Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products

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ABSTRACT

To protect the ecosystem and drinking water resources in Switzerland and in the countries of the downstream catchments, a new Swiss water protection act entered into force in 2016 aiming to reduce the discharge of micropollutants from wastewater treatment plants (WWTPs). As a consequence, selected WWTPs must be upgraded by an advanced treatment for micropollutant abatement with suitable and economic options such as (powdered) activated carbon treatment or ozonation. WWTP Neugut (105'000 people equivalent) was the first WWTP in Switzerland to implement a long-term full-scale ozonation. Differing specific ozone doses in the range of 0.35-0.97 g O_3/g DOC were applied to determine the adequate ozone dose to fulfill the requirements of the Swiss water protection act. Based on this assessment, a specific ozone dose of 0.55 g O_3/g DOC is recommended at this plant to ensure an average abatement of the twelve selected indicator substances by ≥80% over the whole treatment. A monitoring of 550 substances confirmed that this dose was very efficient to abate a broad range of micropollutants by >79% on average. After ozonation, an additional biological post-treatment is required to eliminate possible negative ecotoxicological effects generated during ozonation caused by biodegradable ozonation transformation products (OTPs) and oxidation by-products (OBPs). Three biological treatments (sand filtration, moving bed, fixed bed) and granular activated carbon (GAC, fresh and pre-loaded) filtration were evaluated as post-treatments after ozonation. In parallel, a fresh GAC filter directly connected to the effluent of the secondary clarifier was assessed. Among the three purely biological post-treatments, the sand filtration performed best in terms of removal of dissolved organic carbon (DOC), assimilable organic carbon (AOC) and total suspended solids (TSS). The fresh activated carbon filtration ensured a significant additional micropollutants abatement after ozonation due to sorption. The relative abatement of the indicator substances ranged between 20-89% after 27'000 bed volumes (BV) and was still substantial at 50'000 BV. In an identical GAC filter running in parallel and being fed with the effluent of the secondary clarifier, the elimination was less efficient. Seven primary OTPs (chlorothiazide and six *N*-oxides) formed during ozonation could be quantified thanks to available reference standards. Their concentration decreased with increasing specific ozone doses with the concomitant formation of other OTPs. The seven OTPs were found to be stable compounds and were not abated in the biological post-treatments. They were sorbed in the fresh GAC filter, but less

46 efficiently than the corresponding parent compounds. Two OBPs, bromate (BrO_3^-) and *N*-

47 nitrosodimethylamine (NDMA), were formed during ozonation but did not exceeded 5 µg/L for bromate

48 and 30 ng/L for NDMA at the recommended specific ozone dose of 0.55 g O_3/g DOC. NDMA was well

49 abated in all post-treatments (minimum 41% during fixed bed filtration, maximum 83% during fresh

50 GAC filtration), while bromate was very stable as expected.

INTRODUCTION

More than 100'000 compounds are registered today in Europe (European Chemical Agency 2017), including pharmaceuticals, personal care products, food additives, and industrial chemicals. A large number of them are frequently observed as persistent compounds in surface waters in levels of ng/L-µg/L (Petrie et al. 2014, Richardson and Kimura 2016). Therefore, sensitive species in the aquatic ecosystem may be adversely affected by, *e.g.*, a damage of the nervous systems, feminization and disruption of reproduction, or inhibition of photosynthesis (Stalter et al. 2013). Furthermore, micropollutants in surface waters and in groundwaters can contaminate the drinking water resources (Lopez et al. 2015).

Many micropollutants observed in water bodies originate from WWTP discharges, where polar micropollutants are generally poorly abated by conventional treatments (Loos et al. 2013), as WWTPs are not designed to eliminate micropollutants. The task of conventional WWTPs is to remove nutrients (inorganic nitrogen and total phosphorus), suspended solids and to reduce the biological and chemical oxygen demand (BOD_5 and COD, respectively) (Ternes et al. 2017).

In Switzerland, a new water protection act entered into force as of January 2016 with the objective to improve surface water quality by reducing the load of micropollutants from WWTPs. Within the next twenty years, about 100 of the 700 existing Swiss WWTPs will have to implement an advanced treatment step for micropollutant abatement, following four criteria: (i) large WWTPs to significantly reduce the load; (ii) WWTPs in the catchment of lakes; (iii) WWTPs at rivers with a high fraction of wastewater to protect ecosystems; and (iv) WWTPs at surface waters which serve as drinking water resources.

The aim is to remove organic micropollutants by 80% on average over the whole WWTP from influent to effluent (Eggen et al. 2014). To ensure the efficiency of the upgraded wastewater treatment, the Swiss Federal Office of Environment (FOEN) has established a shortlist of 12 indicator substances (SI, Table S1), which must be abated on average by 80% (FOEN 2017). The 12 compounds were specifically chosen as non-easily biodegradable substances and are therefore normally not well removed during conventional wastewater treatments.

78 Adsorption by powdered activated carbon (PAC) and ozonation are currently the recommended

79 technologies that lead cost-efficiently to a significant abatement of the micropollutant load and toxicity

80 (Hollender et al. 2009, Logar et al. 2014, Margot et al. 2013, Schindler Wildhaber et al. 2015). Besides,

81 a treatment with granular activated carbon filtration has been recently considered as a potential

82 alternative and is already applied on a full-scale WWTP in Germany (Benstoem et al. 2017).

83 Ozone reacts quickly with electron-rich moieties, *e.g.*, olefins, tertiary amines, thioethers and activated

84 aromatics (von Sonntag and von Gunten 2012), while hydroxyl radicals (•OH), which are formed from

85 self-decomposition of ozone (Hoigné and Bader 1975, Staehelin et al. 1984, Staehelin and Hoigné

86 1982), react additionally with alkanes, amides and non-activated aromatic compounds (Buxton et al.

87 1988). If the mechanism and the kinetics of the reactions of a substance or moiety with ozone are

88 known, the possible OTPs and the rate of abatement of a substance can in principle be predicted (Hübner

89 et al. 2015, Lee et al. 2017, Lee and von Gunten 2016, von Sonntag and von Gunten 2012). Even though

90 there is a lot of mechanistic information available, there are still significant knowledge gaps on certain

91 functional groups.

92 Furthermore, ozonation may yield oxidation/disinfection by-products (OBPs) by reaction of ozone and

93 hydroxyl radicals with the different components of the water matrix. Some OBPs such as BrO_3^- and

94 nitrosamines, *e.g., N*-nitrosodimethylamine (NDMA), are known to be (potential) human carcinogens

95 (Kurokawa et al. 1990, Tricker and Preussmann 1991). Therefore, the formation of these OBPs needs to

96 be minimized during ozonation. In Switzerland, the formation of BrO_3^- and NDMA during ozonation

97 needs to be assessed according to a recently introduced test procedure to evaluate the treatability of

98 wastewater with ozone (Schindler Wildhaber et al. 2015). Bromate is formed from the successive

99 oxidative reactions of bromide (Haag and Hoigné 1983, von Gunten and Hoigné 1994) present in water

100 bodies and wastewaters in µg/L-mg/L levels (Soltermann et al. 2016). The main bromide sources in

101 Switzerland are from wastewaters discharged from municipal waste incinerators, industrial landfills and

102 chemical industries (Soltermann et al. 2016). A bromate drinking water standard/guideline value for

103 BrO_3^- was set to 10 µg/L (Commission Directive 2003, U.S. EPA 2006, WHO 2011) and acute and

104 chronic environmental quality standards (EQS) of 50 µg/L were proposed by the Ecotox Centre Eawag-

105 EPFL (Ecotox Center 2017). NDMA is formed during ozonation of precursors such as hydrazines and

106   sulfamides (yield >50%) (Kosaka et al. 2009, Krasner et al. 2013, Lim et al. 2016, Schmidt and Brauch

107   2008, von Gunten et al. 2010). The NDMA guideline value in drinking water was set to 100 ng/L by

108   WHO (2008) and even lower values of 10 ng/L are proposed in countries such as the USA and Germany

109   (California Department of Public Health 2010, Massachusetts Department of Environmental Protection

110   2004, Planas et al. 2008).

111   Some toxicity endpoints may increase after ozonation due to the formation of aldehydes and organic

112   acids. It has been recently concluded that OBPs are toxicologically probably more relevant than OTPs

113   (Lee and von Gunten 2016). However, toxicity was found to decrease again after biological post-

114   treatments (Stalter et al. 2010a, Stalter et al. 2010b), because of the biodegradability of toxic OBPs and

115   OTPs. Therefore, a biological post-treatment is required with the goal to eliminate biodegradable, toxic

116   OTPs and OBPs leading to negative ecotoxicological effects.

117   The present study aims at evaluating a full-scale wastewater treatment with installed ozonation and post-

118   treatment. To this end, three purely biological post-treatments (a sand filter, a moving bed reactor, and a

119   fixed bed reactor) were investigated as well as GAC filtration with additional sorption capacity (a fresh

120   and a pre-loaded GAC filter). Additionally, a fresh GAC filter was run in parallel directly with the

121   secondary effluent for comparison. The effects of the differing treatment steps were assessed on the

122   chemical (current paper) and biological (Kienle et al. in preparation) wastewater quality. Additionally,

123   non-target peaks across the wastewater treatment train were characterized (Schollee et al. 2017). Here,

124   the abatement of 43 micropollutants frequently detected in wastewater, including the indicator

125   substances, was first investigated at various ozone doses to determine the required specific ozone dose to

126   abate the indicator substances by 80% on average, as requested by the new Swiss water protection act.

127   Thereafter, the abatement of micropollutants from an exhaustive list of 550 substances was studied at the

128   optimum specific ozone dose for an overall evaluation of the advanced treatment. With a target and

129   suspect screening approach, the formation of known OTPs and the OBPs BrO_3^- and NDMA during

130   ozonation was investigated. The fate of micropollutants, OTPs and OBPs over the differing biological

131   post-treatments and in the GAC filters was studied and compared.

MATERIAL AND METHODS

Wastewater treatment plant

Neugut WWTP (Dübendorf, Switzerland) (Fig. S1, Text S1) treats wastewater of about 50'000 persons and 105'000 people equivalent (maximum capacity of 150'000 people equivalent) with an approximate industrial contribution of 50% in COD load (mainly from food industries). The flow in the treatment plant ranges between 13'000 and 57'000 m^3/day with an average of 19'000 m^3/day at dry weather conditions. The wastewater treatment originally consisted of a primary clarifier, a conventional activated sludge treatment with a secondary clarifier and a sand filtration. The average sludge retention time in the conventional biological treatment is about 13 days and the hydraulic retention time (HRT) is 18 h (without settling tank). Dissolved organic carbon (DOC) after the conventional biological treatment was 3.5 – 6 mg/L and nitrite below 0.04 mg N/L; other quality parameters are given in Table S2). Although the industrial contribution is relatively high in this WWTP, the quality of the secondary effluent is similar to typical Swiss domestic wastewater (Schindler Wildhaber et al. 2015, Soltermann et al. 2016). In 2014, an ozonation reactor (V = 530 m^3, divided in 6 reactors in series) was installed between the secondary clarifiers and the four sand filters (4x31.5 m^3 operated in parallel, quartz sand, 0.7-2.0 mm granular size with an average empty bed contact time (EBCT) of 10 min). Ozone is produced with two ozone generators (OZAT-CFV5, Ozonia, Dübendorf, Switzerland) from oxygen fed by a liquid oxygen tank. The ozone reactor has an average HRT of 43 minutes at dry weather conditions and of 13 minutes at maximum flow. Furthermore, 4 post-treatments, *i.e.,* a moving bed (MB, 300 L, average EBCT 21 min), a fixed bed (FB, 220 L, average EBCT 25 min), a fresh GAC filter ($GAC_{fresh/OZO}$, 77 L, *i.e.* 34.65 kg Cyclecarb 401, density 450 g/L, 0.425-2.36 mm granular size, average EBCT 14.5 min) and a pre-loaded GAC filter ($GAC_{loaded/OZO}$, 85 L, *i.e.* 40.8 kg Norit GCN 830, density 480 g/L, 1.4-2.36 mm granular size, average EBCT 18 min) were installed in pilot-scale for a comparison with sand filter, run flow proportionally at dry weather water flow. An identical fresh GAC filter ($GAC_{fresh/bio}$, 77 L, Cyclecarb 401, 0.425-2.36 mm granular size, average EBCT 14 min) was installed directly after the secondary clarifier. More details about the differing reactors and the operational parameters are given in Text S1.

Wastewater sampling and chemical analyses

Wastewater sampling

Samples were taken at the effluent of the primary clarifier (WWTP-INF), of the secondary clarifier (BIO-EFF), of the ozonation reactor (OZO-EFF) and of the post-treatments mentioned above (SF-EFF, MB-EFF, FB-EFF, GAC$_{fresh/bio}$-EFF, GAC$_{fresh/OZO}$-EFF and GAC$_{loaded/OZO}$-EFF). On 37 sampling days over a 10-month period (September 2014-June 2015), samples (1 L, 24-h flow proportional) were collected from all sampling points in intervals from 1 day at the beginning to 5 weeks at the end. Note that WWTP-INF was always sampled 1 day before the others to account for the HRT of the plant.

Four sampling campaigns (September/October 2014) were conducted collecting 24-h flow proportional samples (1 L) at WWTP-INF, BIO-EFF, OZO-EFF and SF-EFF on 3 consecutive dry days at differing ozone doses of 2.0 (October 3-5), 3.0 (September 24-26), 4.0 (September 11-13) and 4.9 mg O$_3$/L (September 15-17), corresponding to specific ozone doses of 0.35±0.02, 0.54±0.04, 0.67±0.02 and 0.97±0.07 g O$_3$/g DOC, respectively. Thereafter, ozonation was run at 2.7 mg/L ozone (about 0.54 g O$_3$/g DOC), the ozone dose recommended for continuous full-scale application at the WWTP Neugut. In February and March 2015, two sampling campaigns (48-h flow proportional samples for all sampling points) were carried out to screen for 550 environmentally relevant micropollutants.

The samples were collected at 4°C and were maintained at this temperature until analyses. If chemical analyses could not be carried out within a week, the samples were frozen at -20°C and thawed just before sample preparation.

Quantification of 51 micropollutants and OTPs using an automatized extraction (online SPE-LC-HRMS, method I)

The concentration of 43 micropollutants (acesulfame, aliskiren ,amisulpride, atenolol, atenolol acid, azithromycin, benzotriazole, bezafibrate, candesartan, carbamazepine, carbendazim, cetirizine, citalopram, clarithromycin, DEET, diclofenac, diuron, eprosartan, fexofenadine, gabapentin, hydrochlorothiazide, iopromide, irbesartan, lamotrigine, levetiracetam, losartan, mecoprop, metoprolol, methylbenzotriazole, N4-acetyl-sulfamethoxazole, oxazepam, phenazone, primidone, ranitidine,

186 sucralose, sulfamethoxazole, telmisartan, tramadol, triclosan, trimethoprim, valsartan, valsartan acid,

187 venlafaxine, including parent compounds and metabolites, Table S5) and eight OTPs with reference

188 standards (4'-/5-hydroxydiclofenac, amisulpride *N*-oxide, cetirizine *N*-oxide, clarithromycin *N*-oxide,

189 fexofenadine *N*-oxide, chlorothiazide, tramadol *N*-oxide and venlafaxine *N*-oxide) was determined

190 according to Jeon et al. (2013) (details of method I are presented in Text S2, SI). Shortly, samples were

191 filtered through 2 glass microfiber filters, *i.e.,* GF/D (top, 2.7 µm pore size, Whatman) and GF/F

192 (bottom, 0.7 µm pore size, Whatman). After dilution and spiking with internal standards (IS), the

193 samples were extracted by online solid-phase extraction with a combination of four adsorbents (Oasis

194 HLB and a Strata-X-AW/Strata-X-CW/ENV+ mixture). The extracts were directly analyzed by liquid

195 chromatography (Atlantis T3 column, Waters), coupled to high-resolution mass spectrometry (Q-

196 Exactive, ThermoScientific). Details on quality control measurements (limit of quantification and

197 recoveries) are given in Table S5.

198 Additionally to the eight OTPs mentioned above, other OTPs, presented in the literature (Table S6),

199 without reference standards were screened with their exact mass of the protonated or deprotonated

200 molecular ion. MS/MS spectra from fragmentation did not show high enough intensities for a

201 confirmation.

202 *Quantification of 550 micropollutants using a manual extraction (offline SPE-LC-HRMS, method II)*

203 The fate of 550 environmentally-relevant chemicals was investigated with an offline SPE-LC-HRMS

204 method, adapted from Kern et al. (2009) and described in Text S3, SI. This list included 240

205 pharmaceuticals, 234 pesticides, 38 industrial chemicals and 60 biological TPs. Their physical-chemical

206 properties cover a wide range of molecular weight (120-915 g/mol), log K_{ow} (-2.2 − 5.7), and charge at

207 circumneutral pH (50% neutral, 50% ionic). In brief, 1 L of sample was filtered (as described above) and

208 spiked with IS. The samples were then extracted through a multilayered solid-phase cartridge, consisting

209 of ENVI-Carb activated carbon (bottom), Strata-X-AW/Strata-X-CW/ENV+ mixture (middle layer), and

210 Oasis HLB (top layer). Chemical analyses were carried out with the same LC-HRMS system as

211 described above.

212

Determination of bromide and bromate

For the quantification of bromide and bromate, 1 mL samples (24- and 48-h flow proportional, September 2014-June 2015, *n*=30) were filtered with a 13-mm syringe filter (regenerated cellulose membrane, 0.45μm porosity, Infochroma AG), diluted 100 times with ultrapure water and stored at +4°C until analyses. Bromide and bromate were separated by capillary ion chromatography (Thermo Dionex ICS-4000) using an anion-exchange IC column (IonPac AS19-4μm, Dionex) and detected by a modified tandem mass spectrometry (Thermo TSQ-Vantage) to reach lower detection limit (Shah et al. 2015). The quantification limits of bromide and bromate in wastewater were 25 μg/L and 2 μg/L, respectively, for the 100-fold dilution (0.25 and 0.02 μg/L, respectively, in ultrapure water without dilution).

Determination of N-nitrosodimethylamine (NDMA) by LC-HRMS/MS

The concentrations of NDMA were determined in several samples collected flow proportionally in September-October 2014 (*n*=2, 24-h composite; n=3 72-h composite) and in February-April 2015 (*n*=3, 48-h composite) with LC-HRMS/MS according to a method described previously (Krauss and Hollender 2008), obtaining a limit of quantification at 5 ng/L (Text S5).

Determination of second-order rate constants

For some relevant compounds without available kinetic data, apparent second-order rate constants at pH 7 ($k_{O3,pH7}$) were determined: 1.5×10^5 M^{-1} s^{-1} for amisulpride, 4.9×10^5 M^{-1} s^{-1} for eprosartan, 2.1×10^5 M^{-1} s^{-1} for losartan, 1.2×10^5 M^{-1} s^{-1} for telmisartan, 560 M^{-1} s^{-1} for candesartan, and 24 M^{-1} s^{-1} for irbesartan (See Text S4 for details). These and other rate constants from literature are compiled in Table S4.

234   **RESULTS AND DISCUSSION**

235   **Micropollutant abatement.**

236   *Fate of micropollutants during ozonation and over the whole wastewater treatment*

237   The abatement of 43 wastewater relevant micropollutants (Table 1, parent compounds and metabolites)

238   in biological treatment with conventional activated sludge (BIO) and during ozonation (OZO) with 4

239   specific ozone doses is presented in Table 1 (concentrations can be found in Table S5).

240   During the biological treatment, the abatements were relatively constant for single compounds over the

241   sampling period (n=12), but varied considerably between -131% and >99% among them (SI, Table S8).

242   A limited number of compounds (acesulfame, bezafibrate, DEET, eprosartan, levetiracetam, N4-acetyl-

243   sulfamethoxazole, triclosan, trimethoprim and valsartan) were almost completely eliminated in

244   biological treatment (relative abatement >80%). Half of the compounds ($n=22$) were not significantly

245   eliminated (relative abatement <20%). Some investigated compounds, *e.g.,* lamotrigine, phenazone and

246   the TP valsartan acid, were even significantly formed during this treatment step (negative elimination or

247   detection of the compound only after BIO). For lamotrigine, this is in agreement with recent studies

248   (Bollmann et al. 2016, Zonja et al. 2016) which showed that non-conjugated and conjugated forms

249   (mainly as glucuronide) enter the WWTPs. In conventional biological treatment, conjugated forms were

250   cleaved to lamotrigine, which is relatively stable. Therefore, its concentration significantly increases,

251   typically from about 300 to 800 ng/L (Table S5). Phenazone was also found to be formed from other

252   pharmaceuticals (from metamizole or human metabolites) during biological treatment (Gros et al. 2010,

253   Kovalova et al. 2012, Prasse et al. 2010), and valsartan acid was identified as a biodegradation product

254   of valsartan (Kern et al. 2010).

255   During ozonation, the extent of abatement increased with increasing ozone doses (Table 1 and Fig. S4).

256   At the lowest specific ozone dose of 0.35 g O_3/g DOC, 20 out of the 43 substances were abated by less

257   than 80%. However, this number decreased significantly to 13, 11 and 5 with higher specific ozone

258   doses of 0.54 g O_3/g DOC, 0.67 g O_3/g DOC and 0.97 g O_3/g DOC, respectively. Substances with high

259   reactivity with ozone at circumneutral pH (Table S4), *e.g.,* diclofenac, carbamazepine,

260   hydrochlorothiazide, sulfamethoxazole and tertiary amines such as cetirizine, fexofenadine and

261 tramadol, were very well abated (>80%) even at 0.35 g O_3/g DOC. For higher specific ozone doses,

262 these compounds were abated by >93% and not detected anymore (<LOQ). Compounds with low

263 apparent second-order rate constant for the reaction with ozone at circumneutral pH (*i.e.,* $k_{O3,pH7}$ <10 M^{-1}

264 s^{-1}), for which the reaction with •OH is the predominant abatement pathway, *e.g.,* iopromide, lamotrigine

265 and sucralose, were only slightly abated (<30%) at a specific ozone dose of 0.35 g O_3/g DOC. The

266 concentration of these compounds was reduced by less than 71% at the highest specific ozone dose (0.97

267 g O_3/g DOC).

268 Other studies, presented in Table S9, showed similar abatements for comparable specific ozone doses

269 (Kovalova et al. 2013, Lee et al. 2013, Reungoat et al. 2010, Ternes et al. 2017) or slightly lower

270 (Hollender et al. 2009, Margot et al. 2013). In the latter two studies, the abatement of compounds

271 predominantly reacting with •OH (methylbenzotriazole, benzotriazole, gabapentine, iopromide,

272 irbesartan, mecoprop, oxazepam, primidone and valsartan) was particularly low. These differences may

273 be attributed to varying wastewater qualities, *e.g.,* a differing composition of the dissolved organic

274 matter leading to a lower •OH formation (Schindler Wildhaber et al. 2015) or a higher alkalinity (HCO_3^-

275 being a •OH scavenger (Buxton and Elliot 1986) in these wastewaters. In the study by Margot et al.

276 (2013), the presence of nitrite in high concentrations (average value of 0.4 mg NO_2-N/L, compared to

277 0.01-0.04 mg NO_2-N/L level in other studies) explains at least partially the lower abatements. Nitrite

278 scavenges ozone rapidly in a ratio of about 1 g O_3 per g NO_2^- (1:1 molar ratio), therefore, a specific

279 ozone dose of 0.83 g O_3/g DOC corresponds to an effective specific dose of 0.63 g O_3/g DOC (DOC 7.3

280 mg /L) at 1.4 mg NO_2^-/L (*i.e.,* 0.4 mg NO_2-N/L).

281 Over the entire treatment, including biological treatment and ozonation (BIO+OZO), most of the

282 compounds were abated by >80% at a specific ozone dose of 0.35 g O_3/g DOC, except 10 compounds

283 (Table 1). At specific ozone doses of 0.54 g O_3/g DOC, 0.67 g O_3/g DOC or 0.97 g O_3/g DOC, 6, 7 or 2

284 compounds, respectively, were not abated >80%.

285 To comply with the guidelines established by the Swiss authorities for the evaluation of advanced

286 wastewater treatment, 12 indicator substances need to be eliminated by 80% on average over the whole

287 treatment chain (marked in Table 1, see Table S1 and Table S8 for more details). These 12 indicator

288 substances were abated by 2-44% during biological treatment, except benzotriazole (64±4%).

289   Benzotriazole is often poorly abated in biological treatment (Herzog et al. 2014, Liu et al. 2011), except

290   in some specific WWTPs (Mazioti et al. 2015), for unknown reasons. The average abatement increased

291   to $85 \pm 3\%$ when the biological treatment was followed by a low specific ozone dose (0.35 g O_3/g DOC)

292   and even up to >94% when the specific ozone dose was 0.54 g O_3/g DOC. Note that these 12 substances

293   are not abated in sand filtration, as will be discussed in more detail below.

294   Considering these results, a combination of biological treatment and a specific ozone dose of 0.40 g O_3/g

295   DOC (1.5-2.5 mg O_3/L) is sufficient to reach an average abatement of >80% of the 12 indicator

296   substances as requested by the Swiss water protection act (FOEN 2017). However, to compensate a

297   potential nitrite peak concentration of up to 0.7 mg NO_2^-/L (*i.e.,* 0.2 mg NO_2-N/L, while the usual nitrite

298   concentration at WWTP Neugut is 0.02-0.04 mg NO_2-N/L), a specific ozone dose of 0.55 g O_3/g DOC

299   (2.0-3.3 mg O_3/L) is recommended for routine operation at this site.

300   Two sampling campaigns (48-h flow proportional samples) were carried out to investigate the abatement

301   of an exhaustive list of 550 micropollutants over the whole treatment chain at a specific ozone dose of

302   0.55 g O_3/g DOC (Fig. 1, Fig. S5, Table S7). In WWTP-INF, 175 compounds were found (>LOQ) with

303   a total concentration of 371 µg/L. Most abundant were pharmaceuticals (133 µg/L), caffeine (130 µg/L)

304   and food additives (85 µg/L) in the influent, while pesticides and biocides were detected only in very

305   low concentrations (*ca.* 1 µg/L). Being aware that the sampling was done in winter, it may not be

306   representative for the whole year. In biological treatment, the total concentration of target compounds

307   decreased by 85% to 54 µg/L, although the number of quantified compounds increased to 204

308   substances. This increase can be explained by the formation of biological transformation products that

309   were included in the target list, and the lower LOQ in BIO-EFF compared to WWTP-INF due to

310   differing dilutions used for the analyses and due to higher matrix effects in WWTP-INF (see Text S3).

311   The 4 most abundant compounds in WWTP-INF, *i.e.,* caffeine, cyclamate, metformin and paracetamol

312   (total concentration 260 µg/L), were eliminated by 99%. Without the contribution of these 4 compounds,

313   the abatement of the remaining micropollutant load drops from 85% to 54% during the biological

314   treatment. After ozonation, the total concentration was still 23 µg/L, corresponding to an abatement of

315   the micropollutants load by 58%. In sand filtration, no significant elimination was observed, and over

316   the whole plant, the total load decreased by 94%. Five compounds (acesulfame, sucralose, metformin,

317   iopromide and tris(2-chloropropyl)phosphate) were found in concentrations >0.9 µg/L in OZO-EFF. All

318   were poorly abated during ozonation (<50%). Alternatively, the abatement can be considered for each

319   single substance and an average can be calculated. As a result, the average abatement of all substances

320   (taking a zero abatement for all substances with negative abatement into account) over the biological

321   treatment is 34% (median 22%), during ozonation >67% (median >74%), and over the whole WWTP,

322   with and without sand filter, >79% (median >89%) (Fig. 1). Due to the fact that 64 substances (out of

323   147) were not detected anymore after ozonation, only a minimal abatement relative to the LOQ could be

324   calculated in these cases.

	0.35±0.02 g O$_3$/g DOC			0.54±0.05 g O$_3$/g DOC			0.67±0.03 g O$_3$/g DOC			0.97±0.07 g O$_3$/g DOC	
	BIO	OZO	BIO+OZO	BIO	OZO	BIO+OZO	BIO	OZO	BIO+OZO	BIO	OZO
Acesulfame	95 ± 1	39 ± 5	97 ± 1	90 ± 8	59 ± 9	96 ± 3	95 ± 1	70 ± 8	98 ± 1	88 ± 5	>90 ± 4
Aliskiren	25 ± 4	>84 ± 1	>88 ± 1	23 ± 22	>93 ± 1	>95 ± 1	7 ± 12	>81 ± 1	>82 ± 3	8 ± 11	>92 ± 3
Amisulpride†	2 ± 14	91 ± 1	91 ± 2	3 ± 16	>98 ± 1	>98 ± 1	-1 ± 13	>95 ± 1	>95 ± 1	3 ± 8	>98 ± 1
Atenolol	75 ± 3	70 ± 2	92 ± 1	70 ± 5	92 ± 3	98 ± 1	72 ± 5	93 ± 5	98 ± 1	71 ± 4	>93 ± 1
Atenolol acid	76 ± 2	70 ± 3	93 ± 1	72 ± 3	91 ± 3	98 ± 1	67 ± 4	>92 ± 4	>97 ± 1	69 ± 3	>98 ± 1
Azithromycin	8 ± 28	>90 ± 1	>90 ± 3	n.m.2	>54 ± 3	n.m.	25 ± 14	>88 ± 2	>91 ± 3	23 ± 15	>95 ± 1
Benzotriazole†	66 ± 3	52 ± 1	83 ± 1	62 ± 7	74 ± 3	90 ± 3	63 ± 6	80 ± 7	93 ± 2	64 ± 3	91 ± 4
Bezafibrate	96 ± 1	>62 ± 5	>98 ± 1	>95 ± 2	>75 ± 1	>99 ± 1	>93 ± 2	n.m.1	>97 ± 1	>94 ± 1	>24^Δ
Candesartan†	0 ± 16	63 ± 1	63 ± 6	1 ± 12	82 ± 3	82 ± 5	-24 ± 20	85 ± 6	81 ± 6	-17 ± 19	94 ± 3
Carbamazepine†	-16 ± 12	95 ± 1	94 ± 1	-14 ± 19	>98 ± 1	>98 ± 1	-33 ± 23	>98 ± 1	>98 ± 1	-24 ± 8	>98 ± 1
Carbendazim	8 ± 18	82 ± 2	83 ± 5	-1 ± 23	>94 ± 3	>94 ± 4	7 ± 16$^\#$	>93 ± 5	>89 ± 8$^\#$	-28 ± 50	>89 ± 4
Cetirizine	6 ± 12	92 ± 1	92 ± 2	-9 ± 12	>93 ± 1	>92 ± 1	-25 ± 25	>95 ± 1	>94 ± 1	-19 ± 10	>95 ± 1
Citalopram†	5 ± 4$^\#$	91 ± 3	89 ± 4$^\#$	4 ± 4	>96 ± 3	>96 ± 3	-8 ± 2	>94 ± 1	>93 ± 1	4 ± 8	>97 ± 1
Clarithromycin†	51 ± 2	93 ± 2	97 ± 1	28 ± 19	>95 ± 1	>96 ± 1	45 ± 6	>94 ± 1	>97 ± 1	52 ± 8	>97 ± 1
DEET	96 ± 1	49 ± 9	98 ± 1	>90 ± 3	65 ± 1	>95 ± 2	97 ± 1	52 ± 18	99 ± 1	97 ± 1	70 ± 15
Diclofenac†	22 ± 8	96 ± 1	97 ± 1	23 ± 8	100 ± 1	100 ± 1	11 ± 10	>99 ± 1	>99 ± 1	13 ± 18	>99 ± 1
Diuron	0 ± 30	64 ± 2	64 ± 10	-7 ± 7	>84 ± 8	>83 ± 10	-5 ± 14	>84 ± 6	>84 ± 4	-40 ± 72$^\#$	>90 ± 6
Eprosartan	98 ± 1	>66 ± 3	>99 ± 1	>93 ± 2	n.m.1	>97 ± 1	>97 ± 1	>67 ± 7	>99 ± 1	>88 ± 5	n.m.1
Fexofenadine	13 ± 16	83 ± 3	85 ± 6	9 ± 4	>94 ± 1	>95 ± 1	12 ± 12	>96 ± 3	>97 ± 2	-1 ± 12	>91 ± 1
Gabapentin	44 ± 10	44 ± 4	69 ± 6	43 ± 6	55 ± 4	75 ± 1	37 ± 5	63 ± 10	77 ± 6	44 ± 5	75 ± 6
Hydrochlorothiazide†	9 ± 13	86 ± 2	87 ± 4	13 ± 9	>98 ± 2	>98 ± 2	-2 ± 17	>97 ± 3	>97 ± 2	1 ± 10	>99 ± 1
Iopromide	72 ± 5	28 ± 1	80 ± 4	70 ± 8	43 ± 3	83 ± 5	53 ± 20	53 ± 6	78 ± 8	64 ± 8$^\#$	65 ± 1$^\#$
Irbesartan†	17 ± 18	57 ± 1	64 ± 8	15 ± 15	75 ± 3	78 ± 5	2 ± 20	79 ± 4	79 ± 6	0 ± 25	89 ± 4
Lamotrigine	-125 ± 31	37 ± 1	-42 ± 18	-128 ± 10	50 ± 2	-15 ± 4	-140 ± 30	57 ± 7	-3 ± 21	-132 ± 5	71 ± 6
Levetiracetam	99 ± 1	>66 ± 34	100 ± 1	98 ± 1	>43 ± 36	>99 ± 1	>99 ± 1	n.m.1	100 ± 1	>99 ± 1	n.m.1
Losartan	71 ± 2	93 ± 1	98 ± 1	68 ± 5	>98 ± 1	>99 ± 1	66 ± 5	>98 ± 1	>99 ± 1	67 ± 4	>98 ± 1

Substance											
Mecoprop	-5 ± 2[#]	59 ± 2	56 ± 1[#]	14 ± 7[#]	77 ± 2	81 ± 4[#]	5 ± 30	82 ± 7	84 ± 5	9 ± 14[#]	>91 ± 3
Metoprolol†	41 ± 7	75 ± 2	85 ± 3	38 ± 5	94 ± 3	96 ± 2	37 ± 8	94 ± 5	96 ± 3	38 ± 4	>99 ± 1
Methylbenzotriazole†,*	45 ± 22	66 ± 3	81 ± 9	61 ± 4	89 ± 4	96 ± 2	2 ± 22	90 ± 1	90 ± 7	28 ± 12	98 ± 1
N4-Acetyl-Sulfamethoxazole	>98 ± 1	n.m.1	>99 ± 1	>98 ± 1	n.m.1	>99 ± 1	>98 ± 1	n.m.	>99 ± 1	>95 ± 2	n.m.1
Oxazepam	5 ± 17	55 ± 1	57 ± 7	10 ± 10	73 ± 3	75 ± 5	-13 ± 22	77 ± 5	74 ± 6	-10 ± 9	88 ± 4
Phenazone	n.m.2	>91 ± 1	n.m.1	n.m.2	>92 ± 1	n.m.1	n.m.2	>92 ± 1	n.m.1	n.m.2	>81 ± 4
Primidone	19 ± 12	48 ± 3	58 ± 5	15 ± 17	66 ± 1	72 ± 6	14 ± 14	70 ± 10	75 ± 7	-4 ± 8	86 ± 5
Ranitidine	82 ± 1	>74 ± 2	>95 ± 1	79 ± 4	>80 ± 4	>96 ± 1	66 ± 16	>71 ± 2	>90 ± 5	77 ± 2	>53 ± 19
Sucralose	9 ± 20	21 ± 2	28 ± 14	13 ± 13	27 ± 1	36 ± 10	-9 ± 17	38 ± 4	32 ± 12	-4 ± 13	46 ± 4
Sulfamethoxazole	55 ± 3	85 ± 2	93 ± 1	46 ± 6	>97 ± 1	>98 ± 1	31 ± 6	>97 ± 1	>98 ± 1	34 ± 2	>95 ± 3
Telmisartan	15 ± 3	66 ± 1	71 ± 1	3 ± 16	86 ± 3	86 ± 4	-24 ± 27	88 ± 5	84 ± 8	-7 ± 18	>94 ± 1
Tramadol**	0 ± 11	91 ± 1	90 ± 3	2 ± 7	98 ± 1	98 ± 1	-5 ± 11	>98 ± 1	>98 ± 1	-6 ± 10	>98 ± 1
Triclosan	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	n.m.1	>56 ± 1	n.m.1	n.m.1	n.m.1
Trimethoprim	>89 ± 4	>59 ± 6	>95 ± 1	85 ± 6	>61 ± 15	>95 ± 1	75 ± 6	>58 ± 4	>90 ± 1	83 ± 3	>79 ± 3
Valsartan	94 ± 1	52 ± 3	97 ± 1	93 ± 2	69 ± 3	98 ± 1	96 ± 1	68 ± 8	99 ± 1	93 ± 1	>86 ± 3
Valsartan acid	n.m.2	49 ± 1	n.m.1	n.m.2	67 ± 1	n.m.1	n.m.2	71 ± 5	n.m.1	n.m.2	76 ± 8
Venlafaxine†	4 ± 15	84 ± 2	84 ± 5	9 ± 10	>97 ± 2	>97 ± 2	-12 ± 17	>96 ± 3	>96 ± 2	1 ± 5	>96 ± 1
Average of the 12 indicator substances†	17 ± 8	79 ± 1	85 ± 3	20 ± 7	>91 ± 2	>94 ± 2	7 ± 8	>92 ± 3	>93 ± 2	14 ± 9	>96 ± 1

330 n.m.1: abatement not measurable because the concentrations at the inlet and at the outlet of the reactor were both <LOQ.
331 n.m.2: abatement not measurable because the concentration at the inlet is <LOQ; abatement has a negative value.
332 *: methylbenzotriazole represents the sum of 4- and 5-methylbenzotriazole, which co-elute under the analytical conditions.
333 **: tramadol represents the sum of tramadol and o-desmethyl-venlafaxine, which are isobaric compounds that co-eluted under the analytical conditions.
334 #: abatement was determined for only 2 samples due to high fluctuations of concentrations in one sample.
335 Δ: abatement was determined for only 1 sample due to high fluctuations of concentrations in two samples.
336 †: the 12 indicator substances (**bold** in the table above) are amisulpride, benzotriazole, candesartan, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, irbesartan,
337 methylbenzotriazole, metoprolol and venlafaxine.
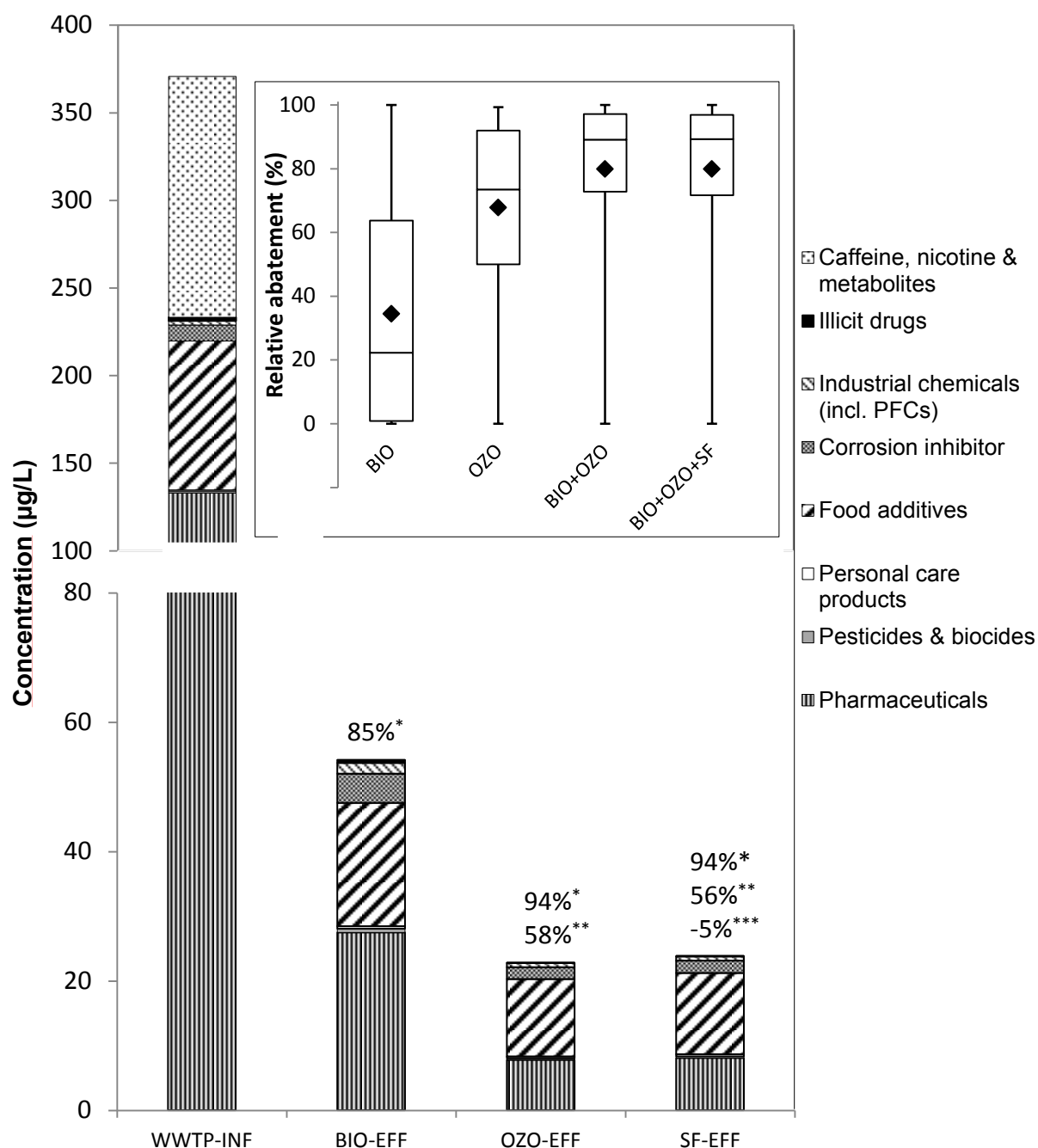
Fig. 1. Sum of concentrations of micropollutants at various WWTP sampling points (*n*=2, 48-h flow proportional samples, specific ozone dose 0.55 g O_3/g DOC, analyzed with method II; for sampling points see Fig. S1). *: abatement of total concentration relative to WWTP-INF (effluent of primary clarifier); **: abatement relative to BIO-EFF (effluent of conventional biological treatment); ***: abatement relative to OZO-EFF (effluent of ozonation reactor). Inset: Box-whisker plot depicting the distribution of calculated abatements for all substances (minimum, 25th percentile, median, 75th percentile, maximum and (♦) average) of micropollutants (analyzed with method II) during all treatment steps. Because nearly half of the compounds were not detected anymore after ozonation, the values given for OZO, BIO+OZO and BIO+OZO+SF represent minimal abatements relative to the LOQ. Negative abatements were taken into account as zero abatements.

Fate of micropollutants during the post-treatments after ozonation

376   Several post-treatments, *i.e.,* sand filtration (SF), moving bed (MB), fixed bed (FB), a fresh granular

377   activated carbon filter (GAC$_{fresh/OZO}$) and a pre-loaded granular activated carbon filter (GAC$_{loaded/OZO}$),

378   were evaluated for their capacity to abate residues of micropollutants still present after ozonation with

379   an ozone dose of 2.7 mg/L ozone (about 0.54 g O$_3$/g DOC). An additional fresh granular activated

380   carbon filter (GAC$_{fresh/BIO}$) was fed with secondary clarifier effluent for a comparison with GAC$_{fresh/OZO}$.

381   Amongst 20 micropollutants (including the indicator substances) frequently detected after ozonation in

382   concentrations >50 ng/L, none showed a significant relative abatement (all <16%) in the three solely

383   biologically active post-treatments, *i.e.,* sand filtration, moving bed and fixed bed (Fig. S8).

384   Similarly, a screening of the selected 550 substances showed that these 3 post-treatments do not

385   significantly impact the number (Fig. S5) and the total concentrations of the compounds detected in the

386   ozonated effluent (22.9 µg/L after OZO *vs.* 24.0 µg/L after SF, 23.5 µg/L after MB and 23.5 µg/L after

387   FB, Fig. S6). The average abatement did not exceed 5% in these biological post-treatments (Fig. S7).

388   Even the compounds abated by >50% during the conventional biological treatment (Table S8), *i.e.,*

389   acesulfame, atenolol, benzotriazole and valsartan, showed a low abatement of <7% in these three post-

390   treatments, due to shorter retention times (10-25 min) compared to the conventional biological treatment

391   (18 h).

392   The abatements in two identical fresh activated carbon filters, GAC$_{fresh/BIO}$ and GAC$_{fresh/OZO}$, was

393   investigated for four compounds with very good sorption on activated carbon (Group I, see Table S1 for

394   definition), two compounds with good sorption (Group II) and two compounds with poor sorption

395   ability (Group III). This grouping is in agreement with the abatement by ozone, and was based on results

396   from sorption to powdered activated carbon, because physical-chemical properties of charged, polar

397   micropollutants like logD$_{ow}$ are not sufficient to predict their sorption behavior (Kovalova et al. 2013). A

398   significant difference in the breakthrough of the compounds was observed. Group I compounds (Fig. 2a

399   and b) showed a much later breakthrough compared to the other compounds with weaker sorption

400   behavior (Fig. 2c and d). Surprisingly, benzotriazole from group II was relatively well abated, as

401   discussed later. In GAC$_{fresh/OZO}$, the breakthrough of Groups I, II, III (Fig. 2) and the 10 additional

402   substances telmisartan, valsartan, valsartan acid, primidone, atenolol, atenolol acid, gabapentin,

403 tramadol, lamotrigine, and oxazepam (Fig. S9-S10) usually occurred later than in GAC$_{fresh/BIO}$. For

404 instance, the abatement of group II/III compounds candesartan and sucralose dropped below 90% at

405 about 3'200 BV in GAC$_{fresh/BIO}$ but only at about 7'000 BV in GAC$_{fresh/OZO}$. As GAC$_{fresh/OZO}$ followed

406 ozonation, the concentrations of the micropollutants were lower and, at the same time, the composition

407 of the matrix is different. It was shown that the breakthrough is independent on micropollutant

408 concentration within certain limits (Zietzschmann et al. 2016). However, during ozonation, effluent

409 organic matter is transformed to smaller compounds, which are generally less aromatic, more

410 hydrophilic and charged, thereby exhibiting a poorer adsorbability on GAC. Measurements showed that

411 small neutral organic substances are further oxidized to charged small organic acids during ozonation

412 (Ramseier and von Gunten 2009, Zietzschmann et al. 2015). As a consequence, micropollutants in

413 ozonated wastewater have fewer competitors for adsorption sites compared to non-ozonated wastewater

414 and the breakthrough of micropollutants may occur later in ozonated wastewater.

415 To compare the two GAC filters, the average relative abatement of the indicator substances was

416 evaluated. Because some of the 12 indicator substances are present in too low concentrations after

417 ozonation to determine an appropriate abatement, only 6 were selected: 4 compounds from Group I

418 (diclofenac, hydrochlorothiazide, metoprolol, venlafaxine), and 2 compounds from Group II

419 (benzotriazole and candesartan). This selection criteria is also recommended by the Swiss legislation in

420 case of low inflow concentrations. An average relative abatement of >80% for the 6 selected indicator

421 substances could be kept up to 10'000 BV for GAC$_{fresh/BIO}$ and up to 15'000 BV for GAC$_{fresh/OZO}$ (Fig.

422 S11). At the two last sampling times for 22'000 and 28'000 BV, the sorption on GAC$_{fresh/BIO}$ increased

423 again. Currently, this effect cannot be explained and would require more investigations for a

424 clarification.

425 In the screening of the 550 substances, the decrease of total concentration in GAC$_{fresh/BIO}$ and

426 GAC$_{fresh/OZO}$ was comparable (47% in GAC$_{fresh/BIO}$ and 41% in GAC$_{fresh/OZO}$ at similar BV in the range of

427 11'000-17'000, Fig. S6). Similarly, the average abatement calculated from the abatement of the same

428 selection of substances was comparable for GAC$_{fresh/BIO}$ and GAC$_{fresh/OZO}$ (54% and 53%, respectively, at

429 the same BV) (Fig. S7).

430   The performance of $GAC_{fresh/BIO}$ can be used to evaluate the effectiveness of GAC filtration. Since this

431   GAC filter has a volume of 77 L and a filling of 34.65 kg GAC, 10'000 BV (where the average

432   abatement of the six indicator substances fell below the limit of 80%) correspond to a carbon usage rate

433   of 45 mg GAC/L. To be comparable to the elimination efficiency of powdered activated carbon, about

434   10 mg/L activated carbon (corresponding to 45'000 BV) should be reached before breakthrough of 80%

435   of the indicator substances (Boehler et al. 2012b). However, a stepwise renewal of several GAC filter

436   cells running in parallel (with differing elimination efficiencies between 100% and below 80%) allows

437   optimal performance with a longer lifetime of the GAC filters (Benstoem et al. 2017). Moreover, it was

438   demonstrated recently that a minimal EBCT is crucial to achieve a good elimination (Wunderlin et al.

439   2017). An EBCT of 25 minutes (compared to 15 minutes in this study) turned out to be sufficient for a

440   good performance for a 1.18 - 2.36 mm granulation at low DOC.

441
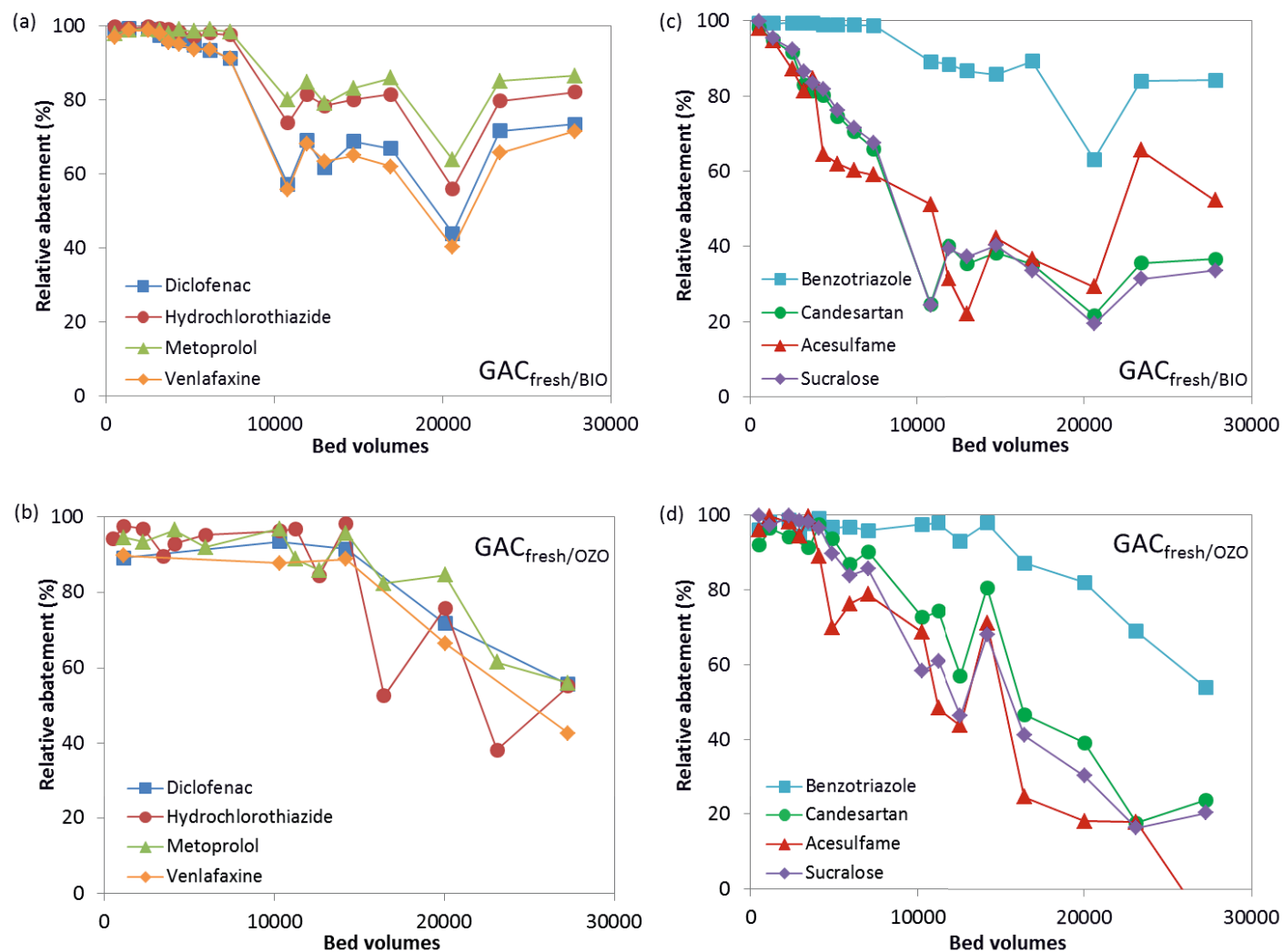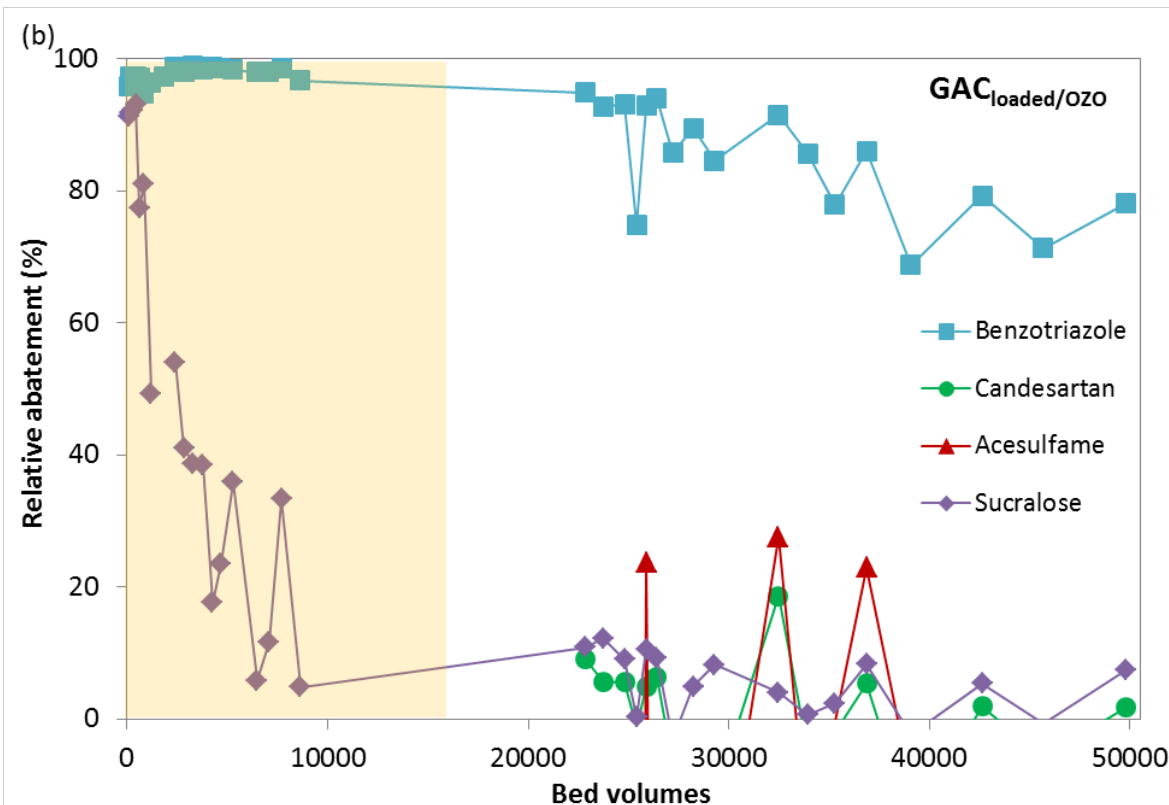
Fig. 2. Relative abatements of group I substances (diclofenac, hydrochlorothiazide, metoprolol and venlafaxine) in (a) $GAC_{fresh/BIO}$ and (b) $GAC_{fresh/OZO}$; of group II (benzotriazole and candesartan) and group III substances (acesulfame and sucralose) in (c) $GAC_{fresh/BIO}$ and (d) $GAC_{fresh/OZO}$ as a function of the bed volumes. 28'000 BV correspond to a run time of 10 months.

445 $GAC_{loaded/OZO}$ had been pre-loaded for 16'000 BV with the effluent of the secondary clarifier from

446 another WWTP (Boehler et al. 2012a), before being installed at WWTP Neugut after ozonation. During

447 this loading phase of $GAC_{loaded/OZO}$, the abatement of selected micropollutants was measured and can be

448 compared to the abatement in $GAC_{fresh/BIO}$ at WWTP Neugut. Micropollutants abatement in $GAC_{loaded/OZO}$

449 (Fig. 3 and Fig. S12, yellow zone) was less efficient than in $GAC_{fresh/BIO}$ (Fig. 2 and Fig. S9), even

450 though the EBCT was slightly higher in $GAC_{loaded/OZO}$ (18 min for $GAC_{loaded/OZO}$ *vs.* 15 min for

451 $GAC_{fresh/BIO}$). For instance, venlafaxine and sucralose broke through immediately in $GAC_{loaded/OZO}$ and

452 their respective abatement at 7'500 BV were around 40% and 30% in $GAC_{loaded/OZO}$, while still at 91%

453 and 68% in $GAC_{fresh/BIO}$, respectively. The wastewater quality (DOC 6.9 mg/L in $GAC_{loaded/OZO}$ vs. DOC

454 5.5 mg/L in $GAC_{fresh/BIO}$) and the GAC properties (different material; higher particle size of 1.4-2.36 mm

455 in $GAC_{loaded/OZO}$ compared to 0.425-2.36 mm in $GAC_{fresh/BIO}$) likely explain why breakthrough occurred

456 faster in $GAC_{loaded/OZO}$.

457 When $GAC_{loaded/OZO}$ was operated with ozonated wastewater (>16'000 BV, to the right of the yellow

458 zone in Fig. 3), abatements were not significantly different to the abatements observed during the pre-

459 loading phase (yellow zone in Fig. 3). Only diclofenac showed a significant increase in the relative

460 abatement in the second phase: its relative abatement was <20% at the end of the first phase at 9'000 BV

461 and 62% when measurements restarted at 23'000 BV. Moreover, the micropollutant's relative

462 abatements decreased only slightly in $GAC_{loaded/OZO}$ over the sampling period between 23'000-50'000

463 BV. Similarly to $GAC_{fresh/BIO}$ and $GAC_{fresh/OZO}$, the relative abatement of poorly sorbing compounds such

464 as acesulfame, candesartan, gabapentin, irbesartan, sucralose, and valsartan acid, was <20% at high BVs

465 (Fig. 3 and Fig. S12). Conversely, abatement was generally still >60% for diclofenac,

466 hydrochlorothiazide, metoprolol, benzotriazole, methylbenzotriazole and atenolol, even at 50'000 BV.

467 When comparing $GAC_{loaded/OZO}$ with $GAC_{fresh/OZO}$ at 28'000 BV, the abatement of all substances was

468 similar, with the exception of benzotriazole. This compound was significantly better abated in

469 $GAC_{loaded/OZO}$ than in $GAC_{fresh/OZO}$ (78% *vs.* 54%). The results of diclofenac and benzotriazole suggest

470 that, in addition to sorption, a biological degradation may also take place in $GAC_{loaded/OZO}$, in analogy to

471 a previous publication (Reungoat et al. 2012). However, it is not possible to differentiate between

472 sorption and degradation by just measuring changes in concentrations. Fig. S11 shows that the average

473 relative abatement of the 6 selected indicator substances (benzotriazole, candesartan, diclofenac,

474 hydrochlorothiazide, metoprolol, venlafaxine) in $GAC_{loaded/OZO}$ was still about 40-50% at 50'000 BV,

475 similar to $GAC_{fresh/OZO}$ at 28'000 BV. In the screening of the 550 substances, the average abatement in

476 $GAC_{loaded/OZO}$ (19% at 35'000-40'000 BV; see Fig. S7) was less efficient than for the 6 selected indicator

477 substances. The reduction of the total concentration was only 6% in $GAC_{loaded/OZO}$ at 35'000-40'000 BV

478 (Fig. S6). This low relative abatement in $GAC_{loaded/OZO}$ can be attributed to the very poor abatement of

479 the compounds still present in high concentrations in OZO-EFF (>0.9 µg/L), *i.e.,* acesulfame, sucralose,

480 metformin, iopromide and tris(2-chloropropyl)phosphate, making up 73% of the overall concentration.

481 These compounds are hydrophilic and known to poorly adsorb to activated carbon (Kovalova et al.
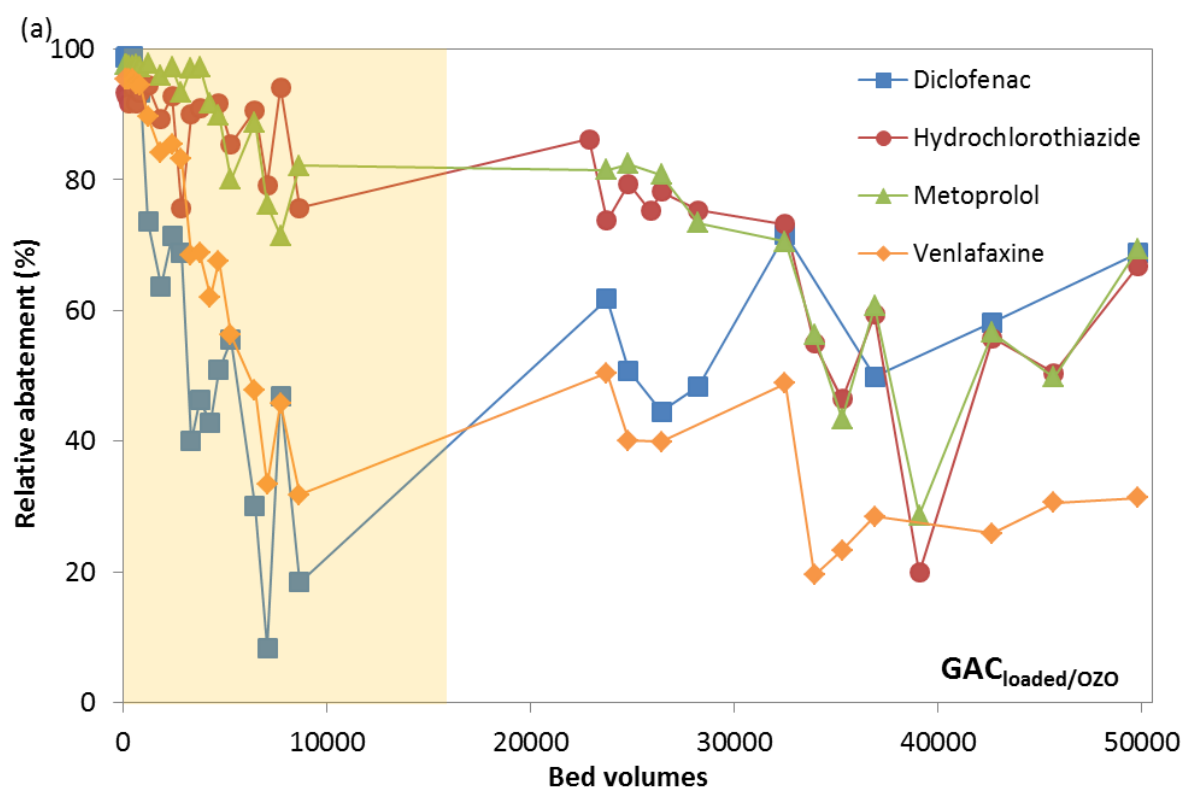
482 2013, Margot et al. 2013, Scheurer et al. 2010).

483

484

485 **Fig. 3. Relative abatements of (a) group I substances (diclofenac, hydrochlorothiazide, metoprolol**
486 **and venlafaxine) and (b) group II (benzotriazole and candesartan) and group III substances**
487 **(acesulfame and sucralose) in GAC$_{loaded/OZO}$. The filter was loaded with the secondary effluent of**
488 **another WWTP until 16'000 bed volumes (yellow area) and thereafter with ozonated effluent**
489 **from the WWTP Neugut.**

Fate of assimilable organic carbon, DOC and oxidation by-products

Formation and fate of AOC and fate of DOC

490 Fig. S13 shows that AOC increased during ozonation at the recommended specific ozone dose (0.55 g

491 O_3/g DOC) by a factor of 3: the AOC level in BIO-EFF was 90 µg C/L and reached about 280 µg C/L at

492 OZO-EFF. The increase of AOC is associated with the oxidation of dissolved organic matter (DOM) in

493 secondary effluent to form biodegradable and potentially toxic products, such as aldehydes, ketones or

494 carboxylic acids (von Gunten 2003). These classes of compounds are generally well removable during

495 biological post-treatments of ozonated drinking water (Hammes et al. 2006). Among the biological post-

496 treatments studied here, the sand filter performed best in reducing the AOC by 40% (Fig. S14), similar

497 to AOC reduction (14-46%) in other sand filters (Zimmermann et al. 2011). MB and FB reactors only

498 slightly reduced AOC (by 17% and 13%, respectively). In FB, an intense growth of snails (*Physidae*)

499 was observed, preventing the formation of a biofilm, which explains the low performance of this filter.

500 The GAC filters showed the highest abatement of AOC (72% in $GAC_{fresh/OZO}$ at 15'000 BV and 57% in

501 $GAC_{loaded/OZO}$ at 35'000 BV) due to additional sorption capability.

502 Ozonation alone induced a relative abatement of DOC of about 10% (Fig. S15), which is relatively high

503 in comparison to other studies where the DOC concentration almost did not change (Haslinger et al.

504 submitted, Hollender et al. 2009). The DOC concentration after ozonation was poorly abated in in MB

505 and FB (6% and 5%, respectively). In contrast, the sand filter showed a better relative abatement of

506 DOC (20%), due to biodegradation of degradable compounds and the deposition of colloidal organic

507 substances on the sand filter material. The GAC filters performed similar to sand filtration with a

508 relative DOC abatement of 15-20% on $GAC_{fresh/OZO}$ or $GAC_{loaded/OZO}$ at 20'000-50'000 BV. The loading

509 of DOC at the beginning (up to 15'000 BV) onto $GAC_{fresh/bio}$ with biologically treated wastewater

510 occurred slightly faster than onto $GAC_{fresh/OZO}$ with the ozonated effluent (Fig. S15-S16). The same

511 behavior was observed by Haslinger et al. (submitted).

512 Similar to DOC, the removal of total suspended solids (TSS) was less efficient in MB or FB (4% or

513 17%, respectively) than in the filter systems, where 75% TSS removal was achieved in SF and 70-80%

516   in the GAC filters (Fig. S17). A filter cloth installed after the MB could enhance the overall TSS

517   elimination to 50%. TSS was relatively low at around 2 mg/L in the influent and effluent of ozonation.

518   *Formation and fate of bromate*

519   The concentration of bromide in the influent to the ozonation reactor (n=30) was on average 60 µg/L

520   ranging 35-85 µg/L (n=26), but a few exceptionally high values (up to 150 µg/L) were measured (Table

521   S10). These values correspond to common bromide concentrations in Swiss municipal WWTPs without

522   discharges from waste incinerators, chemical industries or landfills (Schindler Wildhaber et al. 2015).

523   Bromate, an ozonation product from the oxidation of bromide, was also detected in WWTP-INF and

524   BIO-EFF, mostly below 1 µg/L (n=20), with a maximum concentration of 17 µg/L, concurring with a

525   relatively high bromide concentration (85 µg/L). The presence of bromate before ozonation may be

526   attributed to a pre-oxidation in one of the industrial sites connected to the WWTP.

527   During ozonation, bromide was oxidized to bromate with increasing yields for increasing specific ozone

528   doses, reaching 5.7 µg/L at 0.97 g O_3/g DOC with a bromide level of 60 µg/L (Fig. S18). The bromate

529   yield was calculated as the ratio between the produced bromate and the bromide concentration in the

530   influent (Fig. 4). For specific ozone doses ≤0.45 g O_3/g DOC, the bromate yield was low (<1%, w/w).

531   In this range, ozone and •OH exposures are very low, because ozone is rapidly depleted due to the

532   multiple reactions of ozone with DOM (Chon et al. 2015, Soltermann et al. 2017). For specific ozone

533   doses >0.45 g O_3/g DOC, the lifetime of ozone increases steadily with an increasing bromate yield

534   reaching 14% for 1.07 g O_3/g DOC. For the recommended specific ozone dose of 0.55 g O_3/g DOC, the

535   bromate yield is approximately 3%. At this ozone dose, the bromate formation corresponds to 1.8 µg/L

536   for the average concentration of bromide (60 µg/L), and in worse case 4.5 µg/L at the rare maximum

537   concentration of bromide (150 µg/L). As expected, Fig. S19 shows no significant changes of bromide or

538   bromate concentration in all post-treatments. Since bromate was mostly below 1 µg/L in BIO-EFF, its

539   concentration in the WWTP effluent would range normally between 1 and 3.5 µg/L at bromide levels

540   below 85 µg/L. Taking into account that, after discharge in the river, wastewater effluent is diluted by an

541   average factor of 20 at this site, the WWTP input on bromate concentration in the receiving water is low

542   (normally below 0.18 µg/L, with a maximal level of 0.28 µg/L at the highest bromide concentration),

543   well below the environmental quality standard (50 µg/L) (Ecotox Center 2017), the usual drinking water

544   standards (10 µg/L) (Commission Directive 2003, U.S. EPA 2006, WHO 2011), and even below the

545   most stringent guidelines (1 µg/L) applied for instance in the Netherlands (Knol et al. 2015). In the

546   current study, once a bromate concentration of 17 µg/L (Table S10) was observed in WWTP-INF, which

547   would lead to a bromate concentration as high as 21.5 µg/L in the effluent. In this case, the sources of

548   bromate should be identified and measures should be taken to minimize the bromate discharge.
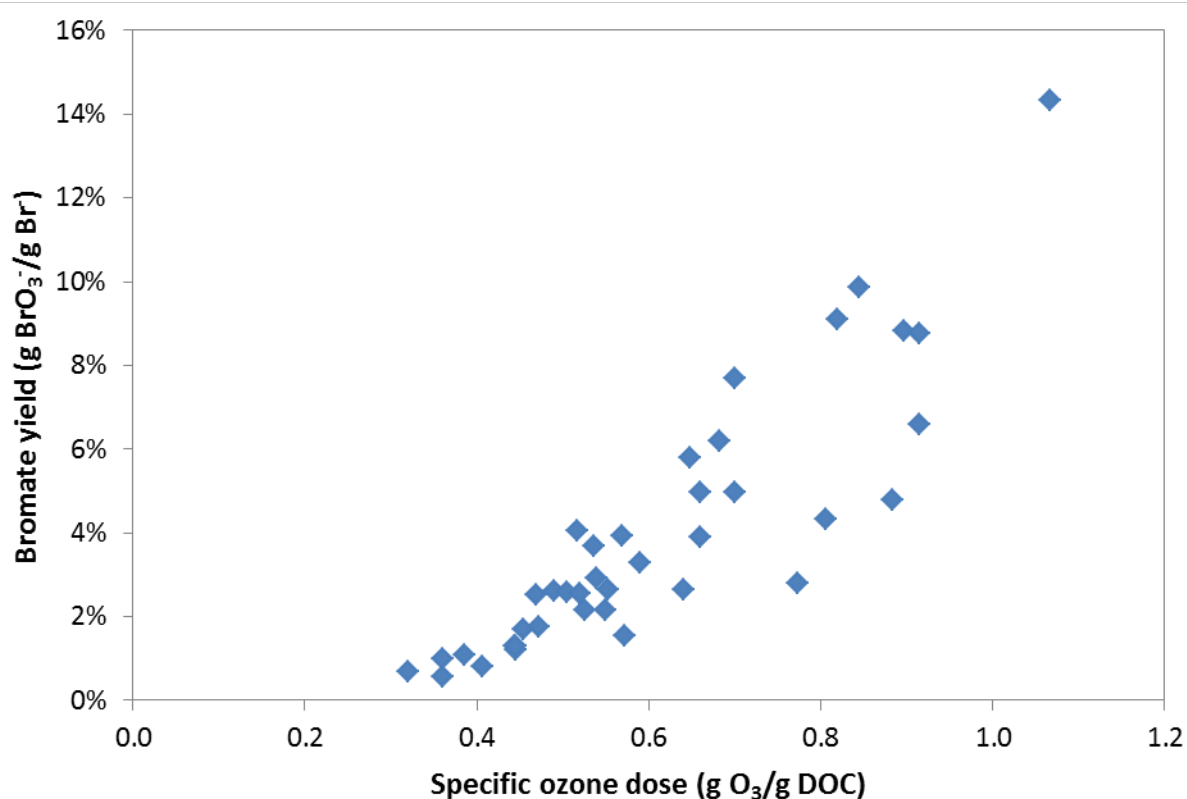
549
550   **Fig. 4. Bromate yields (w/w) in the full-scale ozonation for a range of specific ozone doses from**
551   **0.32-1.07 g O$_3$/g DOC (n=30).**

552   *Formation and fate of nitrosamines*

553   NDMA was regularly detected in relatively high concentrations after the biological treatment (BIO-

554   EFF), with a maximum concentration of 190 ng/L. This is in accordance with previous measurements in

555   20 WWTPs in Switzerland where after the biological treatment NDMA concentrations were found from

556   <LOQ to 188 ng/L (Krauss et al. 2009). In the US, NDMA concentrations in non-chlorinated effluents

557   were found up to 380 ng/L (Pehlivanoglu-Mantas et al. 2006, Plumlee and Reinhard 2007, Sedlak et al.

558   2005). A large variation was also observed from day to day and among differing WWTPs. At WWTP

559   Neugut, the maximum NDMA formation during ozonation for specific ozone doses in the range of 0.54-

560 0.97 g O$_3$/g DOC (Fig. 5) was 30 ng/L. No correlation was observed between the formation of NDMA

561 and the specific ozone dose, in agreement to other studies (Hollender et al. 2009, Schindler Wildhaber et

562 al. 2015, Zimmermann et al. 2011). Thus, the secondary clarifier effluent composition with likely

563 changing concentrations of differing NDMA precursors (not determined here) and varying NDMA

564 formation rates affects the extent of NDMA more than the specific ozone dose. In sand filtration,

565 NDMA was significantly abated always reaching values below 50 ng/L in the WWTP effluent (Fig. 5).

566 Therefore, the expected concentration in the receiving waters after a 20-fold dilution is well below the

567 WHO drinking water guideline of 100 ng/L and also below the tentative drinking water value of 10 ng/L

568 in several countries like Germany (Selin 2011).
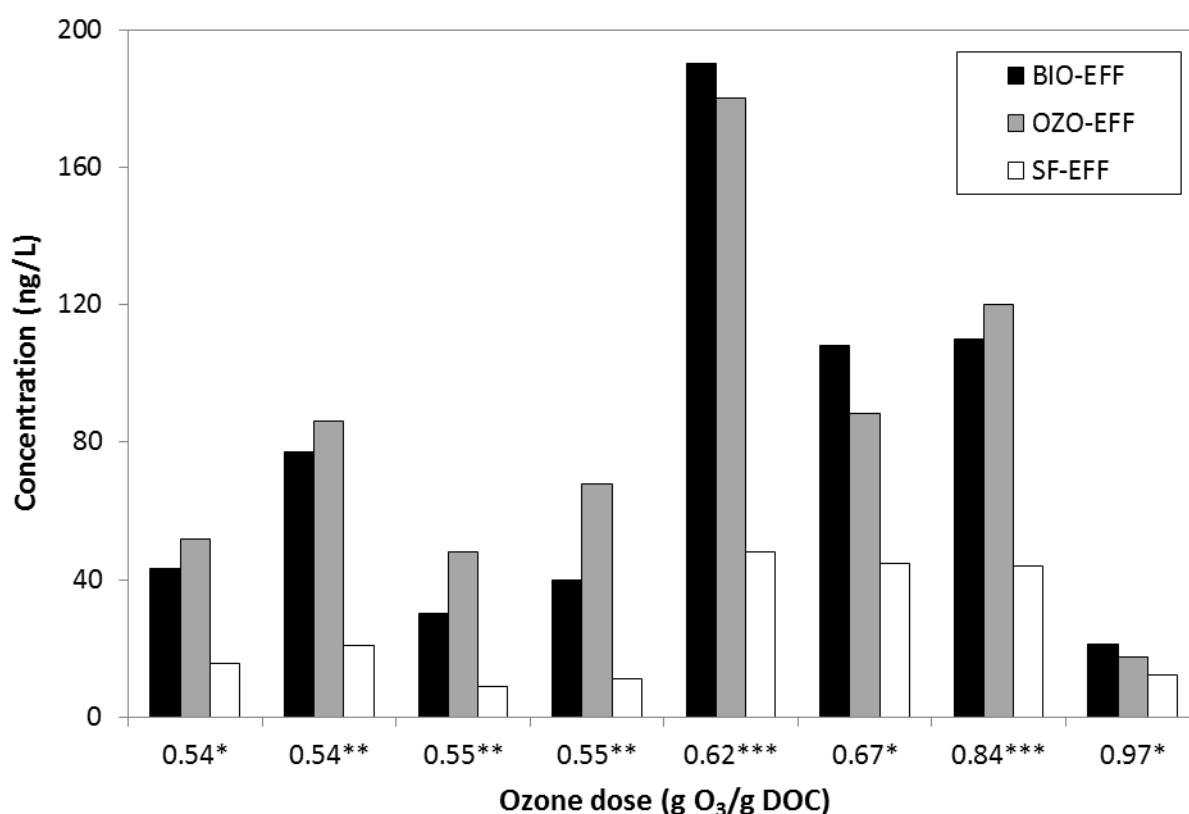
569
570 **Fig. 5. Concentrations of NDMA in BIO-EFF, OZO-EFF and SF-EFF for various specific ozone**
571 **doses ranging between 0.54-0.97 g O$_3$/g DOC. *: 72-h flow proportional samples; **: 48-h flow**
572 **proportional samples; ***: 24-h flow proportional samples.**

573

574 NDMA was abated in all of the investigated post-treatments (Fig. S20). Among the solely biological

575 post-treatments, SF showed the best relative degradation of NDMA by 66%, while MB and FB showed

576 slightly lower relative eliminations (48% and 41%, respectively). The relatively fresh filter GAC$_{fresh/OZO}$

577 (12'500-16'500 BV) showed the highest abatement of 83%, while $GAC_{loaded/OZO}$ at higher BV (35'000-

578 40'000 BV) exhibited a similar efficiency as SF (with 56% removal of NDMA).

579 **Fate of transformation products**

580 *Formation of transformation products during ozonation*

581 Sixty-three ozonation transformation products from a total of 19 parents were screened for, based on

582 evidence of formation in literature (Table S6). Eighteen of them could be quantified because standards

583 were available. However, ten out of these (3-[(4-chlorobenzoyl)amino] propanoic acid, 1-[(4-

584 chlorophenyl) phenylmethyl] piperazine, 4-chlorobenzophenone, *N*-desmethyl-clarithromycin, DCPMU,

585 azacyclonol, gabapentin acid, ranitidine *S*-oxide, *N*-desmethyl-tramadol and *N,N*-didesmethyl-tramadol)

586 were detected in none of the ozonated wastewater samples. 4'-/5-hydroxydiclofenac was detected in

587 high concentrations in most of the wastewater samples, however, its concentration dramatically

588 decreased after ozonation, independently of the specific ozone dose, and was therefore not evaluated

589 further. The following discussion will focus on seven OTPs frequently detected in wastewater samples

590 (Merel et al., 2017).

591 Some of these OTPs are also known to be human metabolites, biological transformation products or

592 used as active ingredients, and were therefore already detected in the wastewater after the conventional

593 biological treatment (Table S5). For instance, chlorothiazide was detected in all BIO-EFF samples

594 (*n*=12) at concentrations ranging 45-67 ng/L during the evaluation of the 4 specific ozone doses.

595 Tramadol *N*-oxide (*n*=5) , clarithromycin *N*-oxide (*n*=3) and cetirizine *N*-oxide (*n*=1) were detected at

596 least once in samples from biological treatment, at a maximum concentration of 35 ng/L.

597 The formation of the seven OTPs and their molar yields decreased with increasing specific ozone doses

598 (Fig. S21 and Table S11). For instance, in the case of chlorothiazide, the concentration of its parent

599 compound, hydrochlorothiazide, was relatively constant in BIO-EFF over the sampling period (*ca.* 1000

600 ng/L), but chlorothiazide concentrations dropped from 421-446 ng/L at 0.35 g O_3/g DOC to 163-308

601 ng/L at 0.97 g O_3/g DOC, respectively, corresponding to a decrease of the molar yield from 40% to

602 21%. At the specific ozone dose of 0.54 gO_3/gDOC, only clarithromycin *N*-oxide (62-74 ng/L),

603 chlorothiazide (364-385 ng/L), fexofenadine *N*-oxide (111-171 ng/L), tramadol *N*-oxide (76-82 ng/L)

and venlafaxine *N*-oxide (27-30 ng/L) were >LOQ in OZO-EFF. Highest molar yields of the OTPs were observed for chlorothiazide (36%), clarithromycin *N*-oxide (34%), and fexofenadine *N*-oxide (30%) at this specific ozone dose. Amisulpride *N*-oxide and cetirizine *N*-oxide were detected only at 0.35 g O_3/g DOC (*n*=3), but their yields did not exceed 4% and 3%, respectively. The selected OTPs were formed rapidly during ozonation due to the high ozone-reactivity of the parent compounds (k_{O3}>10^4 M^{-1} s^{-1}) as recently determined in batch experiments with ozone alone for chlorothiazide, fexofenadine *N*-oxide and cetirizine *N*-oxide (Borowska et al. 2016), but were subsequently further transformed mostly by attack of hydroxyl radical.

For the 45 OTPs without available standard, normalized peak areas were determined in the samples (Fig. S22). Out of these potential OTPs, the exact masses of only 12 were detected after ozonation: four OTPs from hydrochlorothiazide (HCT_TP1-4, Table S6), two from carbamazepine (BQM and BaQD), two from phenazone (PHE_TP2 and TP6), two from sulfamethoxazole (SMX_TP1 and TP3), one from atenolol (ATE_TP1), and one from lamotrigine (LAM_TP2). These results are in agreement with the studies listed in Table S6, where these OTPs were found to be predominantly formed during the ozonation of parent compounds.

Fate of the transformation products during post-treatments

Among the seven quantified OTPs, only five OTPs (chlorothiazide, clarithromycin *N*-oxide, tramadol *N*-oxide, venlafaxine *N*-oxide and fexofenadine-*N*-oxide) were measured regularly in concentrations well above the LOQ and could be evaluated in the post-treatments. SF, MB and FB were all inefficient to biodegrade these OTPs (Fig. S23). This shows that the investigated OTPs are very stable compounds, not being degradable in the selected post-treatments.

In contrast to the three biological post-treatments, GAC$_{fresh/OZO}$ was efficient to remove the selected OTPs due to sorption (Fig. 6 and Fig. S24). Up to about 8'000 BV, the abatement was ≥80% for *N*-oxides and even >96% for chlorothiazide. Thereafter, the abatement of the *N*-oxides started to decrease, but stayed above 80% until 17'000 BV for chlorothiazide. At 23'000 BV, the abatement of *N*-oxides was <40%, while chlorothiazide abatement was still higher (57%). In GAC$_{loaded/OZO}$, only chlorothiazide was efficiently abated by 30-40% at 50'000 BV (Fig. S23b). In general, more polar compounds are

631 produced in ozonation, which are expected to be less efficiently sorbed than their parent compounds,

632 therefore exhibiting an earlier breakthrough. For instance, the sorption of venlafaxine *N*-oxide and

633 tramadol *N*-oxide on $GAC_{fresh/OZO}$ dropped below 80% at 8'000 BV, while for the parent compounds

634 venlafaxine and tramadol, this occurred only after 14'000 BV (Fig. 6). The relative abatement of

635 chlorothiazide was also smaller than for hydrochlorothiazide, but only at higher BVs. However, the

636 abatement of fexofenadine was similar to fexofenadine *N*-oxide (the biggest molecule of the three *N*-

637 oxides, mostly uncharged), where the difference in polarity between the parent and the OTP is probably

638 less pronounced.

639 OTPs without available standards also showed mostly no significant changes of normalized peak areas

640 in SF, MB and FB (Fig. S22). However, significant peak reductions were observed in $GAC_{fresh/OZO}$ (at

641 14'000 BV) and rarely in $GAC_{loaded/OZO}$ (at 37'000 BV), which may be explained by the respective

642 residual sorption capacity. Transformation products of carbamazepine, BQM and BaQD, showed a

643 particular behavior in SF and $GAC_{loaded/OZO}$: The BQM peak area was reduced concomitantly to a BaQD

644 peak increase. The other biological systems, MB and FB, showed no change. These results are in

645 agreement with previous observations (Hübner et al. 2014), where BQM formation was found as the

646 major OTP of carbamazepine, and a successive conversion of BQM to BaQM (not detected in this

647 study) and of BaQM to BaQD was observed in the subsequent biological post-treatments.

648
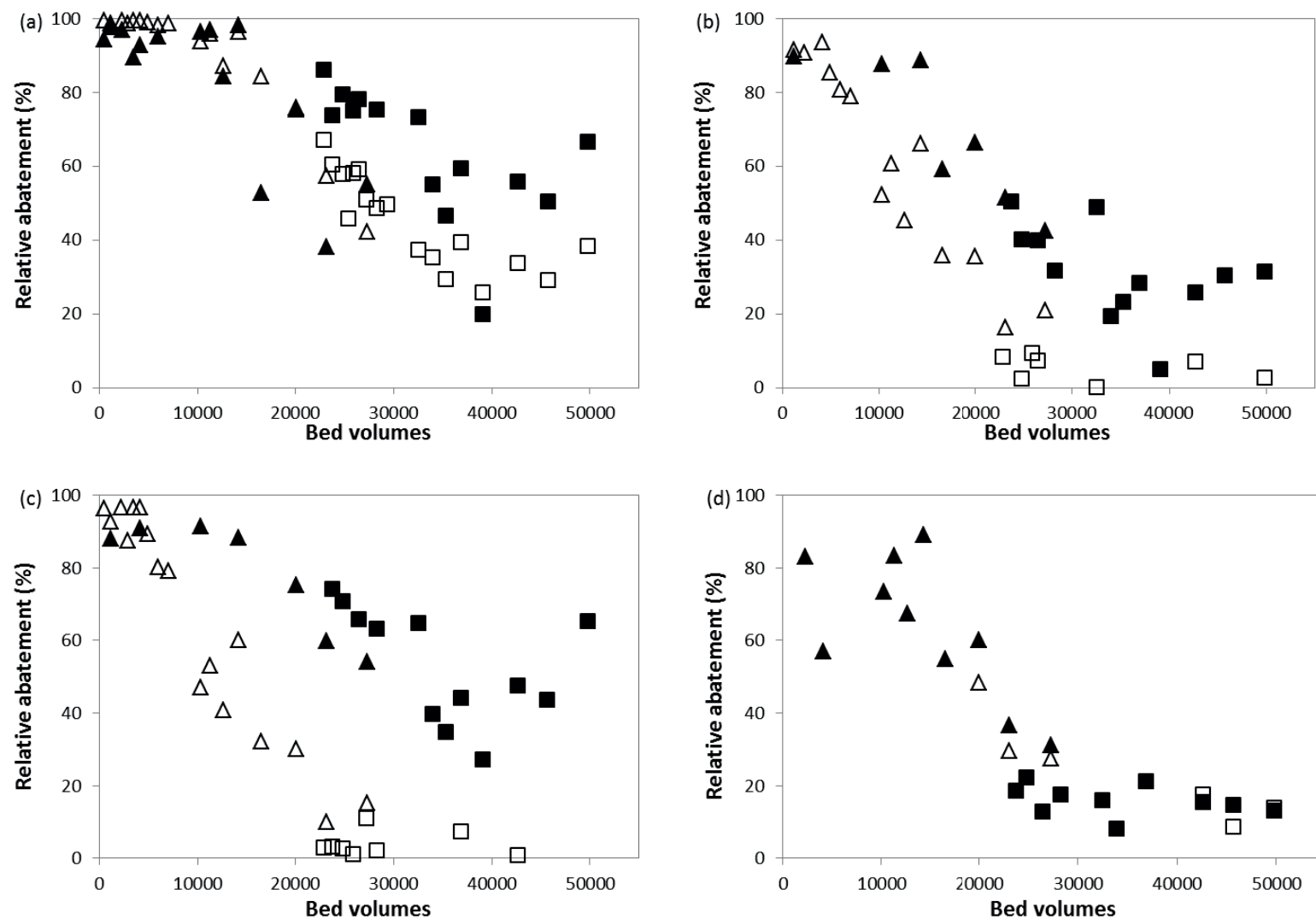
Fig. 6. Comparison of relative abatement of parent compounds (solid) and their respective primary OTP (empty) in GAC$_{fresh/OZO}$ (triangle) and GAC$_{loaded/OZO}$ (square) for (a) hydrochlorothiazide/chlorothiazide, (b) tramadol/tramadol *N*-oxide, (c) venlafaxine/venlafaxine *N*-oxide, and (d) fexofenadine/ fexofenadine *N*-oxide. Tramadol*: sum of tramadol and O-desmethylvenlafaxine (see Text S2).

Cost of new ozone treatment

The cost estimation of the installation and operation of ozonation at WWTP Neugut is presented in detail in SI Text S6. To summarize, investments accounted to 3.27 Mio CHF, and operation costs are 240 CHF/d or 0.013 CHF/m^3 (180 CHF/d for ozone and electricity and 60 CHF/d for manpower). Overall, the total cost accounts to 0.06 CHF/m^3, corresponding to an increase of 10% for wastewater treatment at WWTP Neugut, what is at the lower end of general estimations (Abegglen and Siegrist 2012). According to the new Swiss Water Protection Act, the investment costs will be covered to 75% by a fund established from payments of 9 CHF/y by each Swiss inhabitant who is connected to a WWTP without installation of advanced treatment (Eggen et al. 2014).

CONCLUSIONS

- Ozonation of the effluent of the secondary clarifier in WWTP Neugut resulted in a significant reduction of the micropollutant load in the WWTP effluent. At the recommended ozone dose (0.55 g O_3/g DOC), indicator substances were abated by >80% even at potential high nitrite concentrations of 0.2 mg NO_2^--N/L. For a set of about 200 micropollutants detected in the influent of the WWTP, an average abatement of >79% was observed over the whole treatment chain. Nitrite could be compensated directly by using a feed-back control for ozone dosing by the delta UV_{254nm} signal from in- and outlet of the ozone reactor (Wittmer et al. 2015). In this case, a specific ozone dose of 0.40 g O_3/g DOC (1.5-2.5 mg O_3/L) would be sufficient for the required micropollutant abatement of 80%.

- For the implementation of ozonation, the formation of the oxidation by-products bromate and NDMA needed to be evaluated and were found to be formed also at WWTP Neugut. NDMA was significantly reduced in all post-treatments. As bromide was mostly in a concentration range common for Swiss municipal wastewater, the bromate level was typically < 3.5 ug/L in the WWTP effluent. The concentrations expected after dilution of discharged water were clearly below (potential) drinking water standards (10 μg/L for bromate, 10 ng/L for NDMA).

- While the micropollutants were not significantly abated in the biological post-treatment (SF, MB, FB) as expected, GAC filtration was efficient to remove the majority of micropollutants due to sorption, even after 30'000 bed volumes.

- $GAC_{fresh/OZO}$ (operated with wastewater treated biologically and subsequently by ozonation) showed a later breakthrough of DOC and micropollutants than $GAC_{fresh/BIO}$ (operated with biologically treated wastewater), potentially due to altered organic matter, being less competitive for sorption sites after ozonation.

- $GAC_{loaded/OZO}$ was efficient to abate certain substances even up to 50'000 bed volumes (about 2 years of running time). It cannot be assessed so far whether this is due to a residual sorption capacity of the activated carbon or due to biodegradation. GAC filters operated at high bed volumes should be further investigated as they represent a promising alternative to sand filters for an improved quality of WWTP effluents.

- The investigated OTPs were not abated in the biological post-treatments, except one OTP of carbamazepine, which was degraded to another OTP. The detected OTPs appeared to be very stable compounds, and biodegradable compounds seem to be more difficult to be detected. Only the GAC filters were showing abatement of OTPs due to additional sorption capacities, even at 30'000 bed volumes. However, as demonstrated by the abatement of AOC in the biological post-treatments, degradable compounds are being removed, complying with the task of the post-treatments. Overall, the main goal of the biological post-treatment is the elimination of possible negative ecotoxicological effects generated during ozonation.

- For the evaluation of ozonation and the post-treatments, the water quality needs to be assessed with bioassays. Therefore, various ecotoxicological endpoints, using living cells, organisms and communities, were investigated. The outcomes of these tests will be presented in a follow-up study (Kienle et al. in preparation).

Supporting information

Additional data associated with this article can be found in the Supplementary Material (Text S1-S5, Fig. S1-S24 and Table S1-S11).

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