

24 **Abstract**

25 Concerns have been raised about per- and polyfluoroalkyl substances (PFAS) in sewage
26 sludge given the urgent need of finding suitable disposal methods for sludge. In this study, we
27 evaluated the effect of ultrasonication on PFAS changes in sewage sludge. It was revealed that
28 although ultrasonication at 20 kHz increased the soluble chemical oxygen demand (SCOD) of
29 treated sewage sludge, this technique was ineffective for degrading perfluoroalkyl acids (PFAAs)
30 and their precursors. Ultrasonic treatment for longer time (> 15 min) led to concentration
31 increase of perfluorooctanoic acid (PFOA), perfluoroheptanoic acid (PFHpA), and
32 perfluorohexanoic acid (PFHxA) in the liquid phase, possibly due to their release from disrupted
33 sludge flocs during cavitation. Adding permanganate (10 mM) to the ultrasonic system could
34 also enhance the disruption of sludge particles, resulting in higher concentrations of PFOA and
35 PFHxA in the solid phase and PFOA, PFHpA, PFHxA, and perfluorobutanesulfonic acid (PFBS)
36 in the liquid phase. Overall, ultrasonic pretreatment at 20 kHz and 0.7 W/mL is unlikely to
37 remove PFAS from sewage sludge. Instead, it could increase the risk of PFAS pollution upon
38 final sludge disposal. Effective treatment technologies are thus demanded if PFAS in sludge are
39 regulated.

40

41 **Keywords:** sewage sludge, ultrasonication, per- and polyfluoroalkyl substances, perfluoroalkyl
42 acids, PFAA precursors.

43

44

45

46

47 **1. Introduction**

48 Per- and polyfluoroalkyl substances (PFAS) are of continued concern due to their
49 persistent, bio-accumulative, and potentially toxic nature. Perfluoroalkyl acids (PFAAs) that
50 contain either a carboxylic function group (PFCAs) or a sulfonic functional group (PFSAs) are a
51 major subclass of PFAS. Owing to their extremely high physicochemical stability, PFAAs are
52 often referred to as “terminal PFAS” (Moody et al., 2002; Miralles-Marco and Harrad, 2015).
53 Polyfluorinated compounds also widely exist in contaminated water and soil at aqueous film-
54 forming foam (AFFF)-impacted sites (Guelfo and Higgins, 2013). These chemicals can be
55 transformed to stable PFAAs under certain conditions and are hence termed as PFAA precursors
56 (Wang et al., 2017).

57 Numerous studies have reported occurrence of various PFAS in the environment and
58 engineered systems (Banzhaf et al., 2017; Ghisi et al., 2019; Brusseau et al., 2020). Among a
59 wide range of engineered systems, wastewater treatment plants are one type that is ubiquitous
60 worldwide. It is known that traditional wastewater treatment processes are ineffective in
61 removing PFAS (Sinclair and Kannan, 2006) and PFAA concentrations in the effluent leaving a
62 wastewater treatment plant could be even higher than those in the influent due to transformation
63 of PFAA precursors in the raw wastewater (Schultz et al., 2006; Sinclair and Kannan, 2006). As
64 a by-product from wastewater treatment, sewage sludge has thus become a sink for PFAS and
65 could lead to potential environmental risks upon improper disposal (Higgins et al., 2005; Guo et
66 al., 2008; Yu et al., 2009; Zhang et al., 2010; Sun et al., 2011). The data of 2001 EPA National
67 Sewage Sludge Survey revealed that the mass of PFAS in sewage sludge produced by U.S.
68 wastewater treatment plants was around 2,749 – 3,450 kg/year, of which 1,375 – 2,070 kg went
69 to agricultural land and 467 – 587 kg stayed in landfills (Venkatesan and Halden, 2013).

70 Conventionally, without considering the presence of PFAS in sewage sludge, sludge has
71 been subject to different treatment technologies before final disposal. Among these treatment
72 methods, anaerobic digestion (AD) is an efficient and well-practiced technology for treating
73 sewage sludge, converting biodegradable organic compounds in sewage sludge to methane and
74 carbon dioxide in the absence of oxygen (Appels et al., 2008; Pilli et al., 2011). The advantages
75 of AD include reduction of sludge mass, odor removal, pathogen reduction, low energy input,
76 and high energy recovery in the form of methane (Appels et al., 2008). To enhance yield of
77 biogas and achieve a better performance of the AD process, different pretreatment technologies
78 have been studied and applied at commercial scales to improve sludge's biodegradability. These
79 pretreatments are generally accomplished through mechanical, thermal, chemical, and biological
80 approaches (Zhen et al., 2017).

81 Ultrasonication is a well-established mechanical pretreatment method that can disrupt the
82 polymeric structure of sewage sludge, resulting in the enhancement of sludge digestibility.
83 During ultrasonication, ultrasound waves transport through the sludge and microbubbles are
84 formed due to periodical compression and rarefaction (Onyeche et al., 2002). These
85 microbubbles grow in successive cycles and reach to an unstable diameter. Then, implosive
86 collapse of the microbubbles occurs, producing a localized hotspot region with extreme
87 conditions (temperature of around 5,000 °C and pressure of 500 bars at a lifetime of few
88 microseconds) (Sivakumar et al., 2014). This process of bubbles' formation, growth and collapse
89 is known as cavitation. Cavitation initiates hydro-mechanical shear forces and generates highly
90 reactive radicals (e.g., $H\cdot$, $\cdot OH$) (Pilli et al., 2011). Both mechanisms contribute to the
91 disintegration of sludge flocs. To date, at least 20 full-scale and 17 pilot-scale ultrasonic systems

92 have been installed and used for sludge pretreatment, mostly in Germany (Long and Bullard,
93 2014; Zhen et al., 2017).

94 Ultrasonication treatment has also been demonstrated to degrade PFAS in aqueous
95 solutions. PFAS, especially long carbon chain PFAAs, are surface active compounds and tend to
96 stay at the air-water interface. The high pressure and temperature conditions caused by cavitation
97 could pyrolyze PFAS that accumulate at the air-water interface of the microbubbles (Cao et al.,
98 2020; Lei et al., 2020). The highly reactive radicals (e.g., $H\cdot$, $\cdot OH$) generated during cavitation
99 could also contribute to PFAS degradation through oxidation. To further accelerate degradation
100 rate and reduce energy input, various chemical reagents (e.g., permanganate, persulfate,
101 periodate) have been used in ultrasonic systems as additives to generate extra free radicals for
102 PFAS degradation (Yang et al., 2013; Thi et al., 2014; Lee et al., 2016; Gole et al., 2018b).
103 Although ultrasonication showed promising ability to remove PFAS from contaminated water,
104 its effect on PFAS in sewage sludge that undergoes ultrasonication pretreatment has not been
105 reported in the literature. Thus, to assess the PFAS-related environmental problems caused by
106 disposal of residual sludge after ultrasonication pretreatment followed by AD, it is important to
107 investigate how PFAS change during this pretreatment process.

108 Therefore, the goal of this study was to understand change of PFAS in sludge as a result
109 of ultrasonication treatment. PFAA precursors and a few commonly detected PFAAs were
110 targeted in this study. These PFAAs included perfluorobutanoic acid (PFBA), perfluorohexanoic
111 acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA),
112 perfluorobutanesulfonic acid (PFBS), perfluorohexane sulfonate (PFHxS), and
113 perfluorooctanesulfonic acid (PFOS). Additionally, the effects of ultrasonication time and one
114 additive (permanganate) on changes of sludge PFAS were investigated as well.

115

116 **2. Materials and methods**

117 *2.1 Chemicals and reagents*

118 The details of chemicals used in the experiments were shown in Table S1. The primary,
119 secondary, and combined sewage sludge (primary: secondary = 1: 1) were collected from a local
120 wastewater treatment plant close to the University at Albany. The total solid content of the
121 primary, secondary, and combined sewage sludge was $2.81 \pm 0.27\%$, 6.04 ± 0.28 , and $4.20 \pm$
122 0.02% , respectively. The total volatile solid content of the primary, secondary, and combined
123 sewage sludge was $77.56 \pm 0.33\%$, 75.93 ± 0.78 , and $78.24 \pm 0.25\%$ (dry weight based),
124 respectively.

125 *2.2 Experimental procedures for sonication process*

126 Ultrasonication treatments of sewage sludge for different durations were performed using
127 a Qsonica Q2000 sonicator with a 0.5-inch probe. The sonication frequency was 20 kHz and the
128 amplitude was set at 100%. The sonicator probe was placed in the center of a 150-mL
129 polypropylene (PP) beaker containing 100 mL of sewage sludge and a glass magnetic stirrer for
130 homogenization. The total input of energy (J) and power (W) was displayed by the sonicator
131 instrument. The power density was then calculated by the equation: Power density = power input
132 (W) / sludge volume (mL).

133 It is generally recognized that only soluble compounds are available to and potentially
134 degradable by microorganisms. Thus, soluble chemical oxygen demand (SCOD) has been
135 commonly considered as a key parameter for evaluating effect of pretreatment on sludge
136 disintegration (Ma et al., 2018). Considering this reason, the effects of sonication temperature
137 (40 – 50 °C) and time (0 – 60 min) on fold increase of SCOD of the sewage sludge were first

138 investigated. SCOD was measured by using the HACH kit following manufacturer
139 recommended procedures. According to our results, the SCOD fold increases were similar when
140 sonication temperature was controlled at 40 and 50 °C (Fig. S1). To shorten the total cooling
141 time, 50 °C was selected for the following experiments.

142 To understand how PFAS changed due to sonication treatment, the effect of
143 ultrasonication time (5, 15, and 60 min) on PFAS concentrations in combined sewage sludge was
144 studied. The effect of an oxidant, potassium permanganate (10 mM) on PFAS changes as a result
145 of ultrasonication for 15 min was investigated as well. After ultrasonication treatment, the
146 sewage sludge was centrifuged at 10,000 ×g for 20 min. The semi-solid pellet and the
147 supernatant were named as solid phase and liquid phase, respectively. All experiments were
148 conducted in triplicates.

149 *2.3 PFAS extraction and analysis*

150 The solid phase of each sample was weighed before and after freeze-drying. The solid
151 content of the solid phase was determined as $23.40 \pm 3.01\%$. The dried solid pellet was then
152 homogenized using a mortar and pestle, weighed, and transferred to a new 50-mL PP centrifuge
153 tube. Afterwards, 20 ng of surrogate (^{13}C -PFHxA) was spiked to each sample. The extraction of
154 PFAS was conducted following the method published by Houtz et al. (2013) and Nickerson et al.
155 (2020) with slight modification. Briefly, four mL of basic methanol (0.1 M ammonium
156 hydroxide in methanol) were added to the dry sludge, followed by vortexing for 30 seconds,
157 sonicating at 35 °C for 30 min, and centrifuging at 4,500 rpm for 10 min. The supernatant was
158 then collected. The extraction steps were repeated twice using the basic methanol and the
159 extracts from the three rounds were combined and passed through a Supelclean ENVI-Carb
160 cartridge (250 mg, MilliporeSigma, Burlington, MA, USA). The cleaned extracts were

161 evaporated to dryness with nitrogen in a 45 °C water bath and reconstituted in 6 mL of methanol
162 with 1% acetic acid.

163 The 6 mL of extracts after the extraction were then separated into 2 portions evenly (3
164 mL + 3 mL). One portion was used for PFAA analysis. The other portion was further processed
165 with a total oxidizable precursor (TOP) assay. Under the condition of TOP assay, precursors to
166 both PFCAs and PFSAAs are converted to PFCAs (Houtz and Sedlak, 2012; Houtz et al., 2013).
167 Prior to TOP assay, the 3 mL of extract was evaporated to dryness under nitrogen gas. The dried
168 material was resuspended in 6 mL of deionized water containing 60 mM persulfate and 150 mM
169 NaOH. The samples were then heated at 85 °C for 6 hours. After reaction, all samples were
170 neutralized with HCl and subjected to solid phase extraction (SPE) using HyperSep C18
171 cartridges (Thermo Scientific, Waltham, MA, USA). The cartridges were preconditioned with 4
172 mL of 0.1% NH₄OH in methanol, followed by 4 mL of water. Samples were eluted with 2 mL of
173 methanol, followed by 2 mL of 0.1% NH₄OH in methanol. The concentration of precursors was
174 calculated by subtracting the total concentration of PFCAs in the sample before TOP assay from
175 the total concentration of PFCAs after TOP assay.

176 To quantify PFAS concentrations in the liquid phase after sonication, six replicates of the
177 liquid phase from each treatment were prepared in 15-mL centrifuge tubes. For each of the six,
178 0.228 mL of 10 N NaOH were added to the tube (final NaOH concentration: 150 mM). After 1
179 hour, all samples were centrifuged at 4,500 g for 20 min to remove the suspended solids. The pH
180 of three of the six replicates was then adjusted to 5-9 using HCl. Twenty ng of surrogate (¹³C-
181 PFHxA) was spiked to each of the three replicates. These three replicates were then subjected to
182 SPE and eluted with 2 mL of methanol, followed by 2 mL of 0.1% NH₄OH in methanol. For the
183 other three of the six replicates, 0.24 g of potassium persulfate were added to each tube (final

184 persulfate concentration: 60 mM, NaOH concentration: 150 mM). These samples with NaOH
185 and persulfate went through TOP assay in an oven at 85 °C for 6 hours. The pH of the samples
186 after TOP assay was adjusted to 5 – 9 using HCl. This was followed by SPE and elution with 2
187 mL of methanol, followed by 2 mL of 0.1% NH₄OH in methanol.

188 After extraction, PFAAs were quantified using a 6470 Triple Quad Mass Spectrometer
189 (Agilent Technologies, Santa Clara, CA, USA) following our reported procedures (Cao et al.,
190 2020; Zhang et al., 2020) . Internal standards (i.e., ¹³C-PFOA, ¹³C-PFOS) were spiked to each
191 sample extract before analysis. The analytical column and delay column were Agilent ZORBAX
192 Eclipse Plus C18 (3.0 × 50 mm, 1.8µm) and an Agilent Eclipse Plus C18 (4.6 × 50 mm, 3.5µm),
193 respectively. The column temperature was set at 50 °C and the sample injection volume was set
194 as 5 µL. Water and 95% methanol with 5 mM ammonium acetate were used as mobile phase A
195 and B. The gradient elution started at 70% A and 30% B, shifted to 0% A and 100% B at 8 min.
196 The total running time was 12 min. Other LC-MS/MS running parameters were detailed in Table
197 S2.

198

199 **3. Results and discussion**

200 *3.1 Effect of ultrasonication on sludge SCOD*

201 As introduced above, ultrasonication has been practiced as a pretreatment technology for
202 enhancing biogas production from sludge. The major mechanisms for ultrasonic disintegration of
203 sludge are proposed as hydro-mechanical shear forces and oxidation effect of reactive radicals
204 (e.g., H·, ·OH) (Pilli et al., 2011). During cavitation, the sludge flocs are disrupted, which leads
205 to increased SCOD. Show et al. (2007) found that the flocs in secondary sludge were more
206 readily to be disintegrated by ultrasonication than those in primary sludge. After ultrasonication

207 with a frequency of 20 kHz and sonication density of 0.52 W/mL, the SCOD fold increase for
208 the secondary sludge was around 5. The higher SCOD fold increase observed for the secondary
209 sludge could be explained by its composition (Show et al., 2007). Secondary sewage sludge is
210 mainly composed of biological materials derived from the conventional activated sludge
211 treatment process, while primary sludge contains more solids, such as plastics, sand, and textile
212 that may be resistant to disruption by ultrasonication. In this study, at a power density of 0.7
213 W/mL, the SCOD fold increase of the primary, secondary, and combined sludge all increased
214 with increasing ultrasonication time, indicating the effectiveness of ultrasonication for sludge
215 pretreatment (Fig. 1). Moreover, consistent with findings reported by other researchers, the
216 SCOD fold increase of the secondary sludge was higher than that of the primary and combined
217 sludge.

218 It is known that ultrasonication leads to increased temperature of the ultrasonication
219 medium. The rise in temperature results in higher saturated vapor pressure which makes it harder
220 for the vapor bubbles to collapse and thus decrease the intensity of cavitation and the
221 disintegration efficiency (Huan et al., 2009). In addition, the ultrasonication probe has a
222 temperature limit. For the one used in this study, the upper limit is 60 °C. Considering these
223 reasons, the ultrasonication temperature was controlled at 40 or 50 °C. As shown in Fig. S1,
224 these two temperatures led to no significant difference for SCOD fold increase for the secondary
225 sludge. Thus, for later studies, ultrasonication was conducted at 50 °C. This temperature also
226 required overall shorter treatment time since the frequency of the sonicator pulsing to maintain
227 the set temperature was less than that at 40 °C.

228 *3.2 Determination of PFAS in combined sewage sludge*

229 In practice, primary and secondary sewage sludge are usually combined for treatment
230 processes before final disposal. For the treatment plant where we collected these three types of
231 sludge, primary and secondary sludge (50:50) are mixed before entering anaerobic digesters.
232 Thus, for this study, to investigate ultrasonication effect on PFAS, we mainly focused on the
233 combined sewage sludge.

234 The surrogate recoveries and percent deviations of internal standard responses for the
235 untreated and ultrasonically treated sewage sludge were shown in Fig. 2. Consistent with our
236 previous determination (Zhang and Liang, 2021b), the surrogate recoveries in the solid phase
237 samples were between 50 – 60%, which were lower than the acceptable level (70 – 130%)
238 suggested by EPA method 537.1 (Shoemaker and Tettenhorst, 2018). The surrogate recoveries in
239 the liquid phase of untreated and ultrasonically treated samples, except the treated samples with
240 permanganate, were significantly higher than those in the solid phase and met the requirement of
241 EPA method 537.1. The percent deviation of internal standard responses in measured samples
242 from the average internal standard responses in external analyte calibrations is another index for
243 the quality control of PFAS quantification and should be within $\pm 50\%$ according to EPA method
244 537.1 (Shoemaker and Tettenhorst, 2018). In this study, the solid phase of untreated and treated
245 sludge and the liquid phase of permanganate treated sludge did not meet this requirement.
246 Passing the extracts through ENVI-Carb cartridges repeatedly could not increase the recoveries
247 or decrease the percent deviation in those samples. Significant matrix effect caused by unknown
248 compounds in the extracts may result in the extraction imperfection. Further cleanup approaches
249 beyond the ENVI-Carb cartridges are needed and worth further investigation to improve PFAS
250 quantification in sewage sludge. Moreover, due to the differences of chemical structures and
251 interactions with sludge between surrogate (^{13}C -PFHxA) and the target PFAS, whether the

252 surrogate recoveries can truly represent recoveries of PFAS in sludge or not deserve to be further
253 evaluated.

254 *3.3 Changes of PFAS in sewage sludge after ultrasonication*

255 In this work, all PFAAs and their precursors in the solid phase had significantly higher
256 concentrations than those in the corresponding liquid phase (Fig. 3). PFOS had the highest
257 concentration, followed by PFOA, PFHxA, PFBS, and PFAA precursors. Ultrasonic treatment
258 did not change the concentrations of PFAAs and their precursors in the solid phase, but gradually
259 increased the concentrations of PFOA, PFHpA, and PFHxA in the liquid phase over time (0 – 60
260 min).

261 In an ultrasonic system, ultrasonic frequency determines the maximum size (critical size)
262 of cavitation bubbles before they collapse (Suslick, 1989). Higher ultrasonic frequency results in
263 smaller bubble size and shorter bubble collapse time, thereby leading to an increase of cavitation
264 bubble events per unit time and an enhancement in sonochemical reactions (Petrier and Francony,
265 1997; Manousaki et al., 2004). Ultrasound can be divided into three regions according to its
266 frequency: power ultrasound (20 – 100 kHz), high frequency ultrasound (100 kHz – 1 MHz), and
267 diagnostic ultrasound (1 – 500 MHz). Most of the studies on sonolysis of PFAS in previous
268 literature applied high frequency ultrasound (Campbell et al., 2009; Campbell and Hoffmann,
269 2015; Rodriguez-Freire et al., 2016; Gole et al., 2018a; Gole et al., 2018b; Cao et al., 2020).
270 Campbell and Hoffmann (2015) reported that the optimum ultrasonic frequencies for degrading
271 long chain PFAAs (i.e., PFOA, PFOS, PFHxS, PFHxA) and short chain PFAAs (i.e., PFBA,
272 PFBS) were 358 kHz and 610 kHz, respectively. However, power ultrasound is more commonly
273 used in pretreatment of sewage sludge (Pilli et al., 2011). Tiehm et al. (2001) reported that lower
274 ultrasonic frequency led to higher sludge disintegration efficiency, which is beneficial to the

275 following AD process. Thus, 20 kHz was adopted for pretreating sewage sludge in this study.
276 Apparently, such ultrasonication condition used for sludge pretreatment did not lead to PFAS
277 degradation. Instead, ultrasonication for 60 min increased the concentrations of PFOA, PFHpA,
278 and PFHxA in the liquid phase. This could be explained by two reasons. First, during
279 ultrasonication, precursors to these three PFAAs were degraded to PFAAs. Second, the release of
280 these three PFAAs bound to sludge flocs was promoted by ultrasonication. Since concentrations
281 of PFAAs in the liquid phase did not differ significantly between untreated and treated, the first
282 explanation was not valid. Hence, our results revealed that although ultrasonication can increase
283 floc disintegration and lead to enhanced biodegradability of sewage sludge during the AD
284 process, it is unlikely to degrade PFAS.

285 *3.4 Effect of permanganate on PFAS degradation during ultrasonication*

286 Ultrasonication is an energy-intensive process, raising concerns about its cost
287 effectiveness. Additives that can generate free radicals during ultrasonication treatment were
288 found to be able to intensify the sonochemical reactions and reduce energy input (Phan Thi et al.,
289 2014). Permanganate is a strong oxidant and can be sonochemically reduced to MnO₂ particles
290 ($\text{MnO}_4^- + 3\text{H}\cdot \rightarrow \text{MnO}_2 + \text{OH}^- + \text{H}_2\text{O}$). These particles can act as cavitation nuclei and enhance
291 the degradation of organic pollutants (Okitsu et al., 2009; Zhao et al., 2014). For example, Gole
292 et al. (2018b) reported that ultrasonication at 40 kHz for 120 min with 10 mM of permanganate
293 achieved 84.3% decomposition of PFOA, which was 2.8 times higher than that in a pure
294 ultrasonic system without this additive. Pyrolytic cleavage of C-C bond and permanganate
295 oxidation were proposed to be the main mechanisms for PFOA degradation. In this study, to
296 investigate the effect of permanganate on PFAS changes in sludge treated by ultrasonication for
297 shorter time (15 min), 10 mM of permanganate was dosed to the system. The addition of

298 permanganate, however, did not lead to enhancement of PFAA degradation, except PFBA in the
299 liquid phase (Fig. 4). In contrast, the concentrations of PFOA and PFHxA in the solid phase and
300 PFOA, PFHpA, PFHxA, and PFBS in the liquid phase increased after the ultrasonication
301 treatment with permanganate. This could be explained by the low ultrasound frequency (20 kHz)
302 and the consumption of permanganate and free radicals by sludge flocs. Sewage sludge contains
303 a large number of biological materials that can be oxidized by permanganate and radicals such as
304 H· and ·OH. Similar to the explanations above, the increased PFAS concentrations could be due
305 to enhanced release and extractability of PFAS from either bound or sorbed state with sludge
306 flocs due to sonication. Overall, this study demonstrated that permanganate at 10 mM was not
307 able to improve the sonochemical degradation of PFAS in sewage sludge. Compared to results
308 from hydrothermal treatment of the same sludge, the hydrothermal process is more promising as
309 it leads to degradation of some PFAS (e.g., PFOA, PFHxA, PFHpA) under certain conditions
310 (Zhang and Liang, 2021a). The sonochemical approach toward degrading PFAS in sludge could
311 be enhanced by adopting higher frequencies and harsher conditions that await to be identified.

312

313 **4. Conclusions**

314 In this study, we evaluated the effect of ultrasonication on SCOD and the change of
315 PFAS in sewage sludge. The results indicated that ultrasonication was able to increase SCOD of
316 all three types of sludge, especially the secondary sludge. Concentrations of all studied PFAAs
317 and their precursors in the solid phase of sludge did not change after ultrasonic treatment,
318 indicating the ineffectiveness of ultrasound at low frequency (20 kHz) for PFAS degradation.
319 Ultrasonically treated sludge for longer time (> 15 min) led to concentration increase of PFOA,
320 PFHpA, and PFHxA in the liquid phase, possibly due to their release from disrupted sludge

321 particles during cavitation. Adding permanganate (10 mM) to the ultrasonic system resulted in
322 higher concentrations of PFOA and PFHxA in solid phase and PFOA, PFHpA, PFHxA, and
323 PFBS in the liquid phase. The increases could also be due to the enhancement of PFAS
324 desorption from sludge flocs. Overall, ultrasonication at 20 kHz was not capable of PFAS
325 removal from sewage sludge. Effective treatment technologies are needed if PFAS in sludge are
326 regulated.

327

328 **Acknowledgement:**

329 This material is based upon work supported by the U.S. Department of Energy's Office
330 of Energy Efficiency and Renewable Energy (EERE) under the Bioenergy Technology Office
331 Award Number DE-EE0008932.

332

333 **References**

334 Appels, L., Baeyens, J., Degreève, J., Dewil, R., 2008. Principles and potential of the anaerobic
335 digestion of waste-activated sludge. *Progress in energy and combustion science* 34, 755-781.
336 Banzhaf, S., Filipovic, M., Lewis, J., Sparrenbom, C.J., Barthel, R., 2017. A review of
337 contamination of surface-, ground-, and drinking water in Sweden by perfluoroalkyl and
338 polyfluoroalkyl substances (PFASs). *Ambio* 46, 335-346.
339 Brusseau, M.L., Anderson, R.H., Guo, B., 2020. PFAS concentrations in soils: Background
340 levels versus contaminated sites. *Science of the Total Environment* 740, 140017.
341 Campbell, T., Hoffmann, M.R., 2015. Sonochemical degradation of perfluorinated surfactants:
342 Power and multiple frequency effects. *Separation and Purification Technology* 156, 1019-1027.
343 Campbell, T.Y., Vecitis, C.D., Mader, B.T., Hoffmann, M.R., 2009. Perfluorinated surfactant
344 chain-length effects on sonochemical kinetics. *The Journal of Physical Chemistry A* 113, 9834-
345 9842.
346 Cao, H., Zhang, W., Wang, C., Liang, Y., 2020. Sonochemical degradation of poly-and
347 perfluoroalkyl substances-a review. *Ultrasonics Sonochemistry*, 105245.
348 Ghisi, R., Vamerli, T., Manzetti, S., 2019. Accumulation of perfluorinated alkyl substances
349 (PFAS) in agricultural plants: A review. *Environmental Research* 169, 326-341.
350 Gole, V.L., Fishgold, A., Sierra-Alvarez, R., Deymier, P., Keswani, M., 2018a. Treatment of
351 perfluorooctane sulfonic acid (PFOS) using a large-scale sonochemical reactor. *Separation and*
352 *Purification Technology* 194, 104-110.
353 Gole, V.L., Sierra-Alvarez, R., Peng, H., Giesy, J.P., Deymier, P., Keswani, M., 2018b. Sono-
354 chemical treatment of per-and poly-fluoroalkyl compounds in aqueous film-forming foams by

355 use of a large-scale multi-transducer dual-frequency based acoustic reactor. *Ultrasonics*
356 *sonochemistry* 45, 213-222.

357 Guelfo, J.L., Higgins, C.P., 2013. Subsurface transport potential of perfluoroalkyl acids at
358 aqueous film-forming foam (AFFF)-impacted sites. *Environmental science & technology* 47,
359 4164-4171.

360 Guo, R., Zhou, Q., Cai, Y., Jiang, G., 2008. Determination of perfluorooctanesulfonate and
361 perfluorooctanoic acid in sewage sludge samples using liquid chromatography/quadrupole time-
362 of-flight mass spectrometry. *Talanta* 75, 1394-1399.

363 Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of
364 perfluorochemicals in sediments and domestic sludge. *Environmental science & technology* 39,
365 3946-3956.

366 Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L., 2013. Persistence of perfluoroalkyl acid
367 precursors in AFFF-impacted groundwater and soil. *Environmental science & technology* 47,
368 8187-8195.

369 Houtz, E.F., Sedlak, D.L., 2012. Oxidative conversion as a means of detecting precursors to
370 perfluoroalkyl acids in urban runoff. *Environmental science & technology* 46, 9342-9349.

371 Huan, L., Yiyang, J., Mahar, R.B., Zhiyu, W., Yongfeng, N., 2009. Effects of ultrasonic
372 disintegration on sludge microbial activity and dewaterability. *Journal of Hazardous Materials*
373 161, 1421-1426.

374 Lee, Y.-C., Chen, M.-J., Huang, C.-P., Kuo, J., Lo, S.-L., 2016. Efficient sonochemical
375 degradation of perfluorooctanoic acid using periodate. *Ultrasonics sonochemistry* 31, 499-505.

376 Lei, Y.-J., Tian, Y., Sobhani, Z., Naidu, R., Fang, C., 2020. Synergistic degradation of PFAS in
377 water and soil by dual-frequency ultrasonic activated persulfate. *Chemical Engineering Journal*
378 388, 124215.

379 Long, J.H., Bullard, C.M., 2014. Waste activated sludge pretreatment to boost volatile solids
380 reduction and digester gas production: Market and technology assessment. *Fla Water Resour. J.*
381 44-50.

382 Ma, Y., Gu, J., Liu, Y., 2018. Evaluation of anaerobic digestion of food waste and waste
383 activated sludge: Soluble COD versus its chemical composition. *Science of the total environment*
384 643, 21-27.

385 Manousaki, E., Psillakis, E., Kalogerakis, N., Mantzavinos, D., 2004. Degradation of sodium
386 dodecylbenzene sulfonate in water by ultrasonic irradiation. *Water Research* 38, 3751-3759.

387 Miralles-Marco, A., Harrad, S., 2015. Perfluorooctane sulfonate: a review of human exposure,
388 biomonitoring and the environmental forensics utility of its chirality and isomer distribution.
389 *Environment international* 77, 148-159.

390 Moody, C.A., Martin, J.W., Kwan, W.C., Muir, D.C., Mabury, S.A., 2002. Monitoring
391 perfluorinated surfactants in biota and surface water samples following an accidental release of
392 fire-fighting foam into Etobicoke Creek. *Environmental science & technology* 36, 545-551.

393 Nickerson, A., Maizel, A.C., Kulkarni, P.R., Adamson, D.T., Kornuc, J.J., Higgins, C.P., 2020.
394 Enhanced extraction of AFFF-associated PFASs from source zone soils. *Environmental Science*
395 *& Technology* 54, 4952-4962.

396 Okitsu, K., Iwatani, M., Nanzai, B., Nishimura, R., Maeda, Y., 2009. Sonochemical reduction of
397 permanganate to manganese dioxide: the effects of H₂O₂ formed in the sonolysis of water on the
398 rates of reduction. *Ultrasonics sonochemistry* 16, 387-391.

399 Onyeche, T., Schäfer, O., Bormann, H., Schröder, C., Sievers, M., 2002. Ultrasonic cell
400 disruption of stabilised sludge with subsequent anaerobic digestion. *Ultrasonics* 40, 31-35.

401 Petrier, C., Francony, A., 1997. Incidence of wave-frequency on the reaction rates during
402 ultrasonic wastewater treatment. *Water Science and Technology* 35, 175-180.

403 Phan Thi, L.A., Do, H.T., Lo, S.L., 2014. Enhancing decomposition rate of perfluorooctanoic
404 acid by carbonate radical assisted sonochemical treatment. *Ultrason Sonochem* 21, 1875-1880.

405 Pilli, S., Bhunia, P., Yan, S., LeBlanc, R., Tyagi, R., Surampalli, R., 2011. Ultrasonic
406 pretreatment of sludge: a review. *Ultrasonics sonochemistry* 18, 1-18.

407 Rodriguez-Freire, L., Abad-Fernandez, N., Sierra-Alvarez, R., Hoppe-Jones, C., Peng, H., Giesy,
408 J.P., Snyder, S., Keswani, M., 2016. Sonochemical degradation of perfluorinated chemicals in
409 aqueous film-forming foams. *J Hazard Mater* 317, 275-283.

410 Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006.
411 Fluorochemical mass flows in a municipal wastewater treatment facility. *Environmental science
412 & technology* 40, 7350-7357.

413 Shoemaker, J., Tettenhorst, D., 2018. Method 537.1: determination of selected per-and
414 polyfluorinated alkyl substances in drinking water by solid phase extraction and liquid
415 chromatography/tandem mass spectrometry (LC/MS/MS). US Environmental Protection Agency,
416 Office of Research and Development.

417 Show, K.-Y., Mao, T., Lee, D.-J., 2007. Optimisation of sludge disruption by sonication. *Water
418 Research* 41, 4741-4747.

419 Sinclair, E., Kannan, K., 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater
420 treatment plants. *Environmental science & technology* 40, 1408-1414.

421 Sivakumar, M., Tang, S.Y., Tan, K.W., 2014. Cavitation technology—a greener processing
422 technique for the generation of pharmaceutical nanoemulsions. *Ultrasonics sonochemistry* 21,
423 2069-2083.

424 Sun, H., Gerecke, A.C., Giger, W., Alder, A.C., 2011. Long-chain perfluorinated chemicals in
425 digested sewage sludges in Switzerland. *Environmental pollution* 159, 654-662.

426 Suslick, K.S., 1989. The chemical effects of ultrasound. *Scientific American* 260, 80-86.

427 Thi, L.-A.P., Do, H.-T., Lo, S.-L., 2014. Enhancing decomposition rate of perfluorooctanoic acid
428 by carbonate radical assisted sonochemical treatment. *Ultrasonics sonochemistry* 21, 1875-1880.

429 Tiehm, A., Nickel, K., Zellhorn, M., Neis, U., 2001. Ultrasonic waste activated sludge
430 disintegration for improving anaerobic stabilization. *Water research* 35, 2003-2009.

431 Venkatesan, A.K., Halden, R.U., 2013. National inventory of perfluoroalkyl substances in
432 archived US biosolids from the 2001 EPA National Sewage Sludge Survey. *Journal of hazardous
433 materials* 252, 413-418.

434 Wang, Z., DeWitt, J.C., Higgins, C.P., Cousins, I.T., 2017. A never-ending story of per-and
435 polyfluoroalkyl substances (PFASs)? ACS Publications.

436 Yang, S., Cheng, J., Sun, J., Hu, Y., Liang, X., 2013. Defluorination of aqueous
437 perfluorooctanesulfonate by activated persulfate oxidation. *PloS one* 8, e74877.

438 Yu, J., Hu, J., Tanaka, S., Fujii, S., 2009. Perfluorooctane sulfonate (PFOS) and
439 perfluorooctanoic acid (PFOA) in sewage treatment plants. *Water research* 43, 2399-2408.

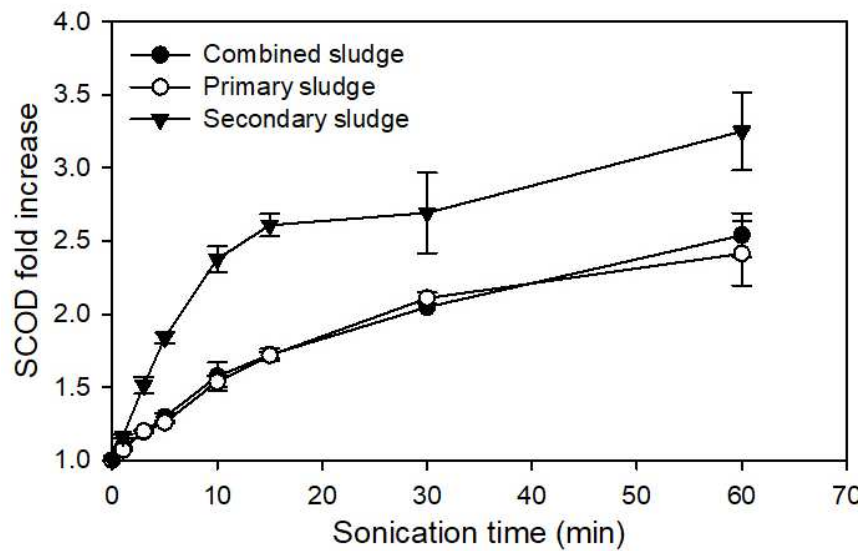
440 Zhang, T., Sun, H., Gerecke, A.C., Kannan, K., Müller, C.E., Alder, A.C., 2010. Comparison of
441 two extraction methods for the analysis of per-and polyfluorinated chemicals in digested sewage
442 sludge. *Journal of Chromatography A* 1217, 5026-5034.

443 Zhang, W., Cao, H., Mahadevan Subramanya, S., Savage, P., Liang, Y., 2020. Destruction of
444 Perfluoroalkyl Acids Accumulated in *Typha latifolia* through Hydrothermal Liquefaction. *ACS
445 Sustainable Chemistry & Engineering*.

446 Zhang, W., Liang, Y., 2021a. Effects of hydrothermal treatments on destruction of per- and
447 polyfluoroalkyl substances in sewage sludge. *Environmental Pollution* 285, 117276.
448 Zhang, W., Liang, Y., 2021b. Effects of hydrothermal treatments on destruction of per-and
449 polyfluoroalkyl substances in sewage sludge. *Environmental Pollution*, 117276.
450 Zhao, H., Zhang, G., Zhang, Q., 2014. MnO₂/CeO₂ for catalytic ultrasonic degradation of
451 methyl orange. *Ultrasonics sonochemistry* 21, 991-996.
452 Zhen, G., Lu, X., Kato, H., Zhao, Y., Li, Y.-Y., 2017. Overview of pretreatment strategies for
453 enhancing sewage sludge disintegration and subsequent anaerobic digestion: current advances,
454 full-scale application and future perspectives. *Renewable and Sustainable Energy Reviews* 69,
455 559-577.

456

457



458

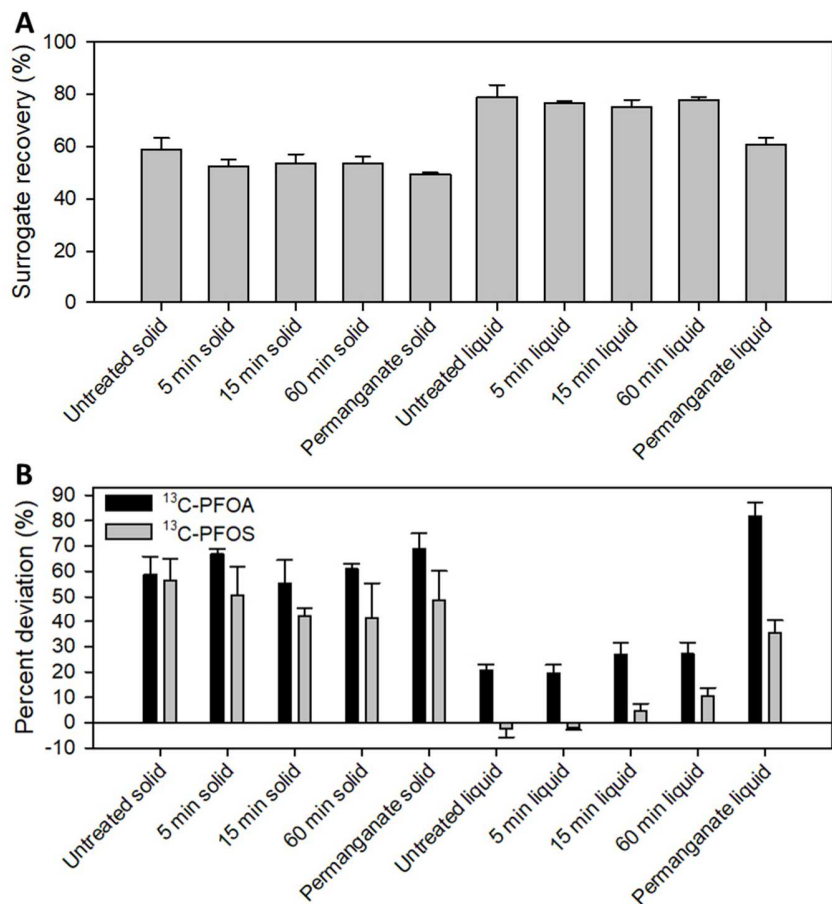
459 Fig. 1. Effects of sonication time on SCOD fold increase for primary, secondary, and combined
460 sewage sludge (n = 3).

461

462

463

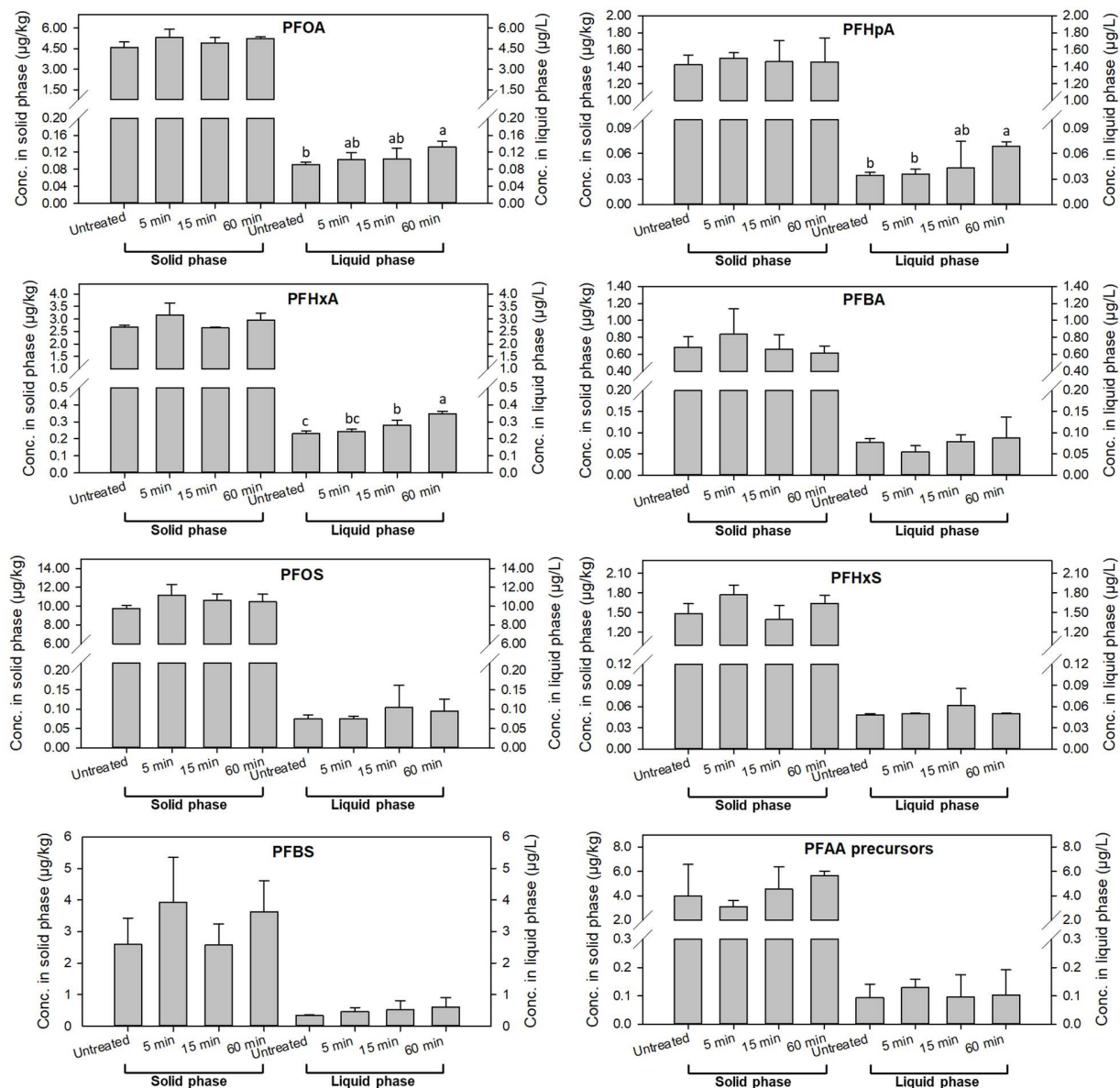
464



465

466 Fig. 2. (A) Surrogate recoveries in the untreated and sonication treated sewage sludge and (B)
 467 percent deviation of internal standard responses in measured samples from the average internal
 468 standard responses in external analyte calibrations (n = 3).

469



470

471

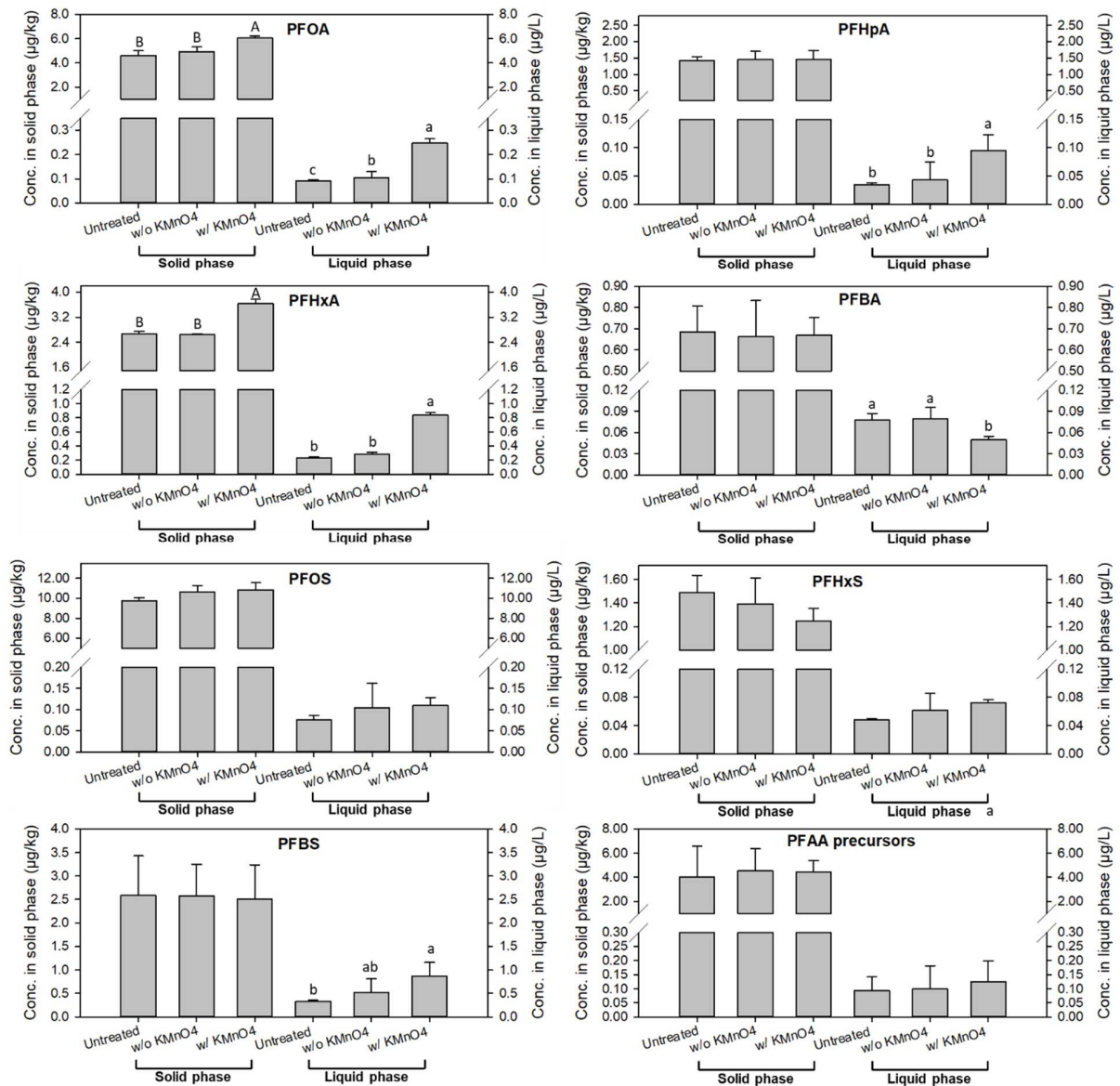
472 Fig. 3. Concentrations of PFAAs and PFAA precursors in sewage sludge (n = 3). Different
 473 letters in upper case (solid phase) and lower case (liquid phase) indicate significant differences
 474 among the concentrations in sewage sludge before and after sonication treatments ($p < 0.05$).

475

476

477

478



479

480 Fig. 4. Concentrations of PFAAs and PFAA precursors in untreated and treated sewage sludge
 481 with (w/) or without (w/o) potassium permanganate (KMnO₄) (n = 3). Different letters in upper
 482 case (solid phase) and lower case (liquid phase) indicate significant differences among the
 483 concentrations in sewage sludge before and after sonication treatments ($p < 0.05$).

484

