The Fate and Transport of Chlorinated Polyfluorinated Ether Sulfonates and other PFAS through Industrial Wastewater Treatment Facilities in China

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Abstract

Wastewater from certain industrial processes can be primary emission sources of per- and polyfluoroalkyl substances (PFAS) and fluorinated alternatives like chlorinated polyfluorinated ether sulfonates (Cl-PFESA). Two such industrial processes are electroplating and textile printing and dyeing (PD). This study focused on the fate of Cl-PFESA in wastewater from these two industrial processes, in comparison to other PFAS, as they went through different wastewater treatment plants located in southeast China. The total target PFAS concentrations were 520±30 ng/L and 4200±270 ng/L at the effluents of the PD WWTP and electroplating WWTP, respectively. Specifically, 6:2 Cl-PFESA (18%) and 8:2 Cl-PFESA (0.7%) were abundant in electroplating-wastewater. Cl-PFESA were also detected in PD wastewater but at trace concentrations and were likely present due to diffuse emissions. The dissolved-phase Cl-PFESA and PFAS mass flow through the WWTPs were fairly constant throughout both facilities. The majority of Cl-PFESA was captured by sludge sedimentation. However, there were individual treatment processes that could cause the wastewater concentrations to fluctuate, and also could lead to relative enrichment of specific Cl-PFESA as indicated by the 6:2/8:2 Cl-PFESA ratios. Cl-PFESA and perfluoroalkyl sulfonic acids were more influenced by the investigated treatment processes than perfluorocarboxylic acids.

Keywords: PFAS; industrial wastewater; water pollution; source apportion

Synopsis: Fate behavior of chlorinated polyfluorinated ether sulfonates and other PFAS were characterized in different industrial wastewater treatment plants

Introduction

Over 4500 per-and polyfluoroalkyl substances (PFAS) exist, and many have been used in various industrial applications and materials found in numerous customer products including papers, textiles, plastics and glass, often to obtain nonstick, water-repellence and low-friction properties[1,2]. Perfluoroalkyl sulfonic acids (PFSAs) and perfluorocarboxylic acids (PFCAs) are the two main groups of PFAS; however, recently due to both increased regulatory action and market forces, new types of fluorinated alternatives are emerging on the market, such as chlorinated polyfluorinated ether sulfonate acids (Cl-PFESAs). Numerous studies have demonstrated that PFAS are wide spread in natural aquatic systems, including rivers[3, 4], lakes[5, 6], groundwater[7, 8] and sea water[9, 10]. Due to their impact on aquatic environments as well as drinking water resources, water contamination by PFAS has been an issue of growing public concern[11-13].

PFAS have been intensively applied in many local industrial activities, where they can become long-term PFAS hotspots for local environments. Studies of PFAS entering wastewater treatment plants (WWTPs)[14-18] have indicated that industrial wastewater can be a substantial source of emissions, particularly those from the electroplating[19], textile manufacturing[20] and chemical production industries [21, 22]. During the last decade PFAS production in China has undergone rapid growth since the restriction and reduction of perfluorooctyl sulfonate (PFOS) and/or perfluorooctanoic acid (PFOA) manufacturing in the U.S. and Europe. In China, PFOS has been in high demand for the chrome plating industry, where PFOS and its salts are applied as chrome mist

67 suppressants to prevent the formation of chrome-containing mist[23]. For almost 40 years

68 monochlorinated polyfluorinated ether sulfonate (Cl-PFESA), particularly 6:2 Cl-

69 PFESA often called F53B, have been applied as PFOS alternatives in the metal plating

70 industries due to their simpler chemical production procedures as well as lower

71 production costs[23, 24]. A recent modeling study estimated that 10−14 tonnes of F53B

72 have been released annually to the environment in China during 2006−2015[24]. Another

73 active PFAS hotpot is textile manufacturing. Side-chain fluorinated polymers or

74 perfluorooctane sulfonyl fluoride (POSF)-based derivatives were commonly used for

75 surface treatment of textiles in order to obtain water-proof and oil-resistant properties.

76 An increasing trend in China was to use shorter-chained homologues as replacement

77 chemicals[25]. For instance, perfluorohexane sulfonyl fluoride (PHxSF) derivatives have

78 been increasingly produced as alternative surface treatment chemicals; these can

79 notably degrade into perfluorohexane sulfonate (PFHxS)[25, 26]. Due to the changing

80 composition of PFAS alternatives as surface treatment chemicals, their fate and that of

81 their degradation products in wastewater still requires better characterization.

82 Different industrial wastewaters often have special emission inventories covering both

83 legacy and alternative PFAS, and therefore might serve as an identifier for PFAS

84 discharge from different sources. PFAS concentrations from these different sources

85 could vary temporally and spatially during individual wastewater treatment, depending

86 on the physiochemical properties of different PFAS as well as their sensitivity to

87 different treatment techniques[27, 28]. Though industrial wastewater treatment plants

88 directly receive PFAS containing wastewaters, water treatment facilities are rarely

89 designed for PFAS removal[29]. WWTP effluents and sludge are considered active

90 sources for the environmental release of both legacy and alternative PFAS[30]. In China

91 Cl-PFESA like F53B represents one of the most important country-specific PFOS

92 alternatives. There is increasing evidence of the emergence of 6:2 Cl-PFESA and 8:2

93 Cl-PFESA in both wastewaters[15, 31, 32] and fresh water environments in China[12, 33].

94 However, the knowledge on diverse industrial uses, in particular, for small-scale

95 manufacturers, and local emission hotspots of Cl-PFESA are still lacking. Hence, there

96 is growing interests to identify different sources of Cl-PFESA and to understand their

97 fate in industrial wastewater streams in comparison to that of legacy PFAS. The main

98 objectives of this study are to characterize the fate and transport of 6:2 Cl-PFESA and

99 8:2 Cl-PFESA from the two different in-situ industrial wastewater treatment plants

100 receiving wastewaters from electroplating and textile printing and dying manufacturing,

101 respectively, and comparing them with legacy PFAS.

102

Materials and methods

Chemicals and Reagents

105 In total eighteen PFAS were included as target compounds. Six isotope-labeled PFAS

106 were employed as internal standards. All the standards were obtained from Wellington

107 Laboratories (Ontario, Canada), with purities greater than 98%. Detailed information

108 regarding the target analytes are summarized in Table S1. Millipore water was produced

109 by a Milli-Q system from Sartorius (Göttingen, Germany). LC-MS grade solvent (i.e.,

110 methanol and ammonium hydroxide; v/v, 25%) were purchased from Merck (Darmstadt,

111 Germany). Glass fiber filters (GFFs, 47 mm diameter, 0.7 μm aperture) were obtained
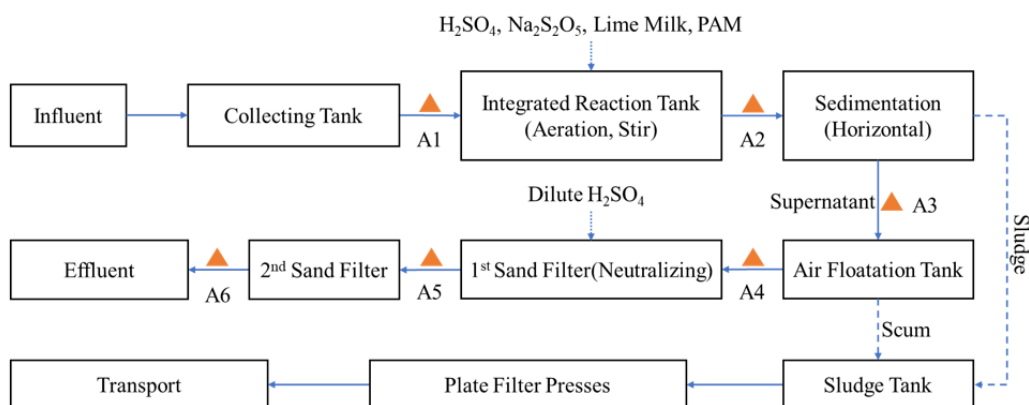
5

from Whatman (Maidstone, UK). Oasis weak anion exchange cartridges (WAX, 150

mg, 6 mL, 30 μm) were purchased from Waters (Milford, USA) and Envi-Carb

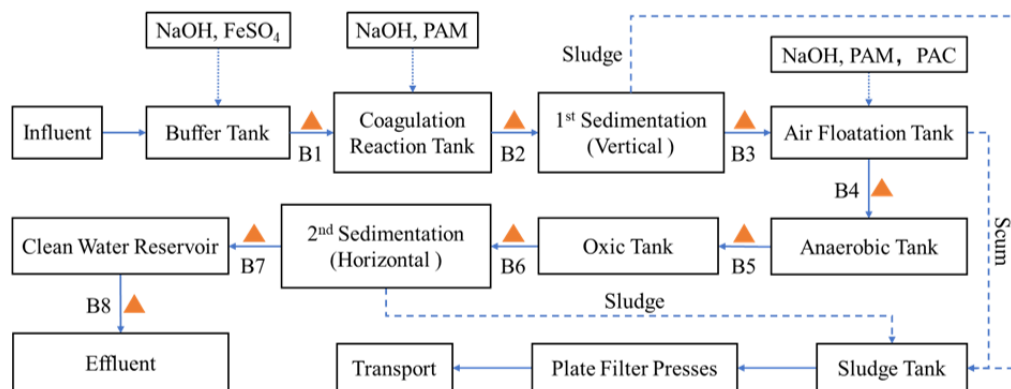cartridge (3 mL, 250 mg) was purchased from Supelco (Bellefonte, USA).

Sample Collection

Industrial wastewater from an electroplating wastewater treatment plant (E-WWTP)

and a textile printing and dyeing wastewater treatment plant (PD-WWTP) were

separately collected during one day in November 2019. Both WWTPs are located in

the Pearl River basin in southeast China, where numerous small-scale industries are

located. The E-WWTP is treating wastewater collected from surrounding chrome

plating factories, and mainly implements chemical precipitation to treat the industrial

wastewater. PD-WWTP is exclusively collecting wastewater generated during textile

printing and dyeing processes in several local factories. The main treatment processes

of PD-WWTP is chemical precipitation (via flocculation), anaerobic digestion and then

aerobic digestion. The flocculent used in both facilities is polyacrylamide (PAM)[34, 35].

The detailed description of the two WWTPs are shown in Figure 1 and Table S2a.

E-WWTP and PD-WWTP are treating a fixed amount (i.e. 1000 m^3/d and 330 m^3/d,

respectively) of the collected industrial wastewater, which goes once through the entire

treatment procedures daily. The wastewater sampling followed the wastewater stream

by considering hydraulic retention time during individual treatment step, and therefore

allowed for tracking the fate of the target PFAS along the wastewater stream as well as

for substantial flow analysis. Though this sampling regime does not give time-

integrated samples, it does prevent biases caused by temporal fluctuations when not

134 following the hydraulic retention time (see Tables S2b and S2c) through the WWTP[36].

135 Treated wastewater was collected in a 1L polypropylene (PP) bottle from the effluent

136 of different treatment units in both WWTPs. All sampling bottles were washed with

137 methanol and rinsed three times with wastewater sample before collection, and sealed

138 with sealing film immediately after sampling. Prior to analysis the samples were stored

139 at 4°C room in the dark. The sludge that accumulated during the treatment processes

140 were sampled (about 250 g per wet sludge sample) before the dehydration treatment.

141 The wet sludge sample was immediately packed with aluminum foil and sealed in

142 polypropylene bags. Prior to analysis, the sludge samples were preserved at -20°C.

a. Electroplating wastewater treatment plant.

H$_2$SO$_4$, Na$_2$S$_2$O$_5$, Lime Milk, PAM

Influent → Collecting Tank → A1 ▲ → Integrated Reaction Tank (Aeration, Stir) → A2 ▲ → Sedimentation (Horizontal)

Dilute H$_2$SO$_4$ | Supernatant ▲ A3

Effluent ← A6 ▲ ← 2nd Sand Filter ← A5 ▲ ← 1st Sand Filter(Neutralizing) ← A4 ▲ ← Air Floatation Tank

Sludge | Scum

Transport ← Plate Filter Presses ← Sludge Tank

b. Printing and dyeing wastewater treatment plant.

NaOH, FeSO$_4$ | NaOH, PAM | Sludge | NaOH, PAM, PAC

Influent → Buffer Tank → B1 ▲ → Coagulation Reaction Tank → B2 ▲ → 1st Sedimentation (Vertical) → B3 ▲ → Air Floatation Tank

B4 ▲

Clean Water Reservoir ← B7 ▲ ← 2nd Sedimentation (Horizontal) ← B6 ▲ ← Oxic Tank ← B5 ▲ ← Anaerobic Tank

B8 ▲ | Scum

Effluent | Sludge

Transport ← Plate Filter Presses ← Sludge Tank

143

144 Figure 1. Water treatment processes of the two in-situ industrial wastewater treatment plants.

7

145　　Panel (a) the E-WWTP and Panel (b) the PD-WWTP. The yellow triangle represents the

146　　sampling locations. The dashed lines represent the removal of sludge from various wastewater

147　　treatment steps.

148　　**Sample pretreatment**

149　　**Filtration.** 500 mL of wastewater samples were filtered by glass fiber filters (0.7 μm,

150　　Whatman, Maidstone, UK), then sealed in PP bottles and stored at 4 °C. All filters were

151　　baked at 450 °C for 12 hours before use. Given that PFAS sorption on glass fiber filters

152　　might underestimate PFAS concentrations [37, 38], after the filtration of water sample, the

153　　filters were washed with about 15 mL methanol to extract PFAS residues on the glass

154　　filters as it was recommended in a previous study[37], and then the methanol solution was

155　　collected and combined later added to the treated water samples extracted in methanol

156　　described below. The sludge samples were pretreated using the dispersive solid phase

157　　extraction (DSPE) method. The detailed treatment protocols were based on a previous

158　　study.[39]

159　　**Extraction.** The aqueous samples were extracted by solid phase extraction (SPE) using

160　　Oasis WAX cartridges. Before water loading, samples were spiked with 5 ng ISs (50

161　　uL, 100 pg/μL). The WAX cartridges were activated with 10 mL acetone, 10 mL

162　　methanol and 10 mL 0.25 % ammonium hydroxide in methanol before use. The loading

163　　speed was adjusted at a flow rate of approximately 2 mL/min.

164　　After water loading, the cartridges were cleaned with 5 mL Millipore water and dried

165　　with a vacuum pump. Then, dried cartridges were eluted with 15 mL 2.5% ammonium

166　　hydroxide in methanol. The eluents were kept in preconditioned PP centrifuge tubes

167 (50 mL, Biosharp). After purification by Envi-Carb cartridges, the eluents were

168 concentrated to 190 μL under a gentle stream of nitrogen. The Envi-Carb cartridges

169 were cleaned with 15 mL methanol. Before instrumental analysis, 1 ng (10 uL,100

170 pg/μL) injection standards ($[^{13}C_2]$-PFOA) were added in each sample.

171

172 **Instrumental analysis**

173 Samples were analyzed by an ultrahigh performance liquid chromatography tandem

174 mass spectrometry (UHPLC-MS/MS) system using a 1290 Infinity II UHPLC (Agilent

175 Technologies) with a 6470 Triple Quad MS/MS (Agilent Technologies). The analytical

176 column used was a ZORBAX Eclipse Plus C18 column (2.1×100 mm, 1.8-micron,

177 Agilent Technologies) with a UHPLC Guard for C18 (2.1×50 mm, 1.8-micron, Agilent

178 Technologies). The column temperature was kept at 40 °C. The mobile phase consisted

179 of A: 10 mmol· L^{-1} ammonium acetate in water and B: 10 mmol· L^{-1} ammonium acetate

180 in methanol. The gradient profile was achieved at a flow rate of 0.30 mL/min and

181 initiated with an equilibration of 90% A, which was decreased to 35% A for 5.5 min

182 and held for 0.5 min, then decreased to 10% A for 2.5 min and held for 3.1 min, and

183 then increased to 90% A for 0.1 min. Finally, 90% A was held for 0.8 min. The detailed

184 instrument parameters of the UHPLC-MS/MS were presented in Table S3.

185

186 **Quality assurance and quality control**

187 To prevent contamination of samples, materials containing Teflon were avoided during

188 whole treatment and analysis processes. All parts that had access to the samples were

189 cleaned using methanol and ultrapure water before use. Instrumental quantification

190 limits (IQLs) were defined as the lowest concentration of target compounds resulting

191 in a signal-to-noise (S/N) ratio of 3. Method quantification limits (MQLs) were defined

192 using a S/N ratio of 10. The IQLs and MQLs of all the target compounds are

193 summarized in Table S4.

194 The wastewater samples collected from the two WWTPs were analyzed separately to

195 avoid cross-contamination during instrumental analysis. Between every 10 samples

196 during sample treatment, one procedural blank using Milli-Q water was prepared by

197 following the same treatment procedures as described above, and the final

198 concentrations of these samples were subtracted from the levels in the blank samples.

199 A standard sample of 20 µg/L was added every 10-15 samples during the instrumental

200 injection in order to monitor instrumental stability (standard deviation less than ±10%).

201 The recoveries of most compounds in the wastewater ranged from 50-120% with

202 standard deviations below 20%. The average recoveries of the Internal Standards

203 ranged from 49% ± 17% ($[^{13}C_2]$-PFDA) to 92% ± 19% ($[^{18}O_2]$-PFHxS). Detailed

204 information of recoveries are listed in Table S5.

205 **Ratios of 6:2 Cl-PFESA to 8:2 Cl-PFESA**

206 The ratio of 6:2 Cl-PFESA to 8:2 Cl-PFESA expresses the variation of the two Cl-

207 PFESA's abundances relative to each other. For instance, increasing ratios could

208 indicate a selective process resulting in relative enrichment of either 6:2 Cl-PFESA.

209 The ratio, $R_{6:2/8:2}$, is given as:

$$210 \qquad\qquad R_{6:2/8:2} = \frac{C_{6:2\ Cl-PFESA}}{C_{8:2\ Cl-PFESA}} \qquad\qquad (1)$$

211   *C* represents the concentration of the two Cl-PFESA.

212   **Results and discussion**

213   **Distribution and profile pattern**

214   Wastewater samples were analyzed for Cl-PFESA and other target PFAS from the entire

215   treatment system of the two different WWTPs following the hydraulic retention time

216   (see Fig. 1). The aqueous concentrations of the target PFAS for the influent waters are

217   shown in Fig. 2. For the E-WWTP, 6:2 Cl-PFESA and 8:2 Cl-PFESA along with

218   seventeen different legacy PFAS were identified (see Fig. 2a). The total PFAS

219   concentration reached 2100±130 ng/L in the influents and went up to 4200±270 ng/L

220   in the effluents, indicating possible transformation and release from the precursors, or

221   variations in sorption/desorption processes, during the treatment processes (Table S6).

222   Concentrations of 6:2 Cl-PFESA and 8:2 Cl-PFESA in the E-WWTP influents were

223   220±23 ng/L and 2.2±0.49 ng/L. After water treatment these values went up to 740±54

224   ng/L and 2.9±0.37 ng/L, respectively (see Fig. 2a). Unlike PFCAs and PFSAs, there are

225   no known precursors of Cl-PFSAs to the authors' knowledge. The major PFSAs in the

226   wastewater, PFOS and PFHxS, occurred at average influent concentrations of 1300±98

227   ng/L and 460±18 ng/L, respectively, and at effluent concentrations of 2700±190 ng/L

228   and 570±37 ng/L, respectively (Fig. 2b). PFOS was the most abundant, accounting for

229   about 62% among the total PFAS in the wastewater, and the corresponding mean

230   concentrations was 1300±98 ng/L, followed by 6:2 Cl-PFESA (220±23 ng/L) and

231   PFHxS (460±18 ng/L), accounting for 10% and 22%, respectively. Additionally,

232 PFCAs including PFPeA, PFHxA, PFHpA and PFOA, contributed only about 4.2% to

233 the ΣPFAS concentrations in total (Fig. 2c).

234 Concerning the PD-WWTP, fifteen PFAS were identified and quantified. The ΣPFAS

235 concentration of the PD-WWTP influent reached 590±39 ng/L, and this value was

236 slightly higher than the ΣPFAS concentration at the effluent (i.e. 520±30 ng/L). Notably,

237 Cl-PFAES were also found in comparatively trace concentrations in the PD-WWTP,

238 with 6:2 Cl-PFAES being detected at 0.21 ± 0.03 ng/L in the influent and 0.04 ± 0.02

239 ng/L in the effluent, indicating PD-wastewater in this area might act as a novel, though

240 minor source for PFESAs environmental release. Given no evidence available for Cl-

241 PFAES applications in PD industries, we speculate that this is likely attributed to

242 "diffuse emissions" from small and unknown industries in this area. In general, PFAS

243 were inefficiently removed by applying the applied wastewater treatment techniques.

244 PFHxS, PFOA, PFHxA and PFOS were among the predominant species, with average

245 influent concentrations of 500±36 ng/L, 52±1.6 ng/L, 21±0.94 ng/L and 8.2±1.39 ng/L,

246 respectively, and effluent concentrations of 450±28 ng/L, 47±1.4 ng/L, 18±1.7 ng/L and

247 2.2±0.71 ng/L, respectively. In comparison, longer chain PFAS (> 8 carbon atoms)

248 were only observed at much lower concentrations (e.g. max < 1.12±0.38 ng/L for

249 PFHxDA in effluent). As described in the Introduction, PFHxS are heavily applied in

250 the textile printing and dyeing process, and these occurred at 500±36 ng/L, which

251 accounts for 85% mass of PFAS in the wastewater. PFOA, PFHxA and PFOS

252 contributed 8.8%, 3.6% and 1.4% to the ΣPFAS concentration, respectively.

253 In general, the composition of PFAS in the two industrial WWTPs are less

254 PFOA/PFOS-dominated comparing with the previous studies[18, 20]. This is likely owing

255 to the fact that the short-chain and polyfluorinated PFAS were increasingly applied in

256 printing and dyeing as well as in electroplating industries[22, 40]. For example, the chrome

257 mist suppressants used in electroplating industries have been most typically PFOS, but

258 now increasingly more alternative PFAS serve as active chemicals in chrome mist

259 suppressants formulations. Our results suggested that PFOS was predominant in the E-

260 wastewater (64%), and PFHxS and 6:2 Cl-PFESA were also abundant and account for

261 14% and 18%, respectively, indicating that these are being used increasingly.

262 Furthermore, the traditional textile PD-industry commonly uses fluorotelomer alcohols

263 (FTOHs) in their textile finishes, which are well-known precursors to PFCAs in textile

264 PD-wastewater[20]. However, our study found that PFHxS (87%) was dominant PFAS,

265 and PFCAs only accounted for 13%. This might be due to increasing production and

266 application of perfluorohexane sulfonyl fluoride (PHxSF) as alternative for textile

267 surface treatment processes in China[25], which could degrade into PFHxS during

268 transformation processes[25, 26].
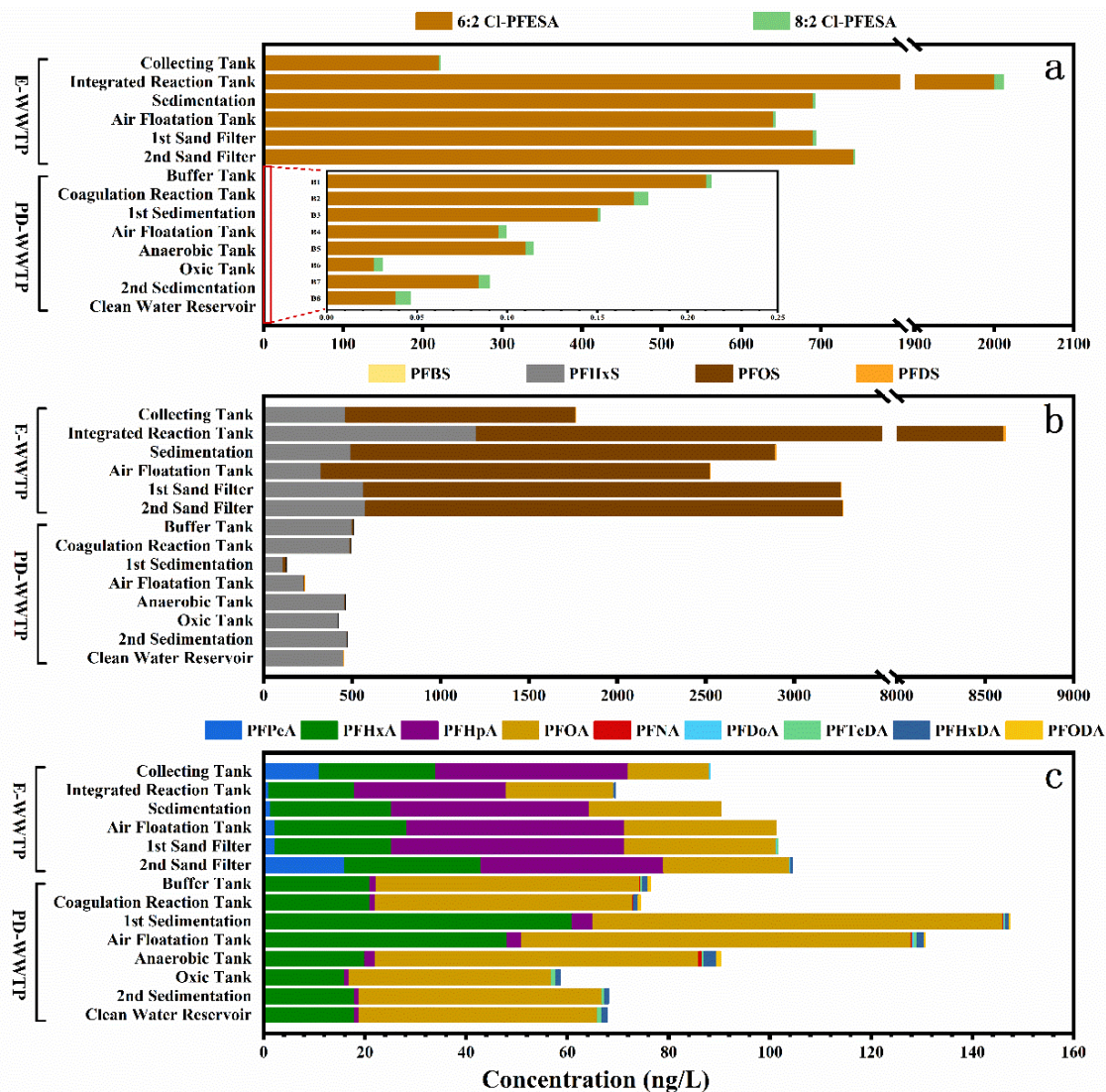
Figure 2. Concentrations of Cl-PFESA and legacy PFAS in the wastewater of the two WWTPs. Panel (a) shows the concentration of 6:2 Cl-PFESA and 8:2 Cl-PFESA; Panel (b) shows the concentration PFSAs; Panel (c) shows the concentration of PFCAs. The y-axis refers to the individual treatment steps for the two WWTPs, as listed in Figure 1.

Mass flow analysis

The mass flow of the individual PFAS in the two WWTPs on the day of sampling were derived (data available in Table S7). The mass flow of the major PFAS through the different treatment processes are shown in Fig. 3. Concerning the E-WWTP, the mass flow of total target PFAS were 2100 ± 130 mg/d in influents and went up to 4200 ± 270 mg/d in effluents. The mass flow of 6:2 Cl-PFESA and 8:2 Cl-PFESA were observed

14

281   at 220 ± 23 mg/d and 2.2 ± 0.49 mg/d in the influents and 740 ± 54 mg/d and 2.9 ± 0.37

282   mg/d in the effluents (Fig. 3 (a1)). For other dominant species including PFOS and

283   PFHxS, the obtained corresponding values were 1300 ± 98 mg/d and 460 ± 18 mg/d

284   and in the influents 2700 ± 190 mg/d and 570 ± 37 mg/d in the effluents, respectively.

285   The mass flow in the effluent almost doubled compared to the influents. This could

286   indicate either large fluctuations in influents that our sampling campaign did not capture,

287   despite following the hydraulic flow of water, or alternatively variations in water

288   concentrations in the response to different treatment steps. A sharp change in the mass

289   flux was observed at the integrated reaction tank, after the "integrated reaction tank",

290   where all the PFSAs and PFESAs increased significantly. Specifically, the mass flow

291   of 6:2 Cl-PFESA increased from 220 ± 23 mg/d (collection tank) to 2000 ± 18 mg/d

292   (integrated reaction tank), and after the same treatment procedures 8:2 Cl-PFESA

293   increased from 2.2 ± 0.49 mg/d to 12 ± 0.26 mg/d; PFHxS increased from 460 ± 18 mg/d

294   to 1200 ± 77 mg/d; PFOS increased from 1300 ± 98 mg/d to 7400 ± 3600 mg/d; PFDS

295   increased from 0.42 ± 0.14 mg/d to 12 ± 2.2 mg/d. We hypothesize that sharp increase of

296   pH by adding lime (pH=12) stimulated desorption of PFAS by deprotonating the anion

297   exchange sites on the suspended solids[38] causing the amount of freely-dissolved PFAS

298   to increase. After this initial spike in the reaction tank, 6:2 Cl-PFESA, 8:2 Cl-PFESA

299   and PFOS concentrations decrease in the sedimentation tank, due to losses to settling

300   sludge. The corresponding log Q_D values at the sedimentation step (log ratio of C_{sludge}

301   to C_{water}) are 4.5 and 6.0 for the 6:2 and 8:2 analogues in the E-WWTP and 3.7 and 5.2

302 in the PD-WTP, indicating strong sorption to sedimented sludge, particularly for the 8:2

303 analogue.

304 Comparing mass flows of Cl-PFESA to sludge and effluent leaving the facility gives

305 further insight.[44, 45] The E-WWTP produces in the range of 2.3-3.0 tons sludge dw/day,

306 corresponding to removal of 50-66 g/day 6:2 Cl-PFESA and 7-10 g/day 8:2 Cl-PFESA

307 via sludge, much larger than the amount released as effluent, being 0.7 and 0.003 g/day,

308 respectively. Similarly, the PD-WWTP produces 0.60-0.75 tons dw/day, corresponding

309 to removal in sludge by 0.0004-0.0005 g/day 6:2 Cl-PFESA and circa 0.0002 g/day 8:2

310 Cl-PFESA, which is larger than the trace emissions from the effluent water of 5E-7 and

311 5E-9 g/day, respectively. This indicates that suspended solids are a substantial reservoir

312 for Cl-PFESA and other high sorbing PFAS. However, despite this removal via sludge,

313 the water concentration during sedimentation nevertheless remains elevated compared

314 to the influent concentration, indicating there still remains suspended solids that desorb

315 the target PFAS, and this concentration remains elevated through all subsequent

316 treatment steps (Figure 2).

317

318 However, other PFCAs did not show the same trend where PFPeA dropping from

319 11±0.93 mg/d (collection tank) to 0.97±0.2 mg/d (integrated reaction tank), PFHxA

320 showing little change from 23±3.7 mg/d to 17±0.28 mg/d and PFHpA showing little

321 change38±7.6 mg/d to 30±8.7 mg/d for PFHpA. The different behavior for the PFCAs

322 may be due the carboxylates having a larger pKa than the sulfonates, and therefore less

323   impacted by the competition with hydroxyl radicals introduced by the pH increase by

324   adding lime [38, 41].

325   Concerning the PD-WWTP, the mass flow of total PFAS were 190±13 mg/d in influents

326   and 170±10 mg/d in effluents. Both 6:2 Cl-PFESA and 8:2 Cl-PFESA were detected in

327   the PD-WWTP at the sub nanogram-per-liter concentrations (see Fig. 3a), resulting in

328   corresponding mass flows of 0.069 ± 0.011 mg/d and 0.0011 ± 0.0003 mg/d at influents

329   (Fig. 3 (b1)), and different but still low concentrations at the effluents (0.013 ± 0.0063

330   mg/d and 0.0029 ± 0.0022 mg/d). In addition, the mass flow of the three predominant

331   compounds PFHxS, PFOA and PFHxA in the influents reached 170 ± 12 mg/d, $17 \pm$

332   0.52 mg/d and 6.9 ± 0.31 mg/d, respectively. There are only small differences on the

333   values obtained in the effluents (i.e. 150 ± 9.2 mg/d, 16 ± 0.46 mg/d, and 6.1 ± 0.57

334   mg/d, respectively). However, the mass flow fluctuated during the treatment processes.

335   For instance, a dramatic change occurred at after the first sedimentation, where PFHxS

336   mass flow decreased from 160 ± 10 mg/d to 37 ± 4.6 mg/d, indicating it was removed

337   by sludge. However, PFOA and PFHxA presented an increasing trend, with increasing

338   PFOA mass loads from 17 ± 0.3 mg/d (reaction tank) to 27 ± 1.8 mg/d (first

339   sedimentation), and from 7 ± 0.43 mg/d (reaction tank) to 20 ± 2 mg/d (first

340   sedimentation) for PFHxA. This could be due to precursor transformation, as the textile

341   PD industry in China is known to emit several PFCA precursors, specifically

342   fluorotelomer alcohols[42, 43]. The individual PFHxS mass flux then went back to their

343   original levels after air floatation and after anaerobic digestion (see Fig. 3); hence, this

344   sudden dip after sedimentation might be due to selective precipitation/aggregation of

345 PFHxS[35], and followed by yield of PFHxS through degradation of perfluorohexane

346 sulfonyl fluoride (PFHxS)-based derivatives during anaerobic tank treatment.

a. E-WWTP   **b. PD-WWTP**
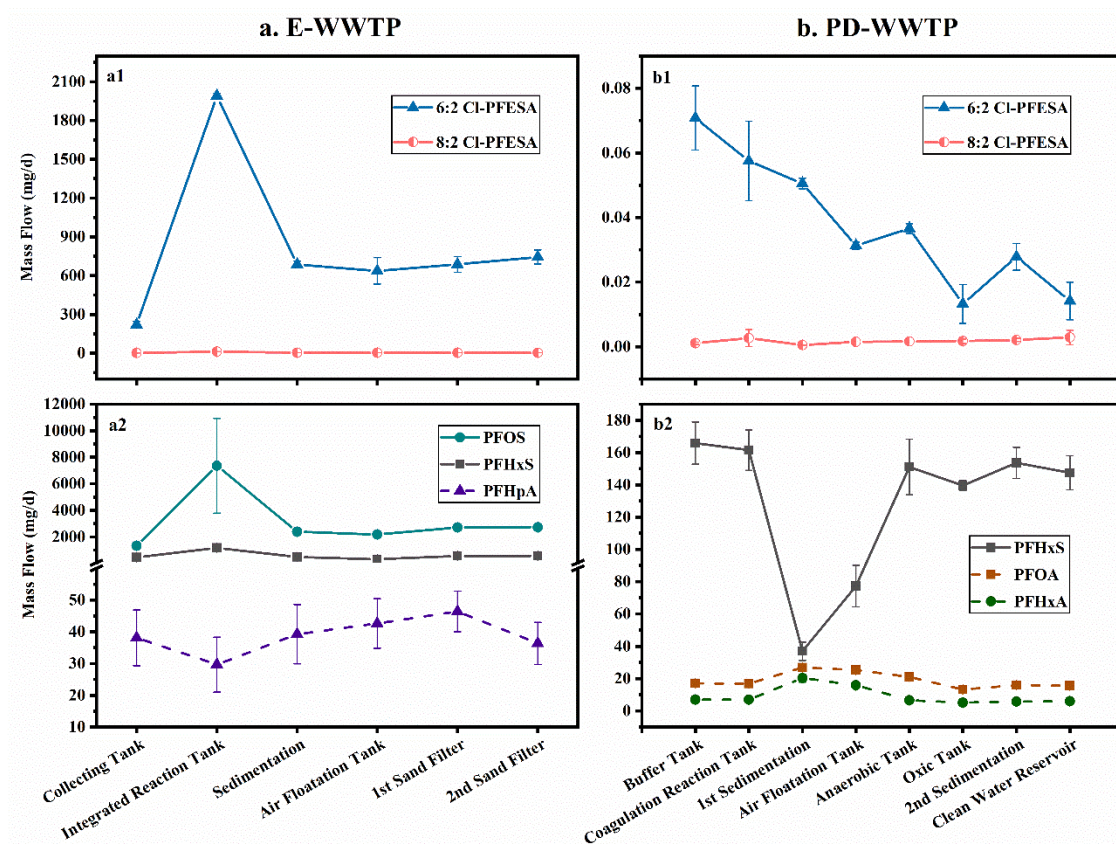
347

348 Figure 3. Mass flow of the Cl-PFESA and predominant PFAS (mg/day) obtained in different treatment
349 steps in the two WWTPs. Panel (a) shows the data for the E-WWTP, and Panel (b) shows the data for the
350 PD-WWTP. The dashed lines represent PFAS with carboxylic acids (PFCAs), and the solid lines
351 represent PFAS with sulfonic acids (PFSAs and Cl-PFESAs).

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Fate behavior of 6:2 and 8:2 Cl-PFESA

356 The fate of 6:2 Cl-PFESA and 8:2 Cl-PFESA in wastewater during treatment processes

357 of the two WWTPs were compared by calculating $R_{6:2/8:2}$ at each stage, as summarized

358 in Fig. 4. An increase in this ratio represents 6:2 Cl-PFESA-enrichment processes due

359 to preferential desorption of 6:2 Cl-PFESA or preferential sorption of 8:2 Cl-PFESA.

360 Trends in such (de)sorption are also evident from the PFAS removal efficiency at each

361 step of the treatment process for 6:2 and 8:2 Cl-PFESA, as presented in Table S10.

362 For the E-WWTP, $R_{6:2/8:2}$ initiated at 100 and went up to 260 for the entire treatment

363 processes, indicating a much higher relative abundance of 6:2 Cl-PFESA (>90%) in

364 both influents and effluents. The corresponding removal efficiency of 6:2 Cl-PFESA

365 and 8:2 Cl-PFESA were -230% and -32%, respectively (where negative values imply

366 an increase in concentration, see Table S10), implying net-desorption from suspended

367 solids with more occurring for 6:2 Cl-PFESA. This net desorption largely occurred

368 from the first aeration step, with a 8-fold vs 4-fold increase in 6:2 and 8:2 Cl-PFESA,

369 respectively. The $R_{6:2/8:2}$ increased most substantially afterafter sedimentation treatment,

370 to a value of 230. This is possibly due to preferential removal of 8:2 Cl-PFESA (73%

371 removed) compared with 6:2 Cl-PFESA (66% removed).

372 For the PD-WWTP, $R_{6:2/8:2}$ at the influent was 66±12 different from the value obtained

373 at the influent of E-WWTP at 100±12. The $R_{6:2/8:2}$ ratio then went down to 7 after entire

374 PD-wastewater treatment processes. This enrichment of the lesser sorbing 8:2 Cl-

375 PFESA seems counter-intuitive, and mainly occurred during the "air flotation" step,

376 which saw an increase in 8:2 Cl-PFESA, yet a decrease in 6:2 Cl-PFESA; a likely

377 explanation for this is the $R_{6:2/8:2}$ for the PD-PFES is much more prone to analytical

378 errors, as the concentrations are quite near the quantification limit, particularly the 8:2

379 Cl-PFESA (Table S6).

380 Considering the sludge fraction, the concentrations of 6:2 Cl-PFESA and 8:2 Cl-

381 PFESA in the sludge are 22000 ng/g and 3200 ng/g (E-WWTP) and 0.72 ng/g and 0.26

382 ng/g (PD-WWTP), respectively (Table S13). The corresponding 6:2/8:2 Cl-PFESA

ratios obtained from the E-WWTP and PD-WWTP are 6.9 ± 0.04 and 2.8 ± 0.16,

respectively, which can be compared to the corresponding water fraction at 230 ± 2.7

and 100 ± 5.3, respectively. A dip of the ratios in the sludge indicates enrichment of 8:2

Cl-PFESA in the sludge during sedimentation, due to its strong sorption interactions

described above. A similar trend was observed in a previous study, where a much

smaller 6:2/8:2 Cl-PFESA ratios were obtained from the sludge in the municipal

WWTP compared to the ratios in the original product solutions.[38]

As presented above, the loss in Cl-PFESA towards the sludge fraction were substantial,

but the impact on the water concentrations minimal. We hypothesize from these results

that one underlying process causing fluctuation of Cl-PFESA flux in the water could be

related to remaining suspended solids to be a substantial source of Cl-PFESA, where

metal ions released from activated sludge or hydroxyl radicals from the lime could lead

to decrease sorption of the Cl-PFESA due to competitive sorption at anionic exchange

sites.[38, 41]

The temporary removal efficiencies of 6:2 Cl-PFESA and 8:2 Cl-PFESA in the waste

water phase during sedimentation tank treatment in E-WWTPs were 66% and 73%; 10%

and 81% for PD-WWTPs, respectively, are worth note that these were not retained or

ultimately effective in subsequent water filtration steps.
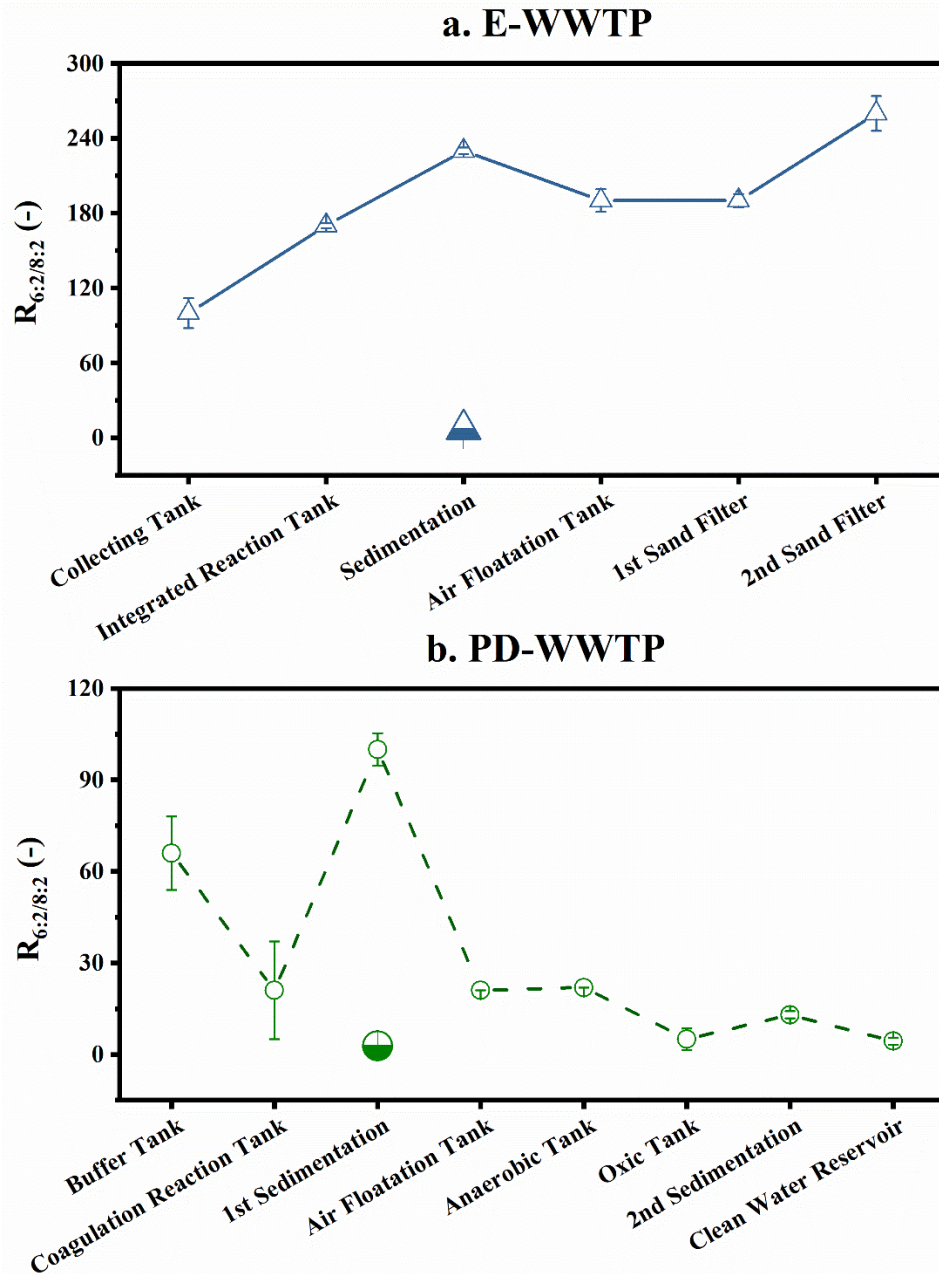
Figure 4. Variation of 6:2 Cl-PFESA over 8:2 Cl-PFESA ratios ($R_{6:2/8:2}$, see Eq. 1) during individual

wastewater treatment processes in E-WWTP (panel a) and PD-WWTP (panel b). The filled symbols

represent the 6:2/8:2 Cl-PFESA ratios obtained from wastewater samples; the semi-filled symbols

show the ratios obtained from sludge samples. The ratio is expected to increase in the case of

preferential sorption of 8:2 Cl-PFESA.

Environmental implications

PFAS were intensively applied at the two industrial sites, which then emitted PFAS towards the wastewater treatment plants. According to the PFAS emission inventories obtained in the effluents (see Fig. 5), PFSAs were predominant in both WWTPs. Both 6:2 Cl-PFESA and 8:2 Cl-PFESA were found in the effluent and sludge of E-WWTP at high abundances due to their extensive applications as chrome mist suppressants in China, but also appeared in trace concentrations in the PD-WWTP likely due to diffuse emission sources. We hypothesize that desorption of Cl-PFESAs from suspended solids, to which they are substantially sorbed, could have occurred during the addition of high pH lime and flocculants (e.g. PAM) in the reaction tank, causing the 6:2 Cl-PFESA and 8:2 Cl-PFESA mass flux to increase in the water phase; testing for this could be the focus of a future study to investigate this hypothesis. A large amount of PFAS-containing wet solid wastes were produced by the two investigated WWTPs. In the present case, these industrial sludges are sent to incineration.

Future work should focus on characterization of loss processes from sludge sedimentation based on dynamic colloidal/suspended particle sorption behavior (e.g. as observed in the reaction tank), in particular, in presence of metal ions, flocculants and pH. Recent advances on non-target screening tools based on high-resolution mass spectrometry could help to identify novel homologue series of n:2 Cl-PFESAs and their degradation intermediates in wastewater and impacted environments[33, 46]. This would also add valuable information to identify local PFAS hotspots as well as to complete emission inventories of different PFAS-relevant manufacturers in China.

430 Cl-PFESA contaminated industrial wastewaters were not efficiently remediated by the

431 WWTPs investigated, even though much was captured by the sludge. Specially, both

432 6:2 Cl-PFESA and 8:2 Cl-PFESA concentrations even increased in the effluents of E-

433 WWTPs. So far, only advanced and relative expensive water treatment techniques

434 including activated carbon filtration, anion exchange methods, and advanced

435 oxidation/reduction processes, provide solutions for removal of some PFAS[47-51], but

436 their efficiency seems to decrease the smaller the size of the PFAS. Currently, only non-

437 PFAS substitutes together with innovative, expensive remediation techniques are the

438 only options for the reduction PFAS and fluorinated alternatives to them. Innovation

439 towards alternatives to PFAS is recommended for both the textile printing and dying

440 industry, as well as the electroplating industry.
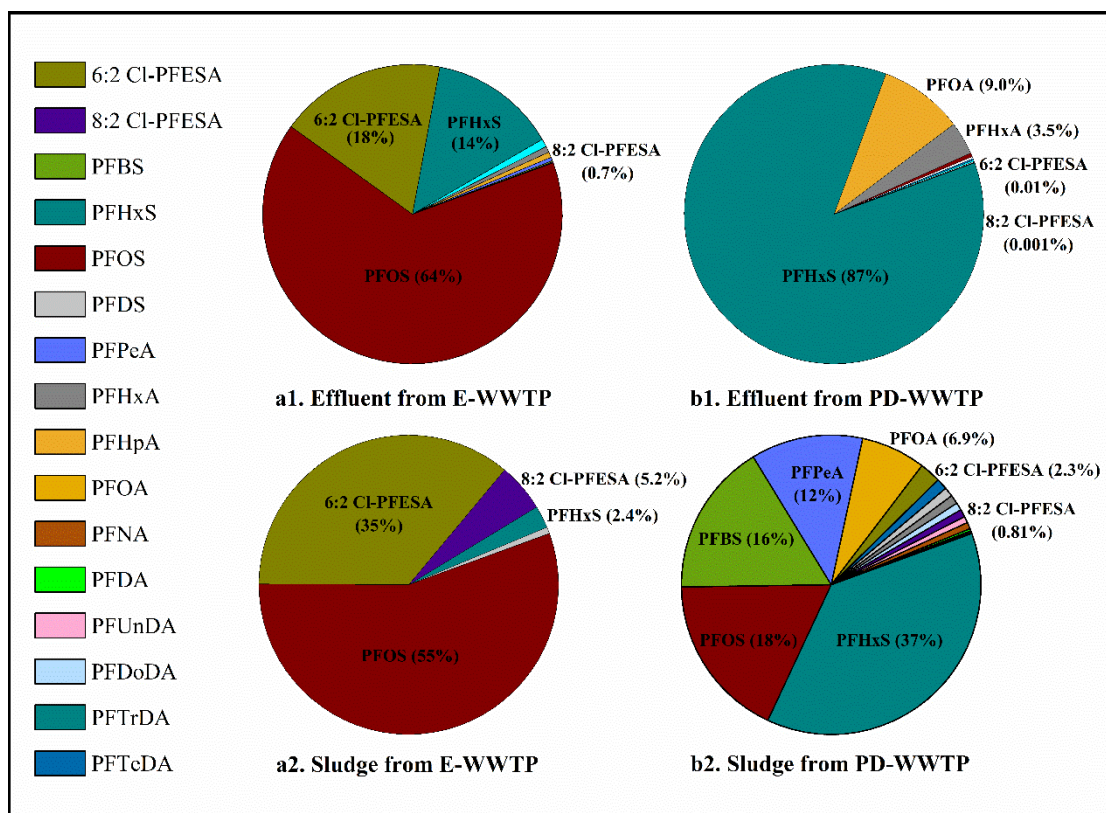
441

442 Figure 5. Alternative and legacy PFAS fraction (%) in the effluents and the sludge collected from the two

443 WWTPs. The pie chart on the left represents the E-WWTP (a1; a2), and the chart on the right represents

444 the PD-WWTP (b1; b2).

Supporting Information

446 The supporting information is available free of charge on the ACS publication website

447 at DOI: XXXXX.

448 Description of calculations for mass flow and removal efficiency; instrumental

449 parameters and relevant information of wastewater treatment plants and target analytes

450 (Table S1-S5); data evaluation of PFAS compositions and dynamics during treatment

451 processes (Table S6-S10, S13; Figure S1); pH values at each treatment step (Table S11-

452 S12); Content (ng/g) of PFASs in the sludge samples collected in the two WWTPs

453 (Table S13).

454

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