554 6:2 Cl-PFESA) were removed by more than 40%, none of the tested methods could
555 remove any of the investigated 22 PFAS by >80%; PFAS were frequently
556 transformed to other congeners without any removal at all. Although the removal of
557 MPs (e.g., CBZ and TMP) can be improved by increasing the interaction with O₃ (i.e.
558 ensure better mixing) this cannot be expected for PFAS since first the reaction even

26

559 at high O₃ doses is low (Eschauzier et al., 2012; Sun et al., 2018; Yang et al., 2014)
560 and second as demonstrated PFAS are transformed only in structure but they stay
561 PFAS. Advanced oxidation processes (AOP, i.e., generate more radicals using
562 additional chemicals) or the use of higher GAC and PAC dosages may provide a
563 better option to remove PFAS in water. In previous literature it was argued that
564 hydroxyl radicals alone cannot degrade PFAA (Dombrowski et al., 2018; Houtz and
565 Sedlak, 2012), which would exclude the AOP/H₂O₂ (i.e., ozonation and additional
566 hydrogen peroxide (H₂O₂)). Moreover, Trojanowicz et al. (2018) reported in their
567 review that almost all tested AOPs which focused on the increase of hydroxyl radical
568 exposure lead to the formation of shorter chain PFAS as the product of
569 decomposition. However, according to Franke et al. (2019) the average PFAA
570 removal efficiencies can be improved by up to 77% using an additional catalyst
571 material and/or persulfate compared to ozone alone. Lin et al. (2012) reported that
572 ozone can degrade PFOA and PFOS better at alkaline conditions (pH ≥11) by the
573 formation of more superoxide radicals ($\cdot\text{O}_2^-$), but first short chain PFAA residuals can
574 still be very much expected and second adjusting a wastewater (or WWTP effluent)
575 to alkaline conditions in a large WWTP is practically impossible.

576 So far solely high-pressure membrane applications such as RO and NF had been
577 reported to effectively remove PFAS including short chain PFAAs (Dai et al., 2019).
578 But besides that this highly energy consuming applications may improve with
579 advances in energy efficiency (Rahman et al., 2014) it is still quite unclear how to
580 dispose the remained PFAS-enriched concentrate (approximately 10% of the treated
581 water volume) properly (Dai et al., 2019), which may makes RO and NF inconvenient

582 for large-scale WWTPs. From our today's point of view an application that is able to
583 degrade PFAS efficiently in (waste)water is needed, which may can be achieved
584 using adequate AOPs (e.g., using catalyzers or additional chemicals to generate
585 more (specific) radicals) or specific microorganisms. Yi et al. (2016) for example
586 reported the discovery of bacteria, which can degrade PFOA.

587

588 **4. Conclusions**

589 In conclusion, none of the tested methods can be considered effective for a minimum
590 PFAS removal of 80% from (waste)water as targeted for micropollutant abatement.
591 Merely PAC alone was able to remove up to 19.3% of the total PFAS molarity in the
592 effluent. However, an optimization of the experimental set up by improving the mixing
593 and increasing the PAC or GAC dosage could improve the removal efficiencies.
594 Since ozone alone is not able to remove PFAS in water it can be used for the
595 application of the TOP assay. Although the small sample size is a limitation of this
596 study and modifications are required, the TOP assay quality controls indicated a
597 good performance of the method. TOP assays should be urgently developed and
598 validated for various matrices. Additionally, considering the availability of different
599 TOP assays, harmonized approaches would be favorable to be able to include them
600 into harmonized guidelines to provide a basis for further regulations. Finally, we
601 would suggest TOP assays as an available applicable method to monitor the limit
602 value for the total PFAS concentration as requested by the European Commission.

603

604 **Acknowledgements**

605 We wish to thank Christina Hartmann, Maria Uhl and Sigrid Scharf for their invaluable
606 support.

607

608 **Appendix A. Supplementary information (SI)**

609

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