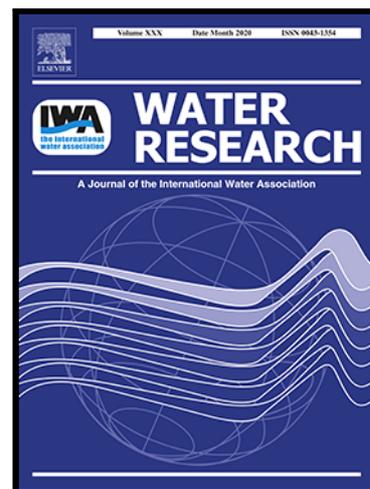


Journal Pre-proof

Removal of trace organic contaminants from wastewater by superfine powdered activated carbon (SPAC) is neither affected by SPAC dispersal nor coagulation

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Highlights:

- The effect of superfine powdered activated carbon (SPAC) aggregation on micropollutant sorption was studied.
- Real not apparent particle size determines micropollutant sorption by SPAC in wastewater.
- At high SPAC doses sorption kinetics are so fast that aggregate dispersal yields no benefit.
- Coagulant can be added with the carbon without compromising micropollutant removal.

Journal Pre-proof

Removal of trace organic contaminants from wastewater by superfine powdered activated carbon (SPAC) is neither affected by SPAC dispersal nor coagulation

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1 Abstract

2 Powdered activated carbon (PAC) is increasingly used as tertiary treatment for the removal of trace
3 organic contaminants (TrOCs) from wastewater (WW). To enhance the sorption kinetics and
4 capacity, the PAC particles can be milled down to super fine powdered activated carbon (SPAC).
5 However, the small-grained SPAC particles are prone to aggregation, which may impact their
6 treatment performance. In this study we examined the effect of SPAC dispersion and aggregation on
7 TrOCs removal kinetics and sorption capacity. Specifically, we assessed how two interventions that
8 modulate the apparent size of SPAC - ultrasonication and coagulation - affect the uptake of TrOCs in
9 secondary WW effluent. We quantified the removal of fourteen TrOCs, of which twelve are indicator
10 substances for micropollutant removal in WWTPs as designated by the Swiss Water Protection
11 Ordinance. We determined that at high SPAC doses (> 1.6 mgSPAC/mg Dissolved Organic Carbon
12 [DOC]), the TrOC removal kinetics were fast even for aggregated SPAC, such that SPAC dispersal by
13 ultrasonication yielded no benefit. At low SPAC doses (< 1.6 mgSPAC/mgDOC) and contact times (< 2
14 minutes) ultrasonication was beneficial, in particular if the SPAC particles reached complete
15 dispersion prior to exposure to TrOCs. However, the energy consumption of such an ultrasonication
16 step should be carefully weighed against the additional energy requirement associated with using a
17 higher SPAC dose. Finally, a coagulant to mitigate membrane fouling can be added simultaneously
18 with the SPAC without compromising the TrOC removal efficiency. We conclude that under realistic
19 SPAC application scenarios in WWTPs, interventions that disperse SPAC during TrOC sorption are not
20 necessary, and processes that aggregate SPAC are acceptable.

21 Keywords:

22 Micropollutants, tertiary treatment, ultrasonication, coagulation, dispersion, aggregation

23 1 Introduction

24 Humans produce and consume thousands of organic compounds that are partly introduced as trace
25 organic contaminants (TrOC) into freshwater environments via municipal and industrial wastewater
26 treatment plant (WWTP) effluents. Even at concentrations below the microgram per liter range,
27 these TrOCs present a risk to freshwater ecosystems (Schwarzenbach et al., 2006). WWTPs only
28 partially remove TrOCs from the wastewater (WW) stream (Luo et al., 2014; Margot et al., 2015;
29 Oulton et al., 2010), and discharge the remainder into the receiving waters (Bonvin et al., 2011; Gälli
30 et al., 2009). In an effort to reduce the contamination of rivers and lakes, the Swiss Water
31 Protection Act and Ordinance of 2016 (Département fédéral de l'environnement, des transports,
32 2016; The Swis Federal Council, 2017, 2018) requires large WWTPs to upgrade their treatment train,
33 such that they achieve an 80% removal of the incoming load of TrOCs. Compliance with this
34 Ordinance is verified by monitoring the average removal of at least six and up to 12 TrOCs indicator
35 compounds.

36 Currently recommended treatment processes for TrOC removal in WWTPs consist of oxidation by
37 ozone, followed by sand filtration, or adsorption onto granular or powdered activated carbon
38 followed by sedimentation/sand filtration (GAC/PAC-SF)(Wunderlin et al., 2017). Both approaches
39 are effective in achieving the required 80% TrOC reduction (Margot et al., 2013), but they each have
40 limitations. Most importantly, not all effluents are suitable for treatment by ozone, which can
41 generate hazardous disinfection by-products (DBPs)(von Sonntag and von Gunten, 2015). While
42 GAC/PAC-SF does not generate DBPs, this treatment method has substantial economic and
43 environmental costs associated with the production of the activated carbon material (Jekel et al.,
44 2016; Margot et al., 2013).

45 The costs of activated carbon-based treatments could be optimized by using a material with a more
46 effective TrOC uptake than currently available PAC/GAC, such that an 80% TrOC removal can be
47 achieved with a lower carbon dose. A possible method to enhance TrOC uptake is to use superfine

48 powdered activated carbon (SPAC), which is produced by wet-milling of PAC. Based on laboratory
49 experiments, Bonvin et al. (2016) showed that the use of SPAC would allow for a shorter contact
50 time compared to PAC to achieve a similar TrOC removal from WW effluents. SPAC has also
51 demonstrated greater removal capacities of taste and odor compounds compared to PAC in drinking
52 water (DW) treatment (Matsui et al., 2013a; Pan et al., 2017, 2016), as well as an enhanced overall
53 dissolved organic material removal (Ando et al., 2010; Matsui et al., 2012, 2013b). Traditional
54 coagulation/flocculation, sedimentation and sand filtration steps, as well as advanced filtration
55 membranes can be implemented downstream to remove the SPAC particles from the water or WW
56 stream (Kweon et al., 2009; Löwenberg et al., 2014; Nakazawa et al., 2018a, 2018b).

57 One possible factor underlying the improved performance of SPAC compared to PAC for TrOC
58 removal is its higher sorption capacity. An increase in the equilibrium sorption capacity was
59 previously observed when the D_{50} of PAC was reduced down to the micron range (1-3 μm).
60 Alternatively, the enhanced performance of SPAC may stem from faster sorption kinetics. Matsui et
61 al. (2013a, 2009), who modeled the sorption of geosmin and 2-methylisoborneol (MIB) in drinking
62 water onto PAC and SPAC, observed that sorption rates increased with decreasing D_{50} . More rapid
63 sorption kinetics for SPAC compared to PAC were also observed by Bonvin et al. (2016) in WW
64 effluents, with SPAC particles with a D_{50} of 1 μm requiring a contact time of 10 min to reach
65 adsorption equilibrium while PAC particles took more than 2 hrs.

66 A potential limitation of the use of SPAC is the tendency of small particles to aggregate in solution,
67 depending on particle concentration and solution conditions (temperature, pH, ionic strength and
68 chemical composition)(Baalousha, 2009; Dempsey, 2006). In drinking water, Pan et al. (2016)
69 reported a slower sorption of MIB onto dry-milled compared to wet-milled SPAC, which they
70 attributed to a combination of lower sorption capacity and aggregation state. These authors suggest
71 that aggregated SPAC particles have interparticle spaces that act as pseudopores, which increase the
72 total diffusive pass length, resulting in a lower sorption rate is lowered for aggregated SPAC

73 compared to single particles (Pan et al., 2016). Based on their findings, they recommended to
74 disperse SPAC particles by ultrasonication if the aggregated particle size is more than twice the
75 dispersed particle size. It is not known, however, if these findings also apply to wastewater, where
76 the higher content of organic matter may lead to competition with TrOCs for the sorption sites on
77 SPAC.

78 The goal of this work was to investigate the impact of particle aggregation on the removal of TrOCs
79 from WW effluent. In particular, we assessed the effect of two interventions that modify the
80 apparent size of SPAC, namely ultrasonication and coagulation. Ultrasonication can be used to
81 disperse particles prior and during TrOC sorption. Coagulation is applied in treatment trains with a
82 SPAC/ultrafiltration process, to facilitate suspended solids removal and mitigate membrane fouling.
83 We monitored the removal of 14 TrOC by SPAC, including the 12 compounds designated as
84 indicators in the Swiss Water Protection Ordinance for removal of TrOCs (Département fédéral de
85 l'environnement, des transports, 2016), and determined the average removal under different
86 treatment scenarios. Ultimately, this work provides operational recommendations for the
87 application of SPAC to treat WW effluents.

88 2 Materials & Methods

89 **SPAC.** Commercially available coal-based PAC (Pulsorb FG4; Chemviron Carbon, Belgium) was used in
90 this study to produce SPAC by wet-milling with a DYNO[®]-MILL ECM-AP 05 (WAB AG, Switzerland).
91 Compared to dry-milling, onsite wet-milling of SPAC in a wastewater treatment plant is a safer
92 procedure, because the dry SPAC powder constitutes an explosion risk. SPAC of three different sizes
93 was produced, namely with a D_{50} around 1, 3 and 5 μm (SPAC 1, SPAC 3 and SPAC 5, respectively) in
94 disperse suspensions. SPAC suspensions with a concentration of 20-30 g/L were produced in
95 deionised water. These suspensions were diluted with deionized water to produce SPAC stock
96 solutions (200 mL) with a targeted concentration range of 1.5-3 g/L, and were stored at 4°C. The
97 SPAC stock concentration was determined by extracting four aliquots of 5 mL from a stirred SPAC

98 stock solution, oven-drying them at 200°C for > 48 hr, and weighing them on a microbalance (AT261;
99 Mettler Toledo). The resulting SPAC concentrations were estimated at 2.3 ± 0.2 (mean \pm stdev) (SPAC
100 1), 1.6 ± 0.2 (SPAC 3) and 2.5 ± 0.1 g/L (SPAC 5). Throughout our work, we use the terms volume-
101 based [mg/L] and specific [mgSPAC/mg dissolved organic carbon (DOC)] dose of SPAC to distinguish
102 between the dose per volume of WW and the dose normalized to the DOC content of the WW.

103 **Water matrices.** Two batches (~30 L) of secondary WW effluent (after primary clarification,
104 activated sludge treatment and secondary clarification; see supplementary information (SI)) were
105 collected from the WWTP of Châteauneuf (Sion, Switzerland). The two batches (WW1 and WW2)
106 were collected six months apart. The WW was collected over 24 hours in a flow proportional
107 manner, mixed and stored in 1 L glass bottles at 4°C. Upon arrival in the lab, ammonium, nitrate,
108 nitrite and phosphate concentrations, as well as the total suspended solids (TSS) concentration,
109 were determined. The ammonium concentration was quantified by ion chromatography (ICS-3000,
110 IonPacCS16 column) with electrical conductivity detection (Dionex, Switzerland). Nitrate, nitrite and
111 phosphate concentrations were measured by ion chromatography (ICS-3000, IonPac AS11-HC
112 column). TSS was determined according to the standard protocol (APHA, 2012). The pH, electrical
113 conductivity (EC), and the DOC concentration of the WW changed during storage and were therefore
114 determined prior to each experiment. The pH and EC were measured with Multi 3430 pH and
115 conductivity meter (WTW). The DOC concentration was determined as non-purgeable organic
116 carbon by TOC analyzer (TOC-L CPN; Shimadzu; Japan). Drinking water (DW) was collected from the
117 tap (Lausanne, Switzerland) and was characterized analogously to WW. Detailed water matrix
118 characteristics are given in the SI (Table S1).

119 **TrOCs.** Fourteen TrOCs were quantified during the course of our different experiments. TrOCs and
120 their deuterated standards were purchased in high purity from Sigma-Aldrich, LGC, Dr. Ehrenstorfer
121 and TRC (Toronto Research Chemicals). Twelve compounds are the indicators TrOC described in the
122 Swiss Water Protection Ordinance for monitoring the removal of trace organic compounds

123 (Département fédéral de l'environnement, des transports, 2016) and were shown to be efficiently
124 removed by AC: amisulpride, benzotriazole, candesartan, carbamazepine, citalopram,
125 clarithromycin, diclofenac, hydrochlorothiazide, irbesartan, methylbenzotriazole, metoprolol,
126 venlafaxine. Two more TrOCs that are weakly adsorbed by AC were added to our list: mecoprop and
127 sulfamethoxazole. TrOC concentrations were determined in each water matrix and prior to each
128 experiment as described below. If the concentration of a given TrOC was too low to detect an 80%
129 removal, this TrOC was spiked into the matrix (SI, Table S1) to raise its concentration. To this end, a
130 methanol (MeOH) solution was prepared containing the TrOCs of interest. This solution was left
131 open for > 12 hours under a fume hood to evaporate the MeOH. Acidified Evian water was added
132 and the solution was shaken for 1 min. The resulting aqueous TrOC solution was then stored for no
133 more than 2 days at 4°C before being used as a spiking solution.

134 TrOC concentrations were quantified by online solid phase extraction (SPE online), followed by ultra-
135 performance liquid chromatography and tandem mass spectrometry (UPLC-MS/MS; Acquity Xevo,
136 Waters). Samples were diluted 1:1 with acidified Evian water (pH ~2.5, HCl 25%) and a deuterated
137 analogue of each target TrOC was spiked into every sample as an internal standard. The analytical
138 method was adapted from previous work (Bonvin, 2013; Margot, 2015; Morasch et al., 2010) and
139 details can be found in the supplementary information. TrOC concentrations were calculated based
140 on calibration curves using all 8 calibration points for high concentrations and only the 5 lowest
141 standards for low concentrations. Correlation coefficients for the calibration curves were typically
142 >0.990. The analytical limit of quantification (LOQ) was defined as the concentration of the lowest
143 standard with a signal-to-noise ratio > 10 (SI, Table S2). The uncertainty associated with the sample
144 concentrations, calculated as the relative standard deviation, was <30% for the large majority of the
145 compounds (Bonvin, 2013).

146 **Sorption kinetics.** Three types of kinetic experiments were conducted to investigate the impact of
147 SPAC characteristics without and with external interventions on TrOC removal kinetics. First, we

148 characterized the influence of SPAC dose and particle size on TrOC uptake from WW effluent.
149 Second, we investigated the effect of ultrasonication (to break up SPAC aggregates) on TrOC uptake.
150 And third, we tested if the impact of Fe coagulant on SPAC size and TrOC removal.

151 *Influence of SPAC dose and particle size on TrOC uptake without interventions.* Samples (500 mL) of
152 WW were stirred by a magnetic stir bar at 300 rpm in glass a beaker. If necessary, the WW was
153 amended with TrOCs of interest (see section TrOCs). Then, the SPAC stock solution of interest was
154 spiked into the WW using a pipettor with a 5 mL tip, which had a mouth wider than 1 mm to avoid
155 particle segregation during the spiking process. Samples (20 mL) were periodically removed and
156 were filtered through a 0.02 μm homemade filter to ensure the complete removal of the SPAC. The
157 filters consist of a single PES hollow fiber from a drinking water filtration membrane, with a syringe
158 glued onto one side and a plug on the other side (SI, Figure S1). The filtration process took between
159 15-20 seconds. Filtered samples were analyzed for TrOCs within hours of the experiment.

160 *Effect of ultrasonication.* TrOC uptake experiments were conducted as described above, except that
161 they were conducted in a temperature-controlled water bath (recirculating cooler F240; Julabo) kept
162 at 18°C. The temperature of the water matrix was checked at the end of each experiment to ensure
163 that it did not rise above 25°C. An ultrasonication power of 13 W (100 % power; Telsonics with
164 ultrasonication probe; 50/60 Hz) was applied. The power was confirmed according to a calorimetric
165 method proposed by Taurozzi et al. (2011) (see SI for detailed procedure). For each experiment, the
166 ultrasonication probe tip was placed in the center of the beaker, around 2 cm above the bottom.
167 Ultrasonication was accomplished either simultaneously to sorption (i.e., sonication was started
168 while spiking the SPAC; sim.) or prior to and simultaneously to sorption (i.e., the sonication started
169 10 min prior to SPAC spiking and was maintained throughout the experiment; prior + sim.). For the
170 latter set of experiments, DW was used instead of WW, to allow for prior sonication in the absence
171 of TrOCs. After 10 min of sonication, the DW was then amended with the TrOCs of interest and
172 sorption was monitored. Sample workup and analysis were conducted as described above.

173 *Impact of Fe coagulant.* Experiments with coagulants were conducted as described above. However,
174 in addition to TrOC and SPAC, the WW was amended with FeCl_3 . Specifically, a coagulant stock
175 solution of 100 ppm Fe (96.8 mg $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ in 200 mL; Acros) was spiked into the reactor to
176 achieve a concentration of 2 ppm Fe in WW. The coagulant was spiked shortly before the SPAC, and
177 the solution was mixed at 300 rpm to ensure SPAC suspension. Sample workup and analysis were
178 conducted as described above.

179 For each set of experiments, SPAC-free control experiments were conducted and analyzed
180 analogously to the SPAC-containing experiments. The different sorption kinetics experiments
181 performed are summarized in the SI (Table S3).

182 **Particle size distribution (PSD).** Besides TrOC removal, the particle size distribution of SPAC without
183 intervention, and while sonicating or adding a coagulant was determined. The measurements were
184 performed with a Mastersizer S (Malvern; UK), with the stirring chamber running at 1400 rpm for all
185 measurements. The D_{50} was calculated from the cumulative distribution derived from the volume
186 distribution that was corrected post-measurement for artifact peaks (i.e. not connected to the rest
187 of the distribution) in the $> 100 \mu\text{m}$ range likely due to air bubbles. The dynamic light scattering (DLS)
188 method assumes spherical properties of particles which is not the case of the AC particles.
189 Nevertheless, the DLS remained the best method to approximate PSD in our experimental system.

190 *Dispersed (D-PSD) and aggregated particle size distribution (A-PSD).* Two droplets of the 20-30
191 g/LSPAC suspension (collected after wet-milling) were spiked into 100 mL of deionized water (DI
192 water) or WW effluent with a plastic Pasteur pipette with an approximately 2 mm wide tip, to
193 achieve a final concentration 20-40 mg/L SPAC. The WW effluent was filtered (mixed cellulose esters
194 membrane, hydrophilic, $0.45 \mu\text{m}$ pore size; Millipore) and pasteurized for 1 hr at 55°C to avoid
195 contamination of the measuring device, while simultaneously conserving the ionic composition and
196 pH of the WW. To determine the D-PSD, the SPAC-spiked samples were stirred for 10 min at ~ 300
197 rpm while sonicating at 13 W in a beaker with water to avoid heating the sample. The A-PSD was

198 determined with the same procedure, except that the mixture was not sonicated. Each D-PSD and A-
199 PSD measurement was performed in triplicate or quadruplicate from the same solution.

200 *Dispersal and aggregation kinetics.* Dispersal or aggregation kinetics were determined under
201 conditions similar to those used in the TrOC sorption experiments. Specifically, 500 mL of filtered
202 and pasteurized WW effluent were amended with SPAC to a concentration around 8 mg/L. Samples
203 were either ultrasonicated at 13 W, or were amended with 2 ppm Fe coagulant. A control sample
204 with a SPAC concentration of ~8 mg/L but without ultrasonication or coagulant was also included.
205 Due to the low concentration of SPAC, a large volume of solution was required to get a high enough
206 obscuration in the Mastersizer, we used sacrificial samples for each time step. Therefore, the results
207 show the average of triplicate samples spiked and treated separately.

208 **Data analysis.** The distribution of the removal values of the different TrOCs were reported as
209 boxplots, where each box represents data from one experiment. For every time step, all
210 experimental conditions were compared by means of a Kruskal-Wallis test, with the null hypothesis
211 being that the median removal for all tested conditions are equal, considering a distribution similar
212 in shape and spread. In case of a significant difference ($p < 0.05$) from the Kruskal-Wallis test, a post-
213 hoc pairwise Mann–Whitney U-test with Benjamini & Hochberg correction was further performed.
214 For every time step, boxplots with different letters are significantly different (rejection of the null
215 hypothesis with a probability of $p < 0.05$). Statistical analyses were conducted in R (R Core Team,
216 2018), using the functions `kruskal.test` and `pairwise.wilcox.test` with `p.adjust.method` equal to "BH"
217 (R package {stats}). Data acquired for the PSD determination were treated in R with the `cumsum` and
218 `approx` functions (R package {stats}).

219 3 Results and Discussion

220 3.1 Characterization of SPAC size

221 Wet-milling of PAC produced three SPAC stock solutions, in which disperse particles (measured
222 under ultrasonication) had a $D_{50,D-PSD}$ of roughly 1, 3 and 5 μm (Table and SI, Figure S2) . This
223 corresponded to an up to 17-fold decrease from the original PAC ($D_{50,D-PSD}$ of 18.5 μm) . In the
224 absence of sonication, the SPAC particles were present in solutions as aggregates, with $D_{50,A-PSD}$
225 values of 5.8, 6.5 and 7.9 μm in WW. Similar $D_{50,A-PSD}$ values were measured in DI water (Table 1 and
226 SI, Figure S2), indicating that the matrix had only a minimal effect on the aggregation of SPAC
227 particles. Interestingly, the smaller the disperse particle size, the larger was the relative increase in
228 D_{50} between disperse and aggregated particles. In DI, PAC, SPAC 5, SPAC 3 and SPAC 1 exhibited
229 $D_{50,A-PSD}:D_{50,D-PSD}$ ratios of 1.3, 1.5, 1.6 and 4.2, respectively. A similar trend was reported by Pan et al.
230 (2016), who observed a higher $D_{50,A-PSD}:D_{50,D-PSD}$ ratio for PAC particles compared to the smaller SPAC.

231 3.2 TrOC uptake by SPAC without interventions

232 To characterize the uptake of TrOCs by SPAC in the absence of any external intervention
233 (ultrasonication or coagulation), we tested the sorption performance for different SPAC doses and
234 sizes.

235 3.2.1 Influence of dose

236 The influence of SPAC dose on the TrOC removal kinetics was assessed using SPAC 1 doses of 6, 12
237 and 15 mg SPAC/L, corresponding to specific SPAC doses of 0.8, 1.6 and 2.7 mg SPAC/mg DOC. These
238 doses approximated the PAC doses typically applied in WW treatment in Switzerland (Horisberger et
239 al., 2019; Margot et al., 2013; Zöllig et al., 2017), which extend from 10 to 20 mg/L.

240 More than 80% TrOC removal was observed after 2 min at specific doses of 1.6 and 2.7 mg
241 SPAC/mgDOC (Figure 1). For these two doses, sorption equilibrium of most compounds was reached
242 within 2-10 minutes (SI, Figure S2). The lower dose of 0.8 mg SPAC/mgDOC also achieved an 80%

243 removal but required a longer contact time of up to 60 min to approach sorption equilibrium (Figure
244 1 and SI, Figure S3). Discrepancies in the effect of dose on removal kinetics were observed at the
245 level of individual compounds (SI, Figure S3). Increasing the dose exhibited no effect on citalopram,
246 clarythromycin and irbesartan, whereas the impact was pronounced for candesartan, mecoprop and
247 sulfamethoxazole (SI, Figure S3). These latter compounds are hydrophilic (low D_{ow} ; see SI, Table S4)
248 and negatively charged at the pH of WW. Compounds with these properties tend to be poorly
249 removed from WW effluent by activated carbon, as was previously shown for GAC and PAC (De
250 Ridder et al., 2011; Margot et al., 2013).

251 The rapid average removal kinetics by SPAC observed herein confirm earlier findings by Bonvin et al.
252 (2016), who demonstrated that for 15 mg/L dose, PAC usually required 1 to 2 hours contact time to
253 reach equilibrium sorption capacity whereas for SPAC less than 10 min were sufficient. However, our
254 results also highlight the importance of the dose on the kinetics, in particular for poorly sorbing
255 TrOCs.

256 Finally, a substantial TrOC removal can likely be achieved at even shorter time intervals than tested
257 herein. Specifically, an average removal of around 30 % with up to 50% for amisulpride,
258 methylbenzotriazole and metoprolol was observed by simply filtering 20 mL of WW through a filter
259 pre- charged with 8 mg/L SPAC 1 (SI, Figure S4A). The filtration step yields a contact time around 10-
260 20 sec. This finding thus demonstrates that even at a low SPAC dose a significant amount of TrOCs is
261 sorbed almost instantaneously.

262 3.2.2 Influence of particle size

263 To determine the effect of SPAC particle size, TrOC removal kinetics were compared for SPAC 1, 3
264 and 5 (Table 1). Because no ultrasonication was applied, the SPAC materials in these experiments
265 had $D_{50, A-PSD}$ values of 5.8, 6.5 and 7.9 μm , respectively (Table 1). As shown in Figure 2, SPAC 1 and 3
266 exhibited similar ($p > 0.05$) average removal kinetics for the totality of TrOCs studied, while SPAC 5
267 μm was significantly slower ($p < 0.05$). At the individual compound level, some significant differences

268 in removal kinetics were observed, with carbamazepine, citalopram, clarithromycin and irbesartan
269 exhibiting significantly slower removal by SPAC 3 compared to SPAC 1 (SI, Figure S5). These
270 compounds have the highest D_{ow} among the TrOCs studied (SI, Table S4), indicating that hydrophobic
271 compounds respond most readily to changes in SPAC particle size. TrOC removal by SPAC 5 was
272 slower than SPAC 1 and 3 for all compounds except candesartan, which was poorly removed by SPAC
273 of all sizes (SI, Figure S5). These findings are consistent with those by Matsui et al. (2013a), who
274 observed slower removal of geosmin and MIB from diluted lake water (~1.5 mgDOC/L) by wet-
275 milled, wood-based SPAC particles with $D_{50, D-PSD}$ of 4.9 μm compared to 0.9 μm .

276 From these results we can infer that the size of SPAC influences the TrOC removal kinetics. However,
277 in these experiments, both the dispersed particle size, as well as the aggregated particle size
278 increased from SPAC 1 to SPAC 3 to SPAC 5 (Table 1). It thus remains to be determined whether it is
279 the dispersed, or the aggregated particle size that determines the uptake kinetics. Therefore, in the
280 following, we applied two interventions, ultrasonication and coagulation, to modify the aggregation
281 state of the SPAC particles, and to disentangle the effects of basic particle size and SPAC aggregation
282 on the TrOC removal.

283 3.3 Effect of ultrasonication on TrOC uptake

284 The consequence of ultrasonication during sorption phase was tested in WW for SPAC 1 with an
285 ultrasonication power of 13 Watts. As shown in section 3.2, variations in TrOC removal under
286 different conditions were mostly evident during the first 10 min of the experiment. The effect of
287 ultrasonication was therefore investigated at low contact times (1, 2, and 5 min), along with the
288 removal well after equilibrium was reached (60 min; Figure S6). Furthermore, the tested SPAC doses
289 ranged from 1.0-1.6 mg SPAC/mgDOC, because this dose range showed greater variability in TrOC
290 removal of the doses tested in section 3.2 and the removal kinetics were slower enough to see
291 potential improvement or decline.

292 Ultrasonication applied during the sorption experiment yielded no significant enhancement of TrOC
293 removal by SPAC 1, neither in the early sorption phase nor after 60 min. Both the average TrOC
294 removal and the removal of individual compounds was comparable to the removal in the absence of
295 ultrasonication (Figure 3.a and SI, Figure S6). The same results were observed for SPAC 5 (SI, Figures
296 S9 and S10). These data contradict results of Pan et al. (2016), who observed a strong enhancement
297 in the removal of MIB with dispersed dry-milled SPAC particles when ultrasonication (150 W/50 mL
298 =3 W/mL for 1 min) was applied prior the sorption experiment ($D_{50,D-PSD} = 1.2 \mu\text{m}$; $D_{50,A-PSD} = 14.2$
299 μm). This effect was smaller for wet-milled SPAC mainly because of its smaller $D_{50,A-PSD}$ (3.8 μm) for
300 the same $D_{50,D-PSD}$. Similarly, Li et al. (2018) reported faster sorption kinetics of Rhodamine B to SPAC
301 particles (<1 μm) if the particles were sonicated during the sorption experiment (100 W/100 mL = 1
302 W/mL for 30 min). The discrepancies in the findings of these two studies and the data shown herein
303 may stem from the differences in experimental design. Both Pan et al. (2016) and Li et al. (2018)
304 used ultrapure water spiked with the compounds of interest as their experimental matrices, and the
305 SPAC was added as a dry powder. In this study, we used wet-milled SPAC, which has a higher
306 equilibrium sorption capacity than dry-milled SPAC (Pan et al., 2016). Furthermore, the experimental
307 matrix used herein (WW) had a higher DOC content than ultrapure water, and rapid sorption of
308 effluent organic matter onto newly available sorption sites produced during ultrasonication may
309 mitigate the effect of SPAC dispersion on TrOC removal. And finally, the ultrasonication energy to
310 disperse the SPAC used herein (13 W/500 mL = 0.03 W/mL for 0-60 min) was lower compared to
311 earlier studies. Those higher energy inputs may alter the sorption capacity by modifying or
312 producing sorption sites.

313 To further rationalize the absence of an effect of ultrasonication, we compared the rate of SPAC
314 dispersion to the rate of TrOC sorption. In the absence of of ultrasonication, SPAC 1 exhibited a $D_{50,A-}$
315 $_{PSD}$ around 6 μm that was stable over 60 min (Figure 3.b and SI, Figure S7). If ultrasonication was
316 applied, complete particle dispersion was achieved after 10 min, resulting in a $D_{50,A-PSD}$ decrease of
317 35 % (from 5.5 to 3.6 μm), 68% (from 5.5 to 1.8 μm) and 78% (from 5.5 to 1.2 μm) after 2, 5 and 10

318 min respectively. The rates of SPAC dispersal and TrOC removal could be directly compared once
319 they were each normalized to their respective values reached at equilibrium (see SI for details). This
320 comparison revealed that the average TrOC removal, as well as the removal of individual
321 compounds, exhibited faster kinetics within the first 5 minutes compared to SPAC particle dispersion
322 (Figure 4). This implies that all the compounds studied herein were more rapidly adsorbed than the
323 SPAC was dispersed from its aggregated state. Thus, the dispersion kinetics under our experimental
324 conditions may not be fast enough to enhance TrOC sorption kinetics.

325 Faster dispersion kinetics may be achieved by applying ultrasonication with a higher power during
326 SPAC exposure to TrOCs. However, even with the low power 13 W device used in this work,
327 ultrasonication of SPAC would require substantial energy beyond that required for SPAC grinding. An
328 estimation based on the conditions used in this study (continuous sonication of 13 W/0.5 L WW)
329 indicates that milling requires around 0.055 kWh/m³ treated WW, whereas ultrasonication
330 consumes approximately 500-fold more energy (see SI for the detailed calculation). Increasing the
331 wattage of the ultrasonication device would further increase the energy consumption of the whole
332 SPAC treatment process and render it more complex in terms of design and operation.

333 Alternatively, the SPAC could be periodically dispersed in the concentrated stock solution, prior to its
334 dilution into WW. Pan et al. (2016) have reported stable D₅₀ for up to 10 days in SPAC stock of 10-50
335 g/L after dispersion by ultrasonication at 150 W for 1 min. We attempted to replicate this result in
336 SPAC stock solutions with different concentrations (2-3 g/L and 20-30 g/L), and with the highest
337 ultrasonication power at our disposition (~60 W; SI, Table S5). Even after 10 min of sonication,
338 however, the SPAC stocks remained aggregated (SI, Table S5). For the SPAC material used in this
339 study, SPAC sonication prior to the addition to WW thus is not feasible.

340 To nevertheless evaluate if there are benefits of using completely dispersed SPAC particles for TrOC
341 removal, ultrasonication was applied to a dilute SPAC solution in (largely TrOC-free) DW. Once the
342 particles were dispersed, TrOCs were then added to the DW from a spiking solution. This approach

343 allowed us to temporarily separate the SPAC dispersion and the TrOC uptake, and avoid TrOC
344 sorption during dispersal. A lower SPAC dose was used (4 mg/L) compared to experiments in WW (6-
345 8 mg/L) to decelerate the sorption process in DW, which has a low DOC (0.8 mg/L) (SI, Table S1).
346 Dispersion of the particles prior to TrOC exposure yielded only a small benefit over ultrasonication
347 applied simultaneously with TrOC exposure, and this benefit lasted for only the first minute of the
348 experiment (Figure 5 and Figure S11). This implies that the slow SPAC dispersal kinetics are not
349 limiting the average TrOC uptake. Interestingly, sulfamethoxazole, and to a lesser extent mecoprop,
350 even showed slower removal kinetics in the case were SPAC was sonicated prior to TrOC exposure
351 (SI, Figure S11).

352 However, unlike in WW (Figure 3 and SI, Figure S6), simultaneous ultrasonication of SPAC in DW
353 enhanced the removal kinetics of TrOCs (Figure 5 and SI, Figure S11). This allows us to draw some
354 conclusions regarding the role of organic matter in TrOC uptake kinetics by SPAC. Specifically, the
355 lower content of organic matter in DW may less efficiently consume new sorption sites created
356 during particle dispersion, such that these sites are more readily available to adsorb TrOCs. A gain in
357 removal kinetics can thus mainly be expected in low DOC matrices. However, even this gain
358 diminishes after 5 min of contact time, such that no further benefit of dispersion could be observed
359 (Figure 5).

360 In summary, particle dispersion benefits TrOC removal only in processes that require a very short
361 contact time and take place in low DOC matrices. In contrast, using a small basic SPAC particle size is
362 also beneficial for TrOC sorption in high DOC waters and over long contact times (Figure 2).

363 3.4 Effect of coagulant on TrOC uptake

364 Lastly, we analyzed the effect of coagulant on TrOC removal in WW to examine if TrOC removal is
365 affected by particle aggregation, or by the coagulant itself. Ferric chloride was chosen as it was
366 previously used in other studies and is commonly used in wastewater treatment (Altmann et al.,
367 2015; Mailler et al., 2016; Margot et al., 2013).

368 Coagulant without SPAC did not show any relevant effect on the average TrOC removal (Figure 3.c),
369 though it reduced the concentration of clarithromycin and hydrochlorothiazide by 30-40% after 5
370 min (SI, Figure S8). The addition of 2 ppm coagulant to WW did not alter the average nor the
371 individual TrOC removal kinetics by SPAC (Figure 3.c & SI, Figure S8). This finding could be
372 rationalized by monitoring of the SPAC size change in presence of the coagulant. During the 10 min
373 of SPAC exposure to TrOCs required to reach sorption equilibrium, the presence of coagulant had
374 only a slight effect on the SPAC size. Specifically, the $D_{50,A-PSD}$ increased by a factor of 1.3 during 10
375 min (from 5.5 to 7.6 μm), though ultimately the D_{50} was > 4 times larger after 60 min (22.2
376 μm)(Figure 3.b).

377 When adding a coagulant in WW at pH 7-8, the negatively charged SPAC particles are neutralized
378 and the repulsion between particles is therefore decreased (Nakazawa et al., 2018b; Pan et al.,
379 2016). The SPAC particles can aggregate, though the aggregation rate depends on their
380 concentration. The slow aggregation rate in our experimental system is consistent with the low SPAC
381 concentration used (Figure 3.b). In addition, the high stir rate (300 rpm) employed to ensure SPAC
382 suspension during WW treatment may cause SPAC aggregates to redisperse and may slow down
383 particle growth and prevent the formation of large aggregates.

384 Finally, a coagulant can also neutralize or remove a fraction of the DOC, and hence may reduce
385 competition with the TrOCs for the sorption sites (Mailler et al., 2016). Under our experimental
386 conditions, DOC removal was not sufficiently pronounced to result in a change in SPAC sorption
387 capacity. We can thus conclude that the Fe coagulant did not interfere in the sorption of the TrOCs
388 and therefore this coagulant can be added in a process with SPAC without implications for the SPAC
389 performance, and without constraints to the sequence at which the SPAC and coagulant are added.

390 Similar to our finding, Mailler et al. (2016 & 2014) reported no or a small positive effect of adding 2.5
391 mg/L Fe coagulant for the removal of 13 pharmaceuticals in a fluidized bed reactor with 10 mg/L PAC
392 ($D_{50,A-PSD} = 16 \mu\text{m}$). Altmann et al. (2015) also observed no significant influence of Fe coagulant at

393 concentrations up to 10 mg/L on the removal of carbamazepine, diclofenac and sulfamethoxazole
394 from WW effluent by PAC ($D_{70} < 40 \mu\text{m}$; 5 to 50 PAC mg/L). They further concluded that the
395 incorporation of PAC particles in coagulated flocs did not limit the adsorption of TrOC for Fe
396 concentration $< 10 \text{ mg/L}$. However at higher coagulant concentrations ($> 10\text{-}20 \text{ mg/L}$ of an aluminum
397 coagulant), Ho et al. (2005) reported a decrease of MIB removal with a coconut-based steam-
398 activated PAC.

399 4 Conclusions

400 We investigated the influence of SPAC aggregation state on TrOC removal. Specifically, we tested the
401 effects of dispersion by ultrasonication and coagulation by addition of FeCl_3 on the removal of up to
402 14 TrOCs from WW effluent. Based on our observations, we can make the following conclusions and
403 recommendations for using wet-milled SPAC around the micron size range in a process of TrOC
404 removal in water with a high dissolved organic matter load (5-10 mgDOC/L):

- 405 • If the SPAC dose applied is high ($> 1.6 \text{ mgSPAC/mgDOC}$), the removal kinetics are very fast
406 even in an aggregated state, such that ultrasonication yields no relevant benefit.
- 407 • If the SPAC dose applied is limited ($< 1.6 \text{ mgSPAC/mgDOC}$):
 - 408 ○ *For a contact time $> 2 \text{ minutes}$* : there are no significant effect of ultrasonication. The
409 removal kinetics increases with decreasing basic particle size, but not with
410 decreasing aggregate size. To limit energy consumption, it is more efficient to spend
411 energy on milling the SPAC to small sizes than to ultrasonicate. Furthermore, the
412 downstream separation step (membrane ultrafiltration, sand filter) might further
413 benefit from particle aggregation to remove SPAC from the final treated effluent.
 - 414 ○ *For a contact time $< 2 \text{ minutes}$* : an ultrasonication step can be beneficial if it is
415 designed such that the SPAC particles reach complete dispersion prior to the
416 sorption step. However, one should consider carefully the energy requirement for

417 the ultrasonication, which could be prohibitive for processes that aim at treating
418 large volumes of water. Further investigations on low-energy consuming methods to
419 keep concentrated SPAC stock in a dispersed state need be conducted.

- 420 • Coagulant can be added simultaneously with the SPAC without compromising the TrOC
421 removal efficiency.

422

423 Declaration of competing interest

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

426

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431

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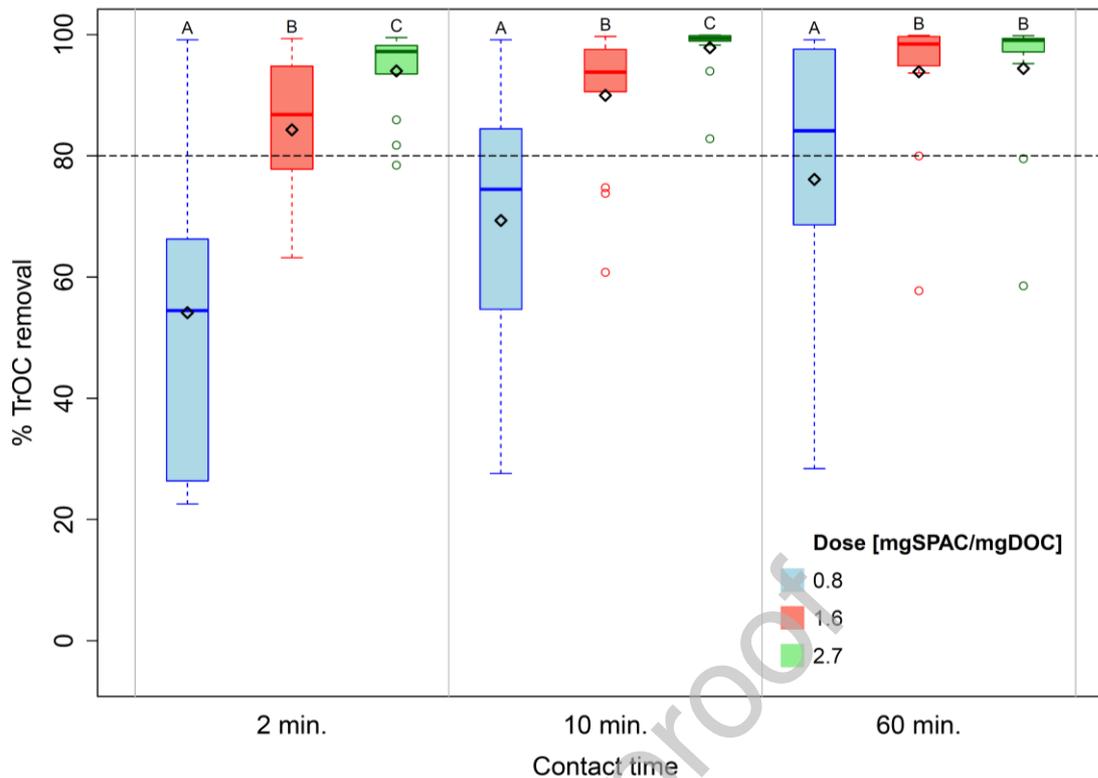
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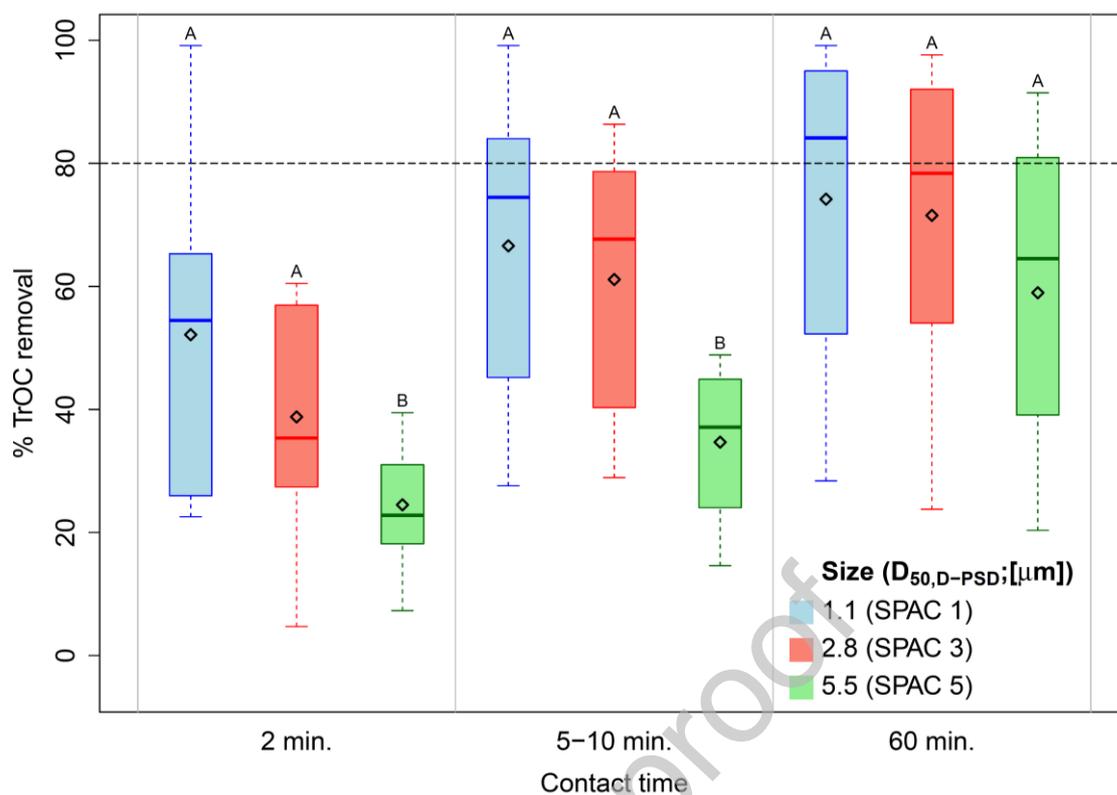
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565

566 *Figure 1: TrOC removal kinetics by SPAC as a function of the specific SPAC dose [mg SPAC/mgDOC].*567 *SPAC 1 ($D_{50,D-PSD} \approx 1 \mu\text{m}$) was applied in volume-based doses of 6, 12 and 15 mg SPAC/L (blue, red and*568 *green respectively), corresponding to specific doses of 0.8, 1.6 and 2.7 mg SPAC/mgDOC. Data are*569 *shown in boxplot format, where the thick line indicates the median removal of the 14 TrOCs studied.*570 *The box is bounded by the first and third quartiles (50% of the data), the whiskers indicate the*571 *minimum and maximum removal measured and the dots are the outliers. Open black diamonds show*572 *the average removal of the 14 TrOC, and the horizontal dashed line indicates the removal objective*573 *set by the Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters*574 *have significantly different ($p < 0.05$) median removal values. Removal kinetics of each individual TrOC*575 *are shown in the SI (Figure S3).*

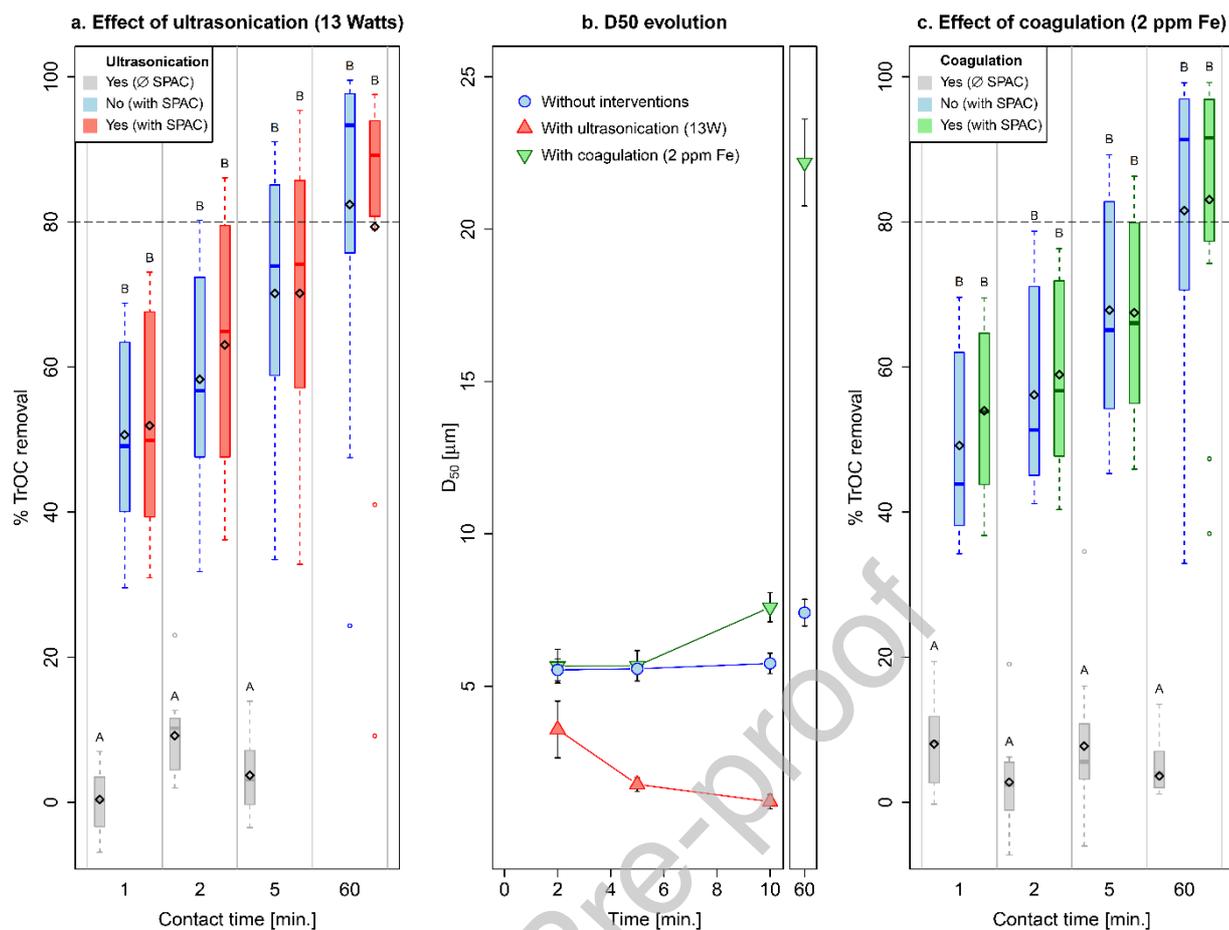
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578 *Figure 2: TrOC removal kinetics as a function of SPAC size. SPAC particles tested had a $D_{50,D-PSD}$ of 1.1,*
579 *2.8 and 5.5 μm , but because no ultrasonication was applied, the SPAC particles had actual ($D_{50,A-PSD}$)*
580 *sizes of 5.8, 6.5 and 7.9 μm (Table 1). The volume-based dose SPAC dose was 6 mg/L (specific dose:*
581 *0.8 mg SPAC/mgDOC for SPAC 1 and SPAC 3, and 1.3 mg SPAC/mgDOC for SPAC 5, respectively).*
582 *Data are shown in boxplot format, where the thick line indicates the median removal of 12 TrOCs*
583 *studied (citalopram and hydrochlorothiazide were omitted for all conditions, because they were not*
584 *quantifiable in the experiment with SPAC 5). The box is bounded by the first and third quartiles (50%*
585 *of the data), the whiskers indicate the minimum and maximum removal measured and the dots are*
586 *the outliers. Open black diamonds show the average removal of the 14 TrOC, and the horizontal*
587 *dashed line indicates the removal objective set by the Swiss Water Protection Ordinance (80%*
588 *average removal). Boxplots with different letters have significantly different ($p < 0.05$) median*
589 *removal values. The removal of each individual compound is shown in the SI (Figure S5). SPAC 1 and 3*
590 *were tested in WW1, and SPAC 5 was tested in WW2.*

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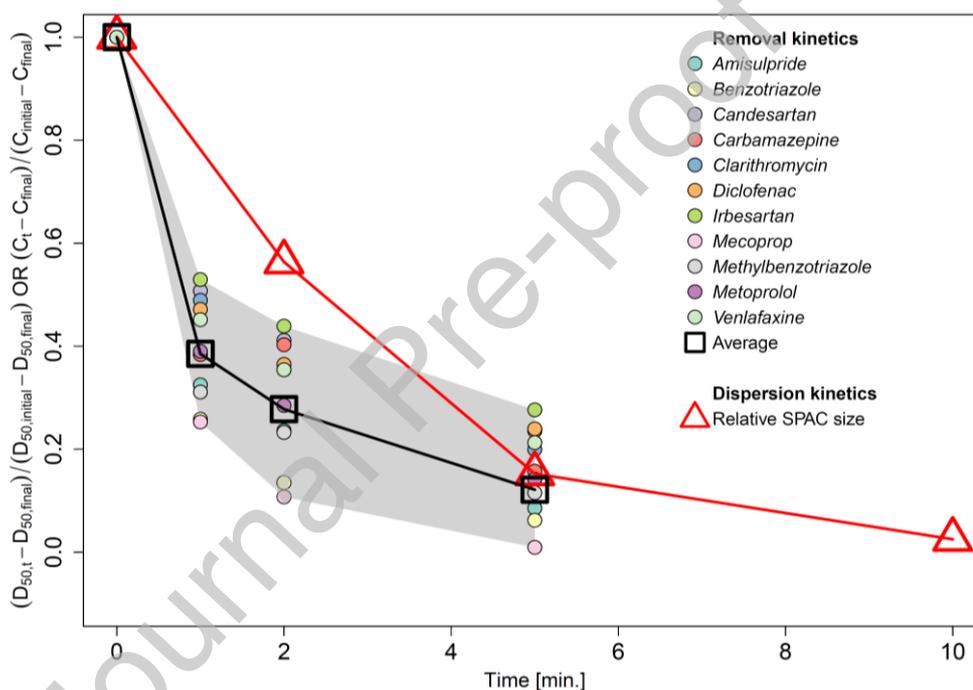


592

593 **Figure 3: Effect of interventions (ultrasonication or coagulation) on TrOC removal by SPAC.** (a) TrOC
 594 removal by SPAC 1 (6 mg/L or 1.3 mg SPAC/mgDOC) without ultrasonication (blue), by SPAC 1 under
 595 simultaneous ultrasonication (red), and with ultrasonication in the absence of SPAC (grey). Data are
 596 shown as boxplots, where the thick line indicates the median removal of 12 TrOCs studied
 597 (citalopram and hydrochlorothiazide were omitted because they were not quantifiable). The box is
 598 bounded by the first and third quartiles (50% of the data), the whiskers indicate the minimum and
 599 maximum removal measured and the dots are the outliers. Open black diamonds indicate the
 600 average removal of the 12 TrOCs. The black dashed line indicates the removal objective set by the
 601 Swiss Water Protection Ordinance (80% average removal). Boxplots with different letters have
 602 significantly different ($p < 0.05$) median removal values. The removal of each individual compound is
 603 shown in the SI (Figure S6). (b) SPAC dispersion or aggregation over time for 8 mg/L of SPAC 1 ($D_{50,D-}$
 604 $_{PSD} \approx 1 \mu\text{m}$) in filtered/pasteurized WW. Data indicate the $D_{50,A-PSD}$ values measured without external

605 interventions (only stirring; blue circles), under ultrasonication (13W; red triangles), and in presence
 606 of a coagulant (2 ppm FeCl_3 ; green inverted triangles). The error bars depict the 95% confidence
 607 intervals ($n = 3$). Detailed PSD data is given in the SI (Figure S7). (c) TrOC removal by SPAC 1 (6 mg/L
 608 or 1.5 mg SPAC/mgDOC) without coagulant (blue), by SPAC 1 with 2 ppm FeCl_3 coagulant (green) and
 609 with 2 ppm FeCl_3 coagulant in the absence of SPAC (grey). Data are shown as boxplots as in panel a,
 610 except that the open black diamonds indicate the average removal of 13 TrOCs (only citalopram was
 611 not quantifiable). Individual compound removal is shown in the SI (Figure S8).

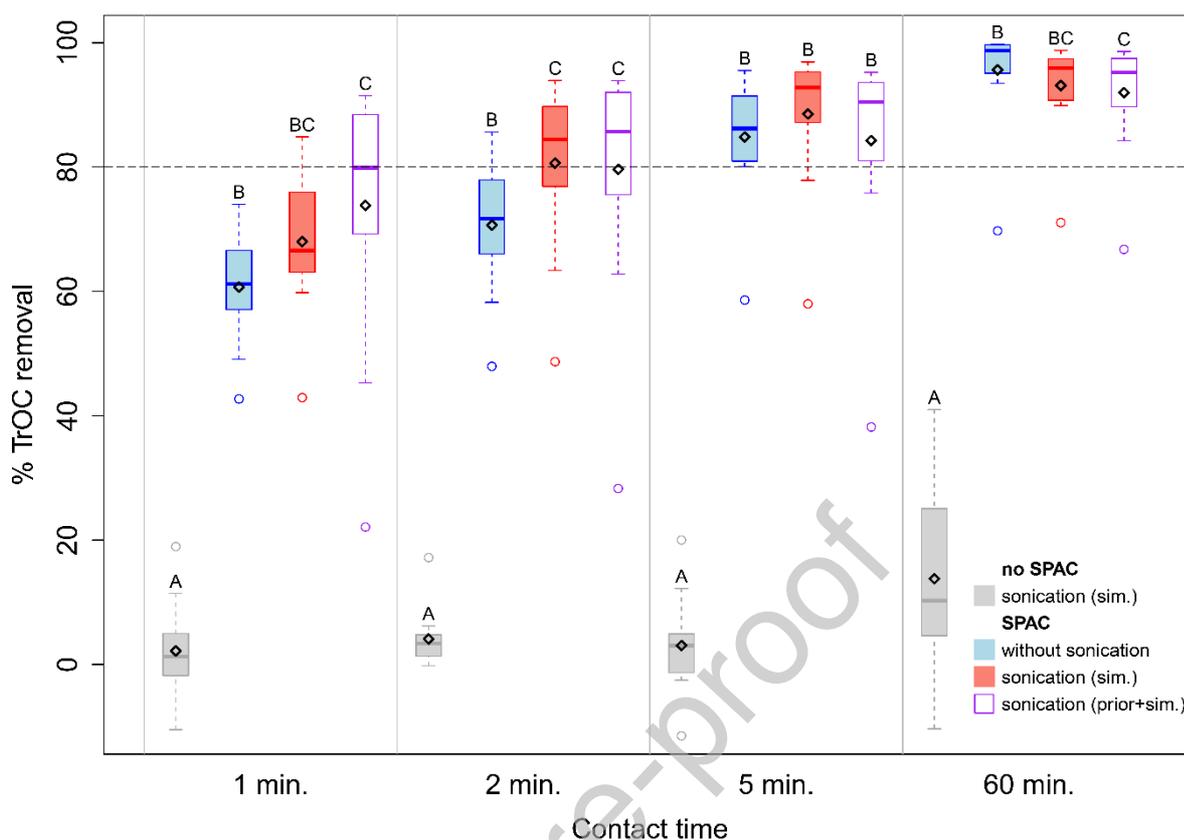
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613

614 **Figure 4: Comparison of TrOC sorption and SPAC dispersion kinetics.** Kinetics of TrOC by SPAC 1
 615 without ultrasonication (black squares) was compared to the kinetics of size change of SPAC 1 during
 616 ultrasonication (red triangles). The removal values of individual compounds are shown in colored
 617 dots, except for citalopram and hydrochlorothiazide and sulfamethoxazole (removal not
 618 quantifiable). The grey area represents the domain between the minimum and maximum removal of
 619 any individual compound. TrOC removal data corresponds to that shown in Figure 3a and SI, Figure
 620 S6. SPAC PSD data corresponds to that in Figure 3b and SI, Figure S7.

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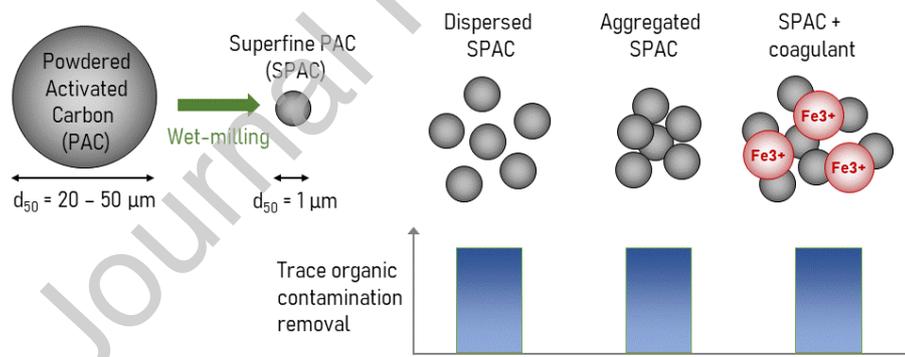
623 *Figure 5: TrOC removal from DW by SPAC. TrOC removal was monitored with ultrasonication applied*
 624 *simultaneously to TrOC exposure (red), and with ultrasonication applied both prior to and*
 625 *simultaneous with TrOC exposure (empty purple). Controls without SPAC (grey) or without*
 626 *ultrasonication (blue) were also included. SPAC 1 ($D_{50,D-PSD} \approx 1 \mu\text{m}$) was used at a dose of 4 mg/L or 5*
 627 *mgSPAC/mgDOC. Data are shown as boxplots, where the thick line indicates the median removal of*
 628 *12 TrOCs studied (Citalopram and diclofenac were not quantifiable). The box is bounded by the first*
 629 *and third quartiles (50% of the data), the whiskers indicate the minimum and maximum removal*
 630 *measured and the dots are the outliers. Open black diamonds indicate the average removal of the 12*
 631 *TrOC. The black dashed line indicates the removal objective set by the Swiss Water Protection*
 632 *Ordinance (80% average removal). Boxplots with different letters have significantly different ($p < 0.05$)*
 633 *median removal values. The removal of each individual compound is shown in the SI (Figure S11).*

634

635 Table 1: D_{50} comparison between D-PSD and A-PSD for SAPC/PAC in DI water and WW used in our
 636 experiments according to the procedure described in the Materials and Methods section (detailed
 637 PSD are shown in SI, Figure S2).

	D-PSD		A-PSD	
	DI water		DI water	WW
	D_{50} (D_{10} , D_{90}) [μm]		D_{50} (D_{10} , D_{90}) [μm]	D_{50} (D_{10} , D_{90}) [μm]
PAC	18.5 (2.2, 61.7)		24.0 (3.6, 78.2)	
SPAC 1	1.1 (0.4, 3.4)		4.6 (2.2, 8.4)	5.8 (2.9, 10.4)
SPAC 3	2.8 (0.7, 17.6)		4.5 (1.9, 41.9)	6.5 (2.8, 18.1)
SPAC 5	5.5 (1.2, 29.5)		8.2 (2.6, 47.2)	7.9 (3.0, 41.1)

638

639 **Graphical**

640

641 **Declaration of interests**

642

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