

Comparative study of PFAS treatment by UV, UV/ozone, and fractionations with air and ozonated air

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Dai, X, Xie, Z, Dorian, B, Gray, Stephen and Zhang, Jianhua (2019) Comparative study of PFAS treatment by UV, UV/ozone, and fractionations with air and ozonated air. Environmental Science: Water Research and Technology, 5. pp. 1897-1907. ISSN 2053-1400

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Environmental Science Water Research & Technology

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Dai, Z. Xie, B. Dorian, S. R. Gray and J. Zhang, Environ. Sci.: Water Res. Technol., 2019, DOI: 10.1039/C9EW00701F.



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PFAS are persistent chemical of concerns and pose significant risk to human health and intrinsice Online environment. In this study, some advanced treatment technologies capable of commercialisation and generating less secondary waste were studied and compared for treating PFAS containing wastewater. This research provides a valuable reference for the employment of the existing technology in the PFAS containinated water treatment.

Comparative study of PFAS treatment by UV, UV/ozone: and control of the study of PFAS treatment by UV, UV/ozone: and control of the study of the stu

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- 10 Abstract:

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Per- and poly fluorinated alkyl substances (PFAS) and their derivatives are persistent organic 11 chemicals, resulting in significant adverse human health and environmental effects. In this 12 paper, UV, ozonated air fractionation, air fractionation and UV/ozone combined treatment for 13 PFAS removal were studied and compared. The feed water was synthesised from the 14 15 firefighting foam, which contained multiple per- and poly fluorinated alkyl substances. Combined UV and ozone equipment patented by EGL were used to compare the performance 16 of different treatment methods, in which a two-unit rig was employed as a benchtop setup and 17 a nine-unit rig using UV/ozone combined treatment was employed as a pilot rig. It was found 18 from the benchtop tests that PFAS removal efficiency was improved with the increases of air 19 and feed flowrates in the UV/ozone combined treatment. The highest PFAS removal efficiency 20 achieved was 87% at an air flowrate of 30 L/min and feed flowrate of 1.4 L/min (10 min 21 residence time). The different treatment techniques including UV only, ozonated air 22 fractionation, and air fractionation were compared with the UV/ozone combined treatment at 23 24 the residence time of 20 min. UV alone removed 16.8% PFAS, which showed the worst 25 performance of all tests. 73% PFAS was destructed by the UV/ozone combined treatment. Air 26 fractionation was able to achieve 81% PFAS removal. Ozonated air fractionation showed the best PFAS removal efficiency, which was more than 95%, as a result of the enriched OH 27 28 radicals in the gas bubble. For the nine-unit pilot rig, the UV/ozone combined treatment achieved about 79% PFAS removal. However, foam fractionation occurred during the 29 treatment, which led to approximately 4% removal of PFAS based on the mass balance. 30 Therefore, the PFAS removal contributed by UV and ozone combined treatment was 75%, 31 which was similar to the result of benchtop rig. All treatment resulted in a concentration 32 increase of at least one type of short-chain PFAS. When foam fractionation with gas bubbles 33 occurred in the treatment, it was easier to remove perfluoroalkyl sulfonate (PFSA) than 34 perfluoroalkyl carboxylate (PFCA), because PFSA is more hydrophobic than PFCA, which 35 makes it more affinity to gas bubbles. In addition, in comparison with long-chain PFAS it is 36 37 much more difficult to remove the short-chain PFAS by fractionation technologies, due to the partition factor declining exponentially with the reduced carbon number. 38

39	DOI: 10.103)/(
40	Key words: PFAS; advanced oxidation; UV; ozone; fractionation; wastewater treatment	
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44 **1. Introduction**

PFAS products have been used since 1940s, and their roles as synthetic pollutants emitted to 45 the natural environment by various pathways were only scarcely considered by environmental 46 chemists, toxicologists, or food chemists. The first observations of organic compounds 47 containing fluorine in humans were made at the end of 1960s and did not attract great attention 48 ¹. At the beginning of 2000s, the works done by Moody and Field ² and Giesy and Kannan ³, 49 raise significant interest in these anthropogenic pollutants. They considered the environmental 50 implications of the use of firefighting foam with PFAS and the global distribution of 51 perfluorooctanoate in wildlife. 52

Australia's national industrial chemicals assessment body concluded that perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are persistent, bioaccumulative, and toxic substances, which undergo long-range transport in water and air and transfer between different media. In 2017, the Australian Government Department of Health regulated the PFOS/ perfluorohexane sulfonate (PFHxS) and PFOA concentrations of 0.07 μ g/l and 0.56 μ g/L in drinking water, respectively ⁴. In 2017, the USEPA proposed the unregulated reference concentrations of PFOA and PFOS to be 0.07 μ g/L in drinking water ⁵.

The primary technologies for PFAS removal from water resources can be divided into two categories:

I. Separation of PFAS from treated water, and destruction of the concentrated PFAS in aseparate process

64 II. Direct destruction of PFAS in-situ the treated water

At present, the technologies in Category I are widely applied in the large-scale water treatment 65 plants, include membrane filtration, adsorption, ion exchange and foam fractionation. 66 Membrane filtration such as reverse osmosis (RO) and nanofiltration (NF) can effectively 67 remove PFAS. However, the treatment cost by filtration is considerable for plants treating large 68 volumes of water. Furthermore, a PFAS concentrated stream (approximately 10% of the treated 69 70 water volume) is produced from RO and NF processes and needs further treatment. Currently, adsorption is the most popular technology used by water utilities. Adsorbents include powdered 71 activated carbon (PAC) and granulated activated carbon (GAC), which are not generally 72 regenerated. The cost of incorporating these adsorbents into existing water treatment processes 73 can be high, because a contact column is essential and the adsorbent needs to be continually 74 purchased. The disposal of the adsorbents is also costly ⁶, usually requiring high-temperature 75 incineration. Ion exchange resin can also remove PFAS efficiently ⁷. However, the exhausted 76 ion exchange resin is difficult to be regenerated, since it produces high salinity PFAS 77 containing wastewater. If no regeneration is undertaken, the considerable solid waste would be 78 produced. Foam fractionation has also been used for separation of the PFAS from wastewater, 79

since PFAS also act as surfactants. The running cost of foam fractionation is low and produce would be would be

only small amounts of highly concentrated PFAS containing water. However, the removal
efficiency is about 80% and is not very effective when dealing with short-chain PFAS.

83 For all treatment methods of Category I, the destruction of concentrated PFAS is still required.

Plasma incineration followed by calcium hydroxide absorption is commonly used to convert

85 PFAS to low hazard compounds 8 .

Category II methods focus on the direct destruction of PFAS, avoiding the concentration step. 86 However, perfluorinated surfactants do not exhibit the preferred reactive sites for reaction with 87 ·OH radicals generated during the advanced oxidation. The abstraction of fluorine from a 88 89 carbon atom is thermodynamically unfavorable because the F-OH bond has a dissociation energy of at least 216 kJ/mol lower than that of the C-F bond (CF₃F 552 kJ/mol, R-CF₂-F 352 90 kJ/mol, R,R'-CF-F 508 kJ/mol) 9. Furthermore, the electron density of the ionic head group 91 92 (e.g., carboxylate and sulfonates) is reduced by perfluorination, hindering electron transfer 93 reactions. The kinetic rate constant for the reaction of trifluoroacetic acid with ·OH has been estimated to be less than 1×10⁶ M⁻¹s⁻¹¹⁰, indicating a slow rate of reaction with practically no 94 95 reactivity of OH towards trifluoroacetic acid. PFOS is resistant to different advanced oxidation treatment methods (Fenton, UV/H₂O₂, ozonation in alkaline solution, and peroxon process 96 (O₃/H₂O₂)) over 120 min at room temperature ¹¹. Hori et al. ¹² found that the addition of 97 hydrogen peroxide in UV treatment method has a detrimental effect on the degradation of 98 PFOA, compared to direct UV-photolysis (radiation source: Xenon-doped mercury lamp), 99 which supports the persistence of PFCs in the presence of OH. It was reported that 83% PFOS 100 was removed under the conditions of 5 h UV dosing with molecularly imprinted polymer-101 modified TiO₂ catalyst ¹³. 102

The combination of ozone and ultraviolet radiation (UV) could achieve better water treatment 103 than the ozone alone, due to the promoted formation of hydroxyl radical intermediates ^{14, 15}. In 104 the UV/O₃ process, the dissolved ozone will be split by UV irradiation ($\lambda < 300$ nm), and reacts 105 with water to form a thermally excited H_2O_2 which decomposes into two $\cdot OH$ subsequently ¹⁵. 106 Houston Research Inc. showed that ozone/UV enhances the oxidation of complexed cyanides, 107 chlorinated solvents, pesticides that contribute to COD and BOD 16-19. In the 108 conventionalozonation, organic compounds are not completely oxidized to CO₂ and H₂O in 109 many cases ²⁰. In some reactions, the intermediate oxidation products remaining in the solution 110 may be as toxic as or even more toxic than the initial compound ²¹. Completion of oxidation 111 reactions, as well as oxidative destruction of compounds immune to unassisted ozone, can be 112 achieved by supplementing the reaction with UV radiation. Many organic contaminants absorb 113 UV energy in the range of 200 -300 nm²² and decompose due to direct photolysis or become 114 excited and more reactive with chemical oxidants. Therefore, the combination of UV/ozone 115 might be able to achieve effective PFAS removal. 116

However, Category II technologies are not favoured by most large-scale water treatment plants
 directly, because strong oxidants/radiation at high dose are required to decompose PFAS, and
 PFAS concentration in the wastewater is generally at PPB to PPT level ^{23, 24}.

Thus, it is necessary to combine both treatment methods in Categories I and II. Through the methods in Category I, the PFAS could be concentrated into a much smaller volume than the original PFAS, which will significantly reduce the load of the subsequent destruction treatments in the Category II. Therefore, minimising the total rejected volume (containing high 127 treatments were also compared in this study.

128 2. Experimental

129 2.1. Benchtop rig tests





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Figure 1. Schematic diagram of the benchtop rig

A schematic drawing of the benchtop UV/ozone rig (Environmental Group Limited, Australia) 132 133 is shown in Figure 1. The benchtop rig consists of two reaction chambers connected to two 134 ozone generators. There are one ozone bubbler stone connected to the ozone generator and two UV lamps ($\lambda = 254$ nm, Cnlight[®], China) in the reaction chamber. The air from a compressor 135 can be partially ozonated in the ozone generator by an ozone lamp ($\lambda = 185$ nm, Cnlight[®], 136 137 China) in the chamber before bubbling into the reaction chambers. A peristaltic pump was used to supply the feed into the benchtop rig. The total volume of the two reaction chambers was 14 138 L. The UV intensity was measured by UV intensity meters (210 - 280 nm, Run-Goal 139 Technology Co. Ltd. China), which showed different readings for the same amount of UV 140 radiation due to the difference of the distance to the UV lamps. The air flowrates were 141 monitored by an air flowmeter (Siargo[®], M5700 Series, China). The PFAS containing feed was 142 synthesized by mixing waste firefighting foam (Cleanaway, Australia) containing about 6.3 143 mg/kg PFAS with tap water to achieve PFAS concentration between 3 to 10 µg/L. 144

145 2.1.1 Blank test

Blank tests were conducted with the tap water to achieve the operation baseline. The UV intensity and ozone residual were measured without the interference from the added PFAS containing firefight foam. The feed flowrates were set at 0.35 and 1.4 L/min to obtain residence times of 40 and 10 min, respectively. The air flowrates during the tests were varied at 10^{102} and 30 L/min, respectively.

151 2.1.2 System PFAS adsorption test

An adsorption test was firstly conducted to check whether PFAS will be absorbed in the benchtop testing rig. The original PFAS wastewater was pumped through the rig at a flowrate of 0.7 L/min (residence time = 20 min). The feed was sampled at the beginning of the test, and

- the effluent was sampled after one hour.
- 156 2.1.3. UV/ozone combined treatment for PFAS wastewater

In the UV/ozone combined PFAS wastewater treatment tests, both the ozone and UV lamps
were set on. The feed flow rate was set at 0.35, 0.7 and 1.4 L/min to achieve the residence time
of 40, 20 and 10 min, respectively. The air flowrate was varied in the range of 15 - 30 L/min.

160 2.1.4. Ozonated air fractionation, air fractionation and UV for PFAS wastewater treatment

As we can see from the schematic diagram of the benchtop rig in Figure 1, it is possible to have UV radiation, air fractionation and ozonated air fractionation/ozone oxidation involved in the treatment. Therefore, it is necessary to identify the dominant PFAS removal mechanism in the treatment. All the tests were conducted at the feed flowrate of 0.7 L/min (residence time of 20 min). The feed was sampled at the beginning of the test, and the effluent was sampled at the end of the test (after one hour).

In the UV test, only UV lamps were switched on, and there was no air bubbling into the reactionchambers.

In the air fractionation tests, only air was bubbled into the reaction chambers at an air flowrateof 20 L/min, and both the UV and ozone lamps were set off.

In the ozonated air fractionation tests, the ozone lamps were set on, and the UV lamps were set
off. The air at a flowrate of 20 L/min was partially ozonated by the ozone lamps and bubbled
into the reaction chambers.

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175 2.2. Pilot UV/ozone rig test

The scale-up of the engineering process may result in great performance differences relative to 176 the benchtop tests ²⁶. Therefore, a pilot test was also conducted under the optimum conditions 177 178 identified from the benchtop tests. In comparison with the benchtop rig, the pilot rig includes nine reaction chambers and sixteen ozone generators. All the reaction chambers were equipped 179 with two UV lamps, but three of them were not connected to the ozone generators, which is 180 different from the benchtop rig. The total volume of the pilot rig was 63 L. Therefore, the feed 181 182 flowrate was set at 3.15 L/min to achieve a 20 min residence time. The feed was prepared by 183 dissolving 100 g firefighting foam into 200 L water. The experiment lasted for one hour. The 184 feed was sampled at the beginning of the test, and the effluent was sampled at the end of the 185 test.

186 2.3. Analysis

187 The PFAS in the water was analysed by ALS, Australia with the LC-MS-MS method, EP22 and the detection limit is in the range of 0.01-0.1 μ g/L. The total PFAS concentration is the 189 sum of the concentration of 28 PFAS analytes, which are listed in Appendix 1.

190 The ozone residual in the reaction chamber was analysed by the Hach DR/800 with AccuVac®

191 method. Triplicate measurements were conducted for the same tests, and the mean value was

192 reported in this paper.

193 3. Results and discussion

194 3.1. Benchtop UV/ozone combined tests

3.1.1. Blank tests with tap water for identification of the maximum UV radiation and ozoneresiduals

197 Blank tests were carried out by using the tap water, which was used to dilute PFAS containing 198 firefighting foam. The purpose of these tests was to understand the baseline performance of the 199 combined UV/ozone system in the absence of PFAS. Besides, the blank tests also help to identify the variations of ozone residuals and UV intensity with the feed and air flowrates, as 200 the reference for the following PFAS water treatment. Table 1 shows the ozone residual and 201 the UV intensity of the blank tests in reaction chambers R1 and R2 at feed flowrates of 1.4 and 202 0.35 L/min respectively, which are also the theoretical maximum value achievable for 203 following PFAS tests under the similar conditions. At the higher feed flowrate of 1.4 L/min 204 (10 min residence time), the total ozone residuals in R1 and R2 were almost the same and in 205 the range of 0.18 - 0.20 mg/L. This difference is in the error range. However, the UV intensity 206 declined about 17% in R1 as the air flowrate was increased to 30 L/min, due to enhanced 207 deflection/reflection of UV beams by increased air bubbles ²⁷. At the lower feed flowrate of 208 0.35 L/min (40 min residence time), the maximum total ozone residuals in R1 and R2 were 0.2 209 mg/L when the air flowrate was 20 L/min. The measured UV intensity also reduced to 210 approximately 12% at an air flowrate of 30 L/min, in comparison with that of an air flowrate 211 of 10 L/min in R1. 212

It is also worth mentioning that in general, the total ozone residuals at high feed flowrate were higher than those at low feed flowrate. That is because of the high liquid turbulence at high flowrate encouraging the ozone transfer from the gas phase to the liquid phase ²⁸. Furthermore, in R1, the UV intensity was also higher at a feed flowrate of 1.4 L/min than that at 0.35 L/min with the same air flowrate, because more and finer air bubbles created at higher feed flowrates will produce more uniform UV scattering ²⁹.

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Feed flowrate	Air flowrate	UV In	tensity	Ozone	residual	
(L/min)	(L/min)	(µW)	$/cm^2$)	(mg	g/L)	
		R1*	R2*	R1	R2	Total
1.4	12	100	44	0.08	0.12	0.20
1.4	20	100	45	0.11	0.08	0.19
1.4	30	83	43	0.09	0.09	0.18
0.35	10	84	43	0.07	0.06	0.13
0.35	20	80	43	0.14	0.06	0.20
0.35	30	74	44	0.06	0.04	0.10

219 Table 1. Blank tests: Ozone residual and UV intensity

* The different readings are due to the different installation distances to the UV lamps.

221 3.1.2. System PFAS adsorption test

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- All the detectable PFAS in the system adsorption test are shown in Table 2. It can be found
- that the PFAS concentrations in the effluent are almost the same as the feed. Thus, there is no
- detectable PFAS adsorption by the benchtop rig in our tests.

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Sample	PFPeS	PFHxS	PFHpS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFAS
	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$
Feed	0.05	0.38	0.07	2.3	0.02	0.18	0.04	0.11	3.15
Effluent	0.04	0.37	0.08	2.4	0.02	0.14	0.04	0.10	3.19

225 Table 2. Analytical results for the system adsorption test

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227 3.1.3. UV/ozone combined treatment for PFAS wastewater

In the UV/ozone combined tests, both UV and ozone lamps were set on, and the ozonated air was bubbled into the reaction chambers. Figure 2a and Figure 2b show the total PFAS concentration in the treated water and the total PFAS removal efficiency under different feed and air flowrates, respectively. Total PFAS removal efficiency is calculated by Equation (1) as below:

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$$Re = (1 - \frac{C_t}{C_f}) \times 100\%$$
 (1)

where Re is the percentage of PFAS removed from the treated water, C_t is the concentration of PFAS in the treated water, and C_f is the PFAS concentration in the feed.

The maximum total PFAS removal was 87% at an air flowrate of 30 L/min and feed flowrate of 1.4 L/min. At the same air flowrate, better PFAS removal was achieved at higher feed flowrate, owing to the higher UV intensity and ozone residual obtained at higher feed flowrate in the blank tests as shown in Table 1. Therefore, it can be concluded that the high ozone transfer rate and UV intensity are able to enhance the PFAS removal.







Figure 2. Performance of treatment at different feed and air flowrate

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Table 3 shows the concentrations of four major per- and poly-fluoroalkyl substances in the feed 246 and treated water. It can be seen that, after the ozone/UV combined treatment, all PFAS 247 concentrations reduced, except for perfluorohexanoic acid (PFHxA). Moreover, the increases 248 of feed and air flowrates could facilitate the PFOS and PFOA removals under all the operating 249 conditions. However, the feed and air flowrates had less influence on PFHxS removal. On the 250 251 other hand, PFHxA concentration increased under almost all the treatment conditions, and up 252 to a 50% increase of PFHxA was observed when 97.3% PFOA removal was achieved. Therefore, it can be confirmed that the UV/ozone combined treatment could convert PFAS into 253 PFHxA ³⁰. It seems that PFHxS also could be generated from other PFAS sources in the 254 treatment process, but it could not be demonstrated unequivocally based on the available 255 256 analytical results. After the treatment under the optimum treatment conditions (air flowrate = 257 30 L/min, feed flowrate = 1.4 L/min), the total concentration of PFHxS (0.48 μ g/L) and PFHxA $(0.22 \ \mu g/L)$ was 0.70 $\mu g/L$ greater than the total concentration (0.60 $\mu g/L$) of PFOS (0.52 $\mu g/L$) 258 and PFOA (0.08 µg/L), although their total concentration in the feed was only one third of that 259 of the PFOS and PFOA. Therefore, to achieve high total PFAS removal, the PFHxA and 260 PFHxS concentrations should be considered, as they could not be easily removed by the 261 UV/ozone combined treatment and PFHxA appeared to be generated by the process. 262

	Feed	Air	PFE	[xS	PFO	OS	PFE	IxA	PFC	DA
Sample	flowrate	flowrate	С	Re	С	Re	С	Re	С	Re
_	(L/min)	(L/min)	(µg/L)	(%)	(µg/L)	(%)	$(\mu g/L)$	(%)	$(\mu g/L)$	(%)
Feed	/	/	2.40	/	5.40	/	0.16	/	2.20	/
S 1	0.35	15	0.44	81.7	2.30	57.4	0.18	-12.5	0.60	72.7
S2	0.35	20	0.46	80.8	1.70	68.5	0.19	-18.8	0.80	63.6
S3	0.35	30	0.48	80.0	1.10	79.6	0.18	-12.5	0.26	88.2
S4	0.7	15	0.70	70.8	2.20	59.3	0.18	-12.5	0.12	94.5
S5	0.7	20	0.58	75.8	1.60	70.4	0.18	-12.5	0.40	81.8
S6	0.7	30	0.60	75.0	0.72	86.7	0.19	-18.8	0.18	91.8
S7	1.4	15	0.58	75.8	1.50	72.2	0.16	0.0	0.24	89.1
S8	1.4	20	0.92	61.7	0.28	94.8	0.24	-50.0	0.06	97.3
S9	1.4	30	0.48	80.0	0.52	90.4	0.22	-37.5	0.08	96.4

263 Table 3.Operation parameters and analytical results

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3.1.4. UV, air fractionation and ozonated air fractionation for PFAS wastewater treatment 265

The purpose of the tests was to verify the overall PFAS removal efficiency and to identify the 266 removal efficiency of specific types of PFAS under differnt treatment methods provided by the 267 benchtop rig. 268

Figure 3 shows images of the observation windows of the UV/ozone combined test, air 269 fractionation test, ozonated air fractionation test, and UV only test. It can be seen from Figures 270 3a and 3d that there was no foaming observed. However, in both fractionation processes where 271 air and ozonated air was bubbled through the reaction chambers, it can be seen from Figures 272 3b and 3c that foaming occurred. Since foaming in the reaction chambers is a sign of 273 fractionation due to existing surfactants (PFAS), no foam observed in the UV/ozone combined 274 275 and UV tests indicated that the PFAS removal in both processes was due to the destruction rather than foam fractionation. 276



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a. UV+Ozone



b. Air fractionation



c. ozonated air fractionation



d. UV only Figure 3. Foaming at different operations

286 In Table 4, the analytical results from the various processes are shown. Feed 1 was used for the air fractionation test, and S1 was the treated water by air fractionation. Feed 2 was used 287 for both UV and ozonated air fractionation tests, and S2 and S3 were the treated waters thereof. 288 The removal efficiencies of all detectable PFAS containing different carbon numbers are 289 290 shown in Figure 4. Since the detection limit was $0.02 \mu g/L$ for the perfluoropentane sulfonate (PFPeS) and perfluoropentanoic acid (PFPeA) containing five carbons, it is impossible to make 291 a solid conclusion based on the analytical method, although some PFPeA removal was found 292 during the ozonated air fractionation. Therefore, the removal efficiency of the PFAS containing 293 five carbons is not shown in Figure 4. Furthermore, since some concentration changes after 294 treatment were less than the detection limit of 0.02 μ g/L, those changes were considered in the 295 analytical error range and are not discussed further. 296

It can be found that the UV treatment could remove 16.8% PFAS in total (Figure 4), which was mainly associated with PFOS removal (Table 4). After the UV treatment, 25% PFOS was removed from 2.8 to 2.1 μ g/L in the treated water, but the PFOA concentration did not change.

View Article Online DOI: 10.1039/C9EW00701F

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However, the PFHxS concentration increased by approximately 33% from 0.3 to 0.4 Weyl Price Online Since only PFOS and/or PFOA was used in the firefighting foam and the variation of perfluoroheptane sulfonate (PFHpS) from 0.06 to 0.05 µg/L is in the range of the detection limit and is negligible, it can be concluded that the newly formed PFHxS was mainly from PFOS degradation.

Based on research from Vecitis et al., perfluoroalkyl carboxylate (PFCA) should have a faster 305 photolytic degradation than perfluoroalkyl sulfonate (PFSA) ³¹However, it can also be seen in 306 Table 4 that PFCA such as PFOA, PFHxA or PFHpA did not show obvious change after the 307 UV treatment, in comparison of the degradation of PFOS (PFSA). Yamamoto, etal. found that 308 one of the photodegradation pathways of PFOS is to transform into PFCA ³⁰. It also can be 309 found that 80% of the total PFAS in the feed is in form of PFOS as shown in Table 4. Therefore, 310 even if the PFCA degrades faster than PFSA, it could be possibly repenlished by the 311 photodegradation of the PFOS in this study. Thus, it would not be possible to make any 312 conclusion whether the PFCA had been destroyed by UV treatement in our study. 313

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Sample	Operation	PFPeS	PFHxS	PFHpS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFAS
		$(\mu g/L)$								
Feed 1	/	0.05	0.38	0.07	2.3	0.02	0.18	0.04	0.11	3.15
S 1	Air fractionation	0.03	0.06	< 0.02	0.3	0.02	0.15	0.02	0.01	0.59
Feed 2	/	0.04	0.3	0.06	2.8	0.02	0.16	0.04	0.09	3.51
S2	UV	0.05	0.4	0.05	2.1	0.02	0.16	0.04	0.1	2.92
S3	Ozonated air fractionation	0.03	< 0.05	< 0.02	<0.04	< 0.02	0.14	< 0.02	< 0.01	0.17

314	Table 4.	Analytical	results	for the	feed	and	treated	water
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From Figure 4, it can be found that air fractionation removed about 81.3% PFAS in total, and 316 80% PFHxS, approximately 100% PFHpS, 87.0% PFOS, 16.7% PFHxA, 50.0% PFHpA, and 317 91% PFOA were removed from the treated water. Since air is not a strong oxidant, foam 318 fractionation should be the dominant separation mechanism for the PFAS removal. For the 319 PFSA, the removal efficiency did not show a clear relationship to the molecular weight. 320 However, the removal efficiency for PFCA declined more than 80% as the carbon number 321 reduced from 8 to 6, because the lower lipophilicity of the shorter alkyl chain PFCA leads to 322 its lower affinity to the air bubbles ^{32, 33}. 323



The total PFAS removal efficiency was about 95% by the ozonated air fractionation, as shown 327 in Figure 4, which is the highest among all the tested treatment methods. After the treatment, 328 329 no PFSA, PFOA and PFHpA was detected in the treated water. However, only 12.5% PFHxA was removed from the treated water. Based on the blank tests, the maximum total ozone 330 residuals in both reaction chambers were 0.2 mg/L, which could not oxidise the PFAS in a 331 contact time of 20 min based on bond energy theory¹¹. Therefore, the dominant PFAS removal 332 mechanism should be ozone-boosted foam fractionation. When ozone is dosed into water, 333 hydroxyl radicals are generated, which are strong electron binders ^{34, 35}. As shown in Figure 5, 334 there will be an OH radical rich layer around the interface of the gas bubbles, due to the ozone 335 diffusion from gas phase into the water phase. Since strong hydroxyl radical electron binders 336 could bind onto the negatively charged hydrophilic SO₃-/COO⁻ ends of the PFOS/PFOA based 337 on affinity theory 36-39, more PFAS will concentrate around the interface of the gas bubbles, in 338 comparison with air fractionation. Therefore, the ozonated air fractionation can achieve higher 339 PFAS separation efficiency than the air fractionation. 340



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Figure 5. Schematic diagram of the proposed PFAS affinity to the gas bubble

PFHxA is highly persistent and mobile in the environment as a short-chain PFAS⁴⁰. Based on 343 the results, it can be seen that none of the tested methods can remove PFHxA as effectively as 344 other PFAS substances. The UV/ozone combined treatment method even caused an increase 345 of the PFHxA concentration in the treated water, when PFOA was presented in the feed water. 346 Therefore, ozone enhanced fractionation or air fractionation could be used to lower the PFOA 347 concentration before applying the UV and ozone combined technology to destroy any PFAS 348 passing fractionation treatment. Although the possibility exists that UV and ozone combined 349 technology could destroy the PFHxA, it could not be confirmed based on our test results and 350 further research is necessary to determine if it is possible and at what rate it might occur. 351

352 3.2. Pilot-scale UV/ozone combined tests

It can be found in Figure 6 that the foaming only occurred in the last two reaction chambers.
During the 1 h experimental period, 189 L water was treated, and 2.5 L of water was collected
from the overflow line due to the foaming in the last two reaction chambers.

From Table 5, after UV/ozone combined treatment, the mass of all short-chain PFCA increased, while the mass of all short-chain PFSA decreased. The 6:2 Fluorotelomer sulfonic acid (6:2 FTS) that was not detected in both the feed and effluent was found in the foam. Therefore, it can be concluded that the advanced oxidation could facilitate the formation of D_{DShort} and D_{DShort}

In Figure 7, the removal efficiency of PFAS during the pilot rig operation by the UV/ozone combined treatment was calculated using Equation (2).

363
$$D_{pfas} = \left(1 - \frac{C_{foam} \times V_{foam} + C_e \times V_e}{C_f \times V_f}\right) \times 100\%$$
(2)

- where D_{pfas} is the percentage of PFAS destroyed by UV and ozone combined treatment; C_{foam}
- and C_e are the PFAS concentrations in the foam and treated water (effluent), respectively; and V_{foam} , V_e and V_f are the volumes of foam, effluent and feed, respectively.



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Figure 6. Foaming in the pilot rig

Table 5. PFAS concentration in the feed, treated water and foam

Sample	PFPeS	PFHxS	PFHpS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	6:2 FTS	PFAS
	$(\mu g/L)$									
Feed	0.04	0.24	0.03	1.20	< 0.02	0.14	0.03	0.07	< 0.05	1.75
Effluent	0.02	0.09	< 0.02	0.05	0.02	0.15	0.03	0.01	< 0.05	0.37
Foam	0.09	0.90	0.13	4.10	0.03	0.23	0.13	0.30	0.06	5.97

³⁷⁰

It can be seen from Figure 7 that about 79% PFAS in total was removed from the treated water (effluent), in which 75% was destroyed by the UV/ozone combined treatment similar to the result achieved by the benchtop at the same residence time. Meanwhile, with the same carbon number, it is easier to remove the PFSA than the PFCA from the feed by either destruction or fractionation, which is attributed to the hydrophobicity or lipophilicity difference between the PFCA and PFSA. With the same alkyl chain length, PFCAs are more hydrophilic than PFSAs ^{32, 33}. Therefore, the affinity of the PFSA molecule to the water-bubble interface is higher than

in the bubble and to partition into the foam compared to PFCA. Furthermore, the concentration
 of the short-chain PFCA including PFHxA and PFHpA increased due to the UV/ozone

381 combined destruction, consistent with the benchtop results.



Figure 7. Percentage of PFAS removed from the effluent and PFAS destroyed by UV and ozone
combined treatment (residence time = 20 min, air flowrate = 160 L/min)

To assess the influence of carbon number on the foam fractionation, the partition factors of the PFAS with different carbon numbers are calculated by Equation (3) using data in Table 5 and shown in Figure 8.

$$388 \qquad \lambda = \frac{C_{foam}}{C_e} \tag{3}$$

389 where λ is the partition factor between the effluent and the foam.

It can be found that the partition factor has an nearly exponential relationship with the PFAS carbon number, due to the octanol-water and air-water partition coefficients increasing exponentially with perfluorinated chain length ⁴². Therefore, partitioning the shorter-chain PFAS from the bulky feed into the foam would be more difficult than that of the long-chain PFAS by the ozonated air fractionation treatment.



View Article Online Figure 8. Distribution factors vs PFAS carbon number 396 DOI: 10.1039/C9EW00701F

4. Conclusions 397

The performance of ozonated air fractionation, air fractionation, UV, and UV/ozone combined 398 treatments on PFAS removal were studied and compared. The benchtop tests were conducted 399 at a hydraulic residence time of 20 min and air flowrate of 20 L/min, and the conclusions were 400 obtained as follow: 401

- ozonated air fractionation achieved the best performance, in which about 95% PFAS 402 was removed from the treated water, 403
 - UV showed the worst performance of 17% PFAS removal, •
 - air fractionation removed 81% of PFAS, and •
 - UV/ozone combined treatment achieved 73% removal of PFAS at a residence time of • 20 min, which was also confirmed in the pilot rig test.

In comparison with the air fractionation, the ozonated air fractionation has higher PFAS 408 removal efficiency, because of the affinity of OH radical to the negatively charged hydrophilic 409 SO₃-/COO- ends of the PFOS/PFOA. 410

It is relatively easier to remove PFSA than PFCA by both the air and ozonated air fractionations 411 and the UV/ozone combined treatment, attributing to the involvement of gas bubbles and the 412 413 greater lipophilicity of PFSA.

When PFAS destruction treatment is involved, the short-chain PFAS concentration will 414 generally increase after the treatment. Both the air and ozonated air fractionations could not 415 effectively partition the short-chain PFAS from the contaminated water into the foam, due to 416 the exponential decline of the partition factor with the redcuing carbon number of the PFAS. 417

Acknowledgement 418

Funding from the Environmental Group Limited and Australian Department of Industry, 419 Innovation and Science are gratefully acknowledged. Pilot and benchtop testing rigs were 420 supplied by the Environmental Group Limited. All Intellectual Property relating to this project 421 and equipment design are covered by the EGL's existing Patent. 422

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527		Appendix I
	PFA	AS - Perfluorobutane sulfonic acid (PFBS)
	PFA	AS - Perfluoropentane sulfonic acid (PFPeS)

PFAS - Perfluorohexane sulfonic acid (PFHxS)

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PFAS - Perfluoroheptane sulfonic acid (PFHpS)	w Article Online C9EW00701F
PFAS - Perfluorooctane sulfonic acid (PFOS)	
PFAS - Perfluorodecane sulfonic acid (PFDS)	
PFAS - Perfluorobutanoic acid (PFBA)	
PFAS - Perfluoropentanoic acid (PFPeA)	
PFAS - Perfluorohexanoic acid (PFHxA)	
PFAS - Perfluoroheptanoic acid (PFHpA)	
PFAS - Perfluorooctanoic acid (PFOA)	
PFAS - Perfluorononanoic acid (PFNA)	
PFAS - Perfluorodecanoic acid (PFDA)	
PFAS - Perfluoroundecanoic acid (PFUnDA)	
PFAS - Perfluorododecanoic acid (PFDoDA)	
PFAS - Perfluorotridecanoic acid (PFTrDA)	
PFAS - Perfluorotetradecanoic acid (PFTeDA)	
PFAS - Perfluorooctane sulfonamide (FOSA)	
PFAS - N-Methyl perfluorooctane sulfonamide (MeFOSA)	
PFAS - N-Ethyl perfluorooctane sulfonamide (EtFOSA)	
PFAS - N-Methyl perfluorooctane sulfonamidoethanol	
PFAS - N-Ethyl perfluorooctane sulfonamidoethanol	-
PFAS - N-Methyl perfluorooctane sulfonamidoacetic acid	
PFAS - N-Ethyl perfluorooctane sulfonamidoacetic acid	
PFAS - 4:2 Fluorotelomer sulfonic acid (4:2 FTS)	
PFAS - 6:2 Fluorotelomer sulfonic acid (6:2 FTS)	
PFAS - 8:2 Fluorotelomer sulfonic acid (8:2 FTS)	
PFAS - 10:2 Fluorotelomer sulfonic acid (10:2 FTS)	

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Conducted by a multifunctional equipment, the comparative study showed a 95% PFAS removal achieved by the ozonated air fractionation.

View Article Online DOI: 10.1039/C9EW00701F