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# Perfluorinated alkyl substances: Sewage treatment and implications for receiving waters

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- 1 • **PRE PROOF ACCEPTED MANUSCRIPT FOR STOTEN -**  
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5 **Perfluorinated Alkyl Substances: Sewage treatment and implications for receiving waters.**

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14

15 **Abstract**

16 This study comprises a detailed analysis of data for perfluorooctanesulfonic acid (PFOS), and  
17 perfluorooctanoic acid (PFOA) for over 600 wastewater treatment works effluents (WwTW) as well as  
18 samples upstream and downstream of each discharge of effluent into its receiving water. This has  
19 allowed an investigation of not only the effectiveness of removal of the perfluoroalkyl substances  
20 (PFAS) compounds during wastewater treatment but also implications for compliance with the  
21 environmental quality standard (EQS) set for PFOS under the Water Framework Directive. It is shown  
22 that effluents contain concentrations of PFOS that exceed the annual average EQS by a factor between  
23 1.1-fold and 40-fold. The corresponding factors for PFOA are between 2-fold and 22-fold. The presence  
24 of high concentrations upstream, means that between a quarter and a third of individual effluents are  
25 found to reduce the concentration of fluorocarbons in the river downstream of the discharge point. The  
26 elevated concentrations upstream of the studied wastewater treatment works suggest inputs of these  
27 perfluoro compounds into the aquatic environment are ubiquitous and therefore difficult to address from  
28 simply setting permit conditions for individual WwTW. The freshwater EQS set for PFOS is based on  
29 several worst-case accumulation coefficients and large safety factors, which, when combined, result in  
30 a sub ng/L EQS. Consequently, the use of the biota derived quality standard may be a more realistic  
31 measure of environmental risk. It may be prudent, to assess the effectiveness of controls implemented  
32 in the last few years before considering widespread end-of-pipe treatment.

33  
34 **Key words:** PFAS; wastewater treatment works; removal; PFOS; PFOA; rivers.  
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## 39 **1. Introduction**

40 Per-fluoroalkyl substances (PFAS), once globally taken up for a variety of applications, are now being  
41 recognised as having a detrimental impact on the environment owing to their persistence,  
42 bioaccumulation and toxicity. First invented in the 1930s, PFAS are an extensive group of chemicals  
43 varying in chemical and physical properties (Ross, et al., 2016). At least 4730 different types of PFAS  
44 have been identified (OECD, 2018). Major examples include perfluorooctanesulfonic acid (PFOS), and  
45 perfluorooctanoic acid (PFOA) which have come to particular attention of regulators (European  
46 Chemicals Agency, 2020). The physico-chemical properties of these compounds: high  
47 electronegativity, low polarizability, and small molecular size provided by strong C-F bonding, weak  
48 intermolecular interactions lead to unusually high chemical and thermal stability as well as hydrophobic  
49 and lipophobic properties making them ideal for certain applications. Typically, PFOS has been used in  
50 the semiconductor and photographic industries, and some firefighting foams. It is also used as a  
51 protective coating for carpets, textiles, and leather. PFOA found uses in fluoropolymers, which are used  
52 in electronics, textiles, and non-stick cookware (Public Health England, 2009). PFASs can enter the  
53 environment through the production, use, and disposal of the products. For example, PFAS have been  
54 used as fabric coatings to enhance stain-resistance in various clothes. It is reported (Lassen et al.,  
55 2015) that after wearing and washing the clothes 20-30 times, the coating can break down and release  
56 the PFAS. Finally, when the clothes are disposed of to landfill, the PFAS can enter the environment  
57 through leaching.

58  
59 PFAS tend to be mobile, when released either into the atmosphere or surface water/groundwater. Loads  
60 of as much as 25-850 kg/year of PFAS have been reported to be transported to polar regions (Yeung  
61 et al., 2017). Consequently, with respect to bioaccumulation, PFAS in the oceans and freshwater bodies  
62 can enter the food chain and bioaccumulate and biomagnify across all trophic levels. Risks to human  
63 health thus arise via contaminated drinking water, consumption of fish and shellfish or foods that are  
64 grown in contaminated soil (Christensen et al., 2017). Toxicity has been reported for fish and dolphins  
65 (Guillette et al., 2020; Soloff et al., 2017); and human exposure to PFAS is of concern as illustrated by  
66 effects in animals on reproductive, developmental, liver, kidney, and endocrine systems (US EPA,  
67 2020a). Phasing out of production and implementation of action plans were initially instigated in the  
68 USA (Zanolli, 2019; US EPA, 2020b). Other countries such as Canada have implemented bans on  
69 manufacture, sales and imports (Canada.ca, 2019). Within Europe PFOS and PFOA are restricted  
70 under the EU POPs Regulation (Regulation (EU) 2019/1021) and some short chain PFAS controlled  
71 under the REACH EU chemical legislation (ECHA, 2020). Most significantly, globally PFOA and PFOS  
72 have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs). There are  
73 some exemptions for use under specified circumstances such as within photoresists or anti reflective  
74 coatings for photolithography processes and photographic coatings (EC, 2017). Use of PFOA appears  
75 to have been slightly less than PFOS (ECHA, 2014, 2015). Controls imposed on the production and  
76 use of these fluorocarbons means that concentrations should be declining in the environment. Specific  
77 high risk uses such as the use in firefighting foams can result in direct release of PFASs into the  
78 environment, as was reported for a major fire in the UK in 2005 (EA, 2007).

79

80 Concerns regarding the environmental impacts of PFAS chemicals have led to PFOS being categorised  
81 as a Priority Hazardous Substance with a freshwater Environmental Quality standard of  $6.5 \times 10^{-4}$   $\mu\text{g/L}$   
82 (0.65 ng/L), as an annual average (EU, 2000). There is no equivalent value for PFOA. PFOS and PFOA  
83 have been reported in river samples downstream of WwTW in countries such as Japan and USA where  
84 concentrations range from low ng/l up to 1000's of ng/l (Hansen et al., 2002; Lien et al., 2008; Zushi et  
85 al., 2008). Further data are required on the occurrence, sources, routes of transport and removal of  
86 PFAS in wastewater treatment.

87

88 The UK Chemical Investigation Programme (CIP) is a monitoring programme undertaken over the past  
89 ten years as a collaborative programme between UK water companies and the relevant regulatory  
90 organisations. An initial phase (CIP1), carried out in 2010-2013, addressed the need for data relating  
91 to newly regulated substances. The second phase (CIP2 - 2015-2020) was intended to quantify risk of  
92 non-compliance with EQS values at a site-specific level in order that appropriate and justifiable remedial  
93 action can be taken. This included monitoring of the quality of river water and sewage effluents at more  
94 than 600 wastewater treatment works' (WwTW) sites. The CIP2 dataset generated monitoring data for  
95 WwTW effluents and receiving waters (upstream and downstream of the discharge point) for over 50  
96 determinands including PFOS and PFOA (UKWIR, 2018). The aim of this work was to assess the fate  
97 of PFOS and PFOA during wastewater treatment as well as compare upstream and downstream  
98 concentrations across England to determine the impact of WwTW effluent on concentrations and  
99 compliance. By thoroughly analysing the data it was possible to make conclusions regarding the  
100 ubiquity of occurrence, the significance of WwTW as sources of PFAS as well as determine the  
101 compliance against the critiqued EQS, there by providing information vital for considering future  
102 management options.

## 103 **2. Methodology**

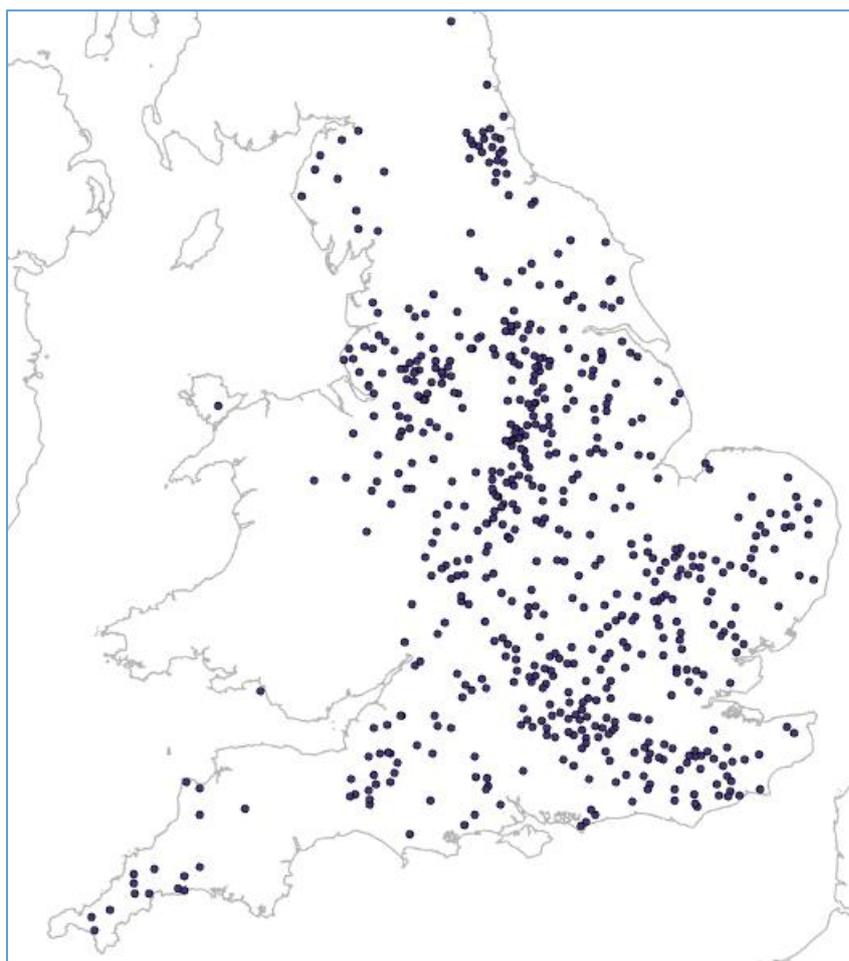
### 104 **2.1 Sampling**

105 Results from 2015 to 2017 have been obtained for over 600 WwTW sites (20 sampling occasions per  
106 substance in effluent and 36 per substance in river water upstream and downstream of the effluent  
107 discharge) over a period of two years between June 2015 and June 2017 (Figure 1). Samples of  
108 effluent, upstream and downstream samples were collected at the same time on each occasion to  
109 ensure consistent hydrological conditions in the river. Numbers of results per substance therefore  
110 corresponded to over 12000 for effluents and over 43,000 for river samples taken upstream and  
111 downstream of effluent discharges.

112

113 Samples were collected as grab samples taken at approximately evenly spaced intervals over (for each  
114 site) a two-year sampling period, rather than as composite sampling. This latter approach was  
115 precluded by concerns about sample stability raised in tests prior to the commencement of the  
116 programme (Gardner et al., 2012). Taking randomly scheduled discrete samples is a guarantee of an

117 unbiased estimator of the variables of interest, such as mean, median and variance etc. Alternative  
118 approaches such as composite sampling, whilst it does provide a nominally more precise estimate of  
119 mean etc (for a given sampling effort) is not a sound approach to generate a ready appreciation of  
120 variance. A minimum of 15% of sampling was undertaken in non-working hours (evenings and  
121 weekends) and included in the data analysis to account for any possible systematic effects in the  
122 sample collection process.  
123



124  
125

126 **Figure 1 Location of sites for CIP2 programme for which samples of WwTW effluent,**  
127 **upstream and downstream were taken**

128  
129

## 130 **2.2 Sample treatment and analysis**

131 Samples were collected in stainless steel samplers, stored in glass containers and transported at 4° C  
132 to the analytical laboratories. The maximum sample storage period was determined for key  
133 determinands prior to the beginning of the programme by undertaking tests of sample stability. A period  
134 of 3 to 5 days storage for trace determinands (depending on substance) was shown not to lead to more  
135 than a 20% change in concentration. Detailed sampling, filtration and preservation requirements are  
136 provided in S1 of the Electronic Supporting Information (ESI). Analytical work was commissioned from

137 contracted laboratories, who used their own in-house analytical methodologies, which were not  
138 standardised but had to meet minimum and exacting performance criteria. Given the variety of potential  
139 methods used and allowing for commercial sensitivities it is not possible to detail specific Gas and/or  
140 Liquid Chromatographic-Mass Spectrometry techniques employed by the laboratories. However, to  
141 ensure analytical quality was paramount the programme management team specified analytical  
142 performance characteristics for laboratories to meet before participating. This included ISO17025  
143 accreditation, the requirement to undertake tests of analytical performance to demonstrate that they  
144 met the stated programme requirements for limit of detection (LOD), precision and recovery in relevant  
145 sample matrices at relevant concentrations. The required LOD values for PFOS and PFOA was 0.00065  
146 (in effluents) and 0.00009 (in river waters) µg/L. LOD was defined as 3.3x the standard deviation of  
147 blank-corrected results of determinations made on a sample containing essentially no determinand  
148 (where possible in a relevant sample matrix) (Thompson and Ellison, 2013). In some cases, it was not  
149 possible to find effluent samples free from determinands in which case a synthetic sample was used).  
150 The full dataset for PFOS showed that <2%, <2% and <0.5% of samples were <LOD for the effluent,  
151 upstream and downstream river samples respectively. The equivalent data for PFOA were <1%, <2%  
152 and <0.5% of samples were <LOD for the effluent, upstream and downstream river samples  
153 respectively. See section S1 and Table S1 of the electronic supporting information for more detail.

154

155 Quality control determinations were undertaken for both laboratory tests and field sampling.  
156 Laboratories also took part in a bespoke proficiency testing scheme. Details of the proficiency testing  
157 scheme used to confirm data quality is provided in S1 of the Electronic Supplementary Information  
158 (ESI). Where reported concentrations were below the required LOD, the result was substituted at half  
159 face value - as stipulated in the relevant Directive (EC, 2009). For PFOS and PFOA there were no  
160 important instances of inter-laboratory bias or inter-regional variation (data not shown), which would  
161 indicate important bias in the methodology of sample handling and analysis.

162

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164 **3. RESULTS and DISCUSSION**

165  
166 **3.1 PFOS and PFOA in UK rivers, upstream and downstream of WwTW**  
167 **effluent discharges**

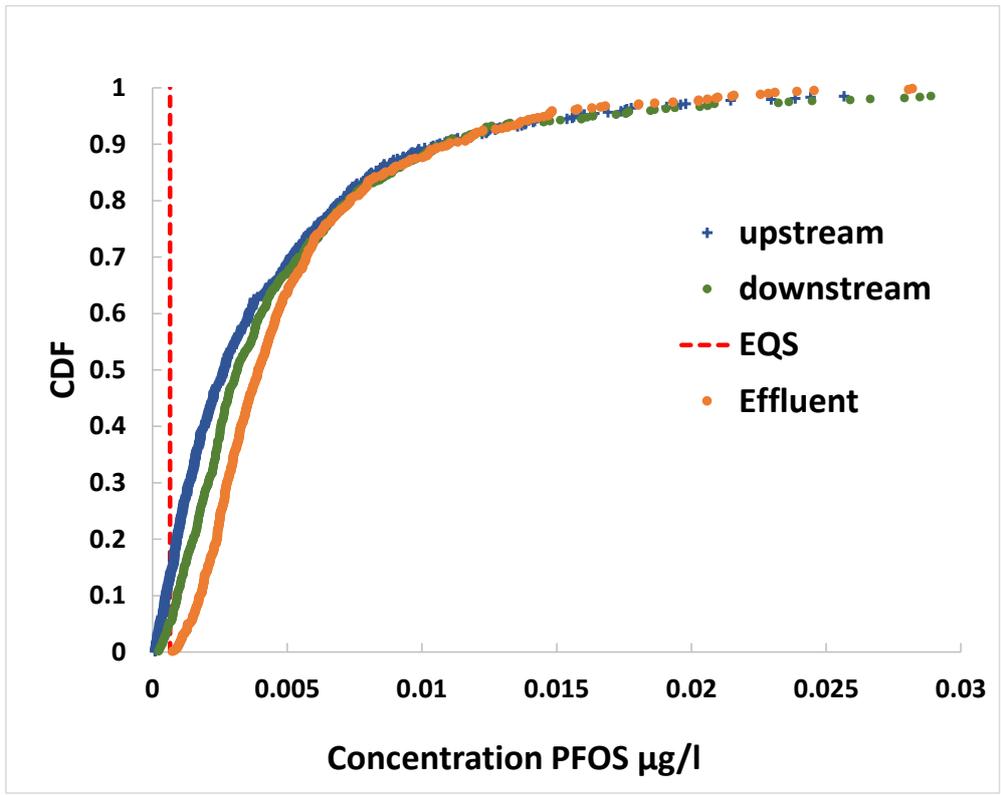
168 Figure 2 shows cumulative distribution function (CDF) plots for PFOS and PFOA, including data for  
169 average river water concentrations upstream and downstream of each of the CIP WwTW discharges  
170 as well as data for the corresponding effluents.

171  
172 The plots illustrate the widespread EQS exceedances at upstream sites as well as the influence of the  
173 WwTW discharge on downstream water quality. This impact is shown by the degree to which the  
174 downstream curve is displaced to the right (to higher values of x) with respect to the upstream curve.  
175 The occurrence of a large displacement rightwards, should it occur, indicates that downstream  
176 concentrations are increased. There are some clear conclusions to be drawn; namely that for PFOS in  
177 particular the increase in concentration downstream is small and that concentrations of PFOS and  
178 PFOA upstream of WwTW discharges predominantly exceed EQSs by a large margin. The mean  
179 increase for both substances is 10% of the upstream value and the median increase for PFOS is 19%  
180 and for PFOA 35%. This is a consequence of the upstream concentrations being already markedly  
181 elevated, such that the percentage of EQS non-compliance only changes from the high eighties to the  
182 mid to high nineties for both substances. The UK situation reflects similar reports for developed  
183 countries with similar concentration profiles between PFOS and PFOA and elevated concentrations in  
184 WwTW effluents (Lein et al., 2008). Other studies have showed an increasing concentration of PFAS  
185 compounds down a catchment owing to their persistence combined with increasingly urban populations  
186 in the lower parts of the catchment. The Danube for example exhibits concentrations up to 30 ng/L for  
187 PFOS and PFOA (Lindim et al., 2015). However, a recent review noted the positive effect of phase-  
188 outs and regulations but noted the impacts on the environment have not always been well studied and  
189 longer-term surveillance monitoring is required to increase the power of the trend analysis (Land et al.,  
190 2018).

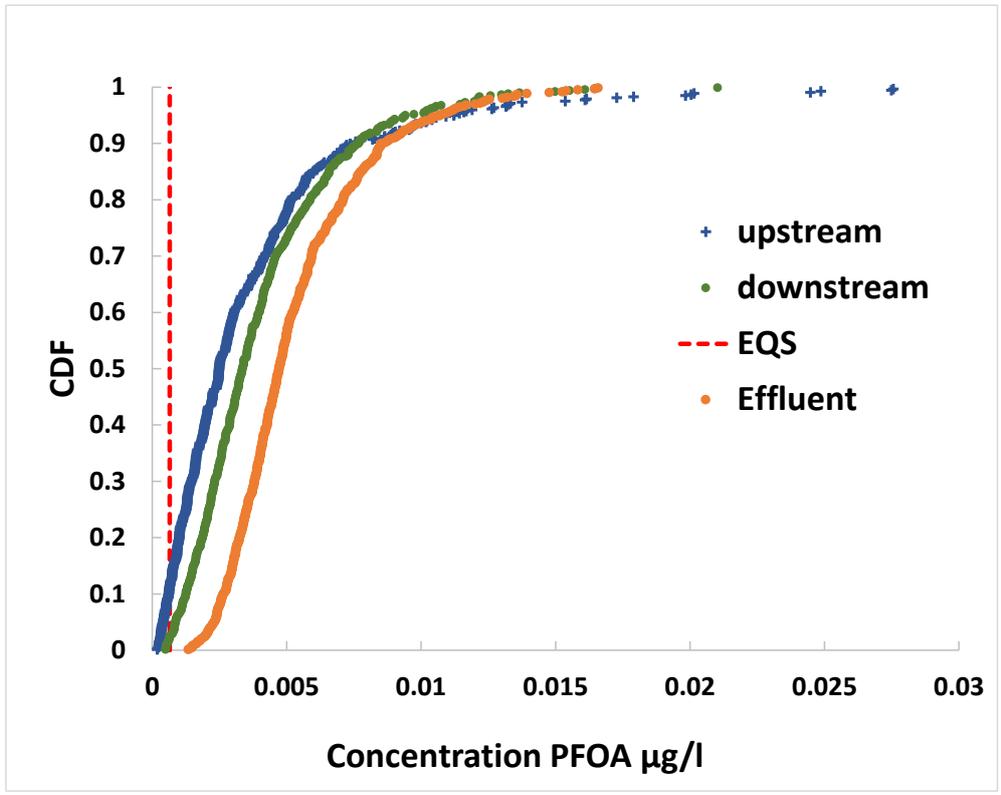
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Figure 2 CDF plots for concentrations in WwTW effluents and in rivers and upstream and downstream of effluent discharges

199 A fundamental issue relating to the implementation of pollution control measures is the extent to which  
200 changes in riverine contaminant concentrations are apparently brought about by specific effluent  
201 discharges. For instance, it is possible to envisage at least three different categories of situation:

202

203 a) The predominantly local problem – where a small number of effluents have a marked impact  
204 on downstream river concentrations of a contaminant. In this case the remediation strategy  
205 likely to be favoured might involve implementation of improved treatment methodologies as well  
206 as (where possible) control of inputs to the WwTWs concerned.

207 b) The problem of widespread in-river noncompliance with EQS values that appears to be caused  
208 by a large proportion of WwTW discharges. This is essentially pollution by sewage effluent  
209 where the concentrations upstream of effluent discharges tend to be low, but concentrations  
210 downstream are elevated to an important extent. Remedial measures in this case might be  
211 similar to a) above but, given the difficulty and cost of upgrading large numbers of treatment  
212 processes, a greater focus on blanket controls of inputs at source (as has been already  
213 employed for PFOS and PFOA) might be more appropriate and cost effective.

214 c) Widespread EQS non-compliance that is not demonstrably caused by the local effluent  
215 discharge. That is, where the change in concentration from upstream to downstream is, in the  
216 majority of cases, small in relation to both the upstream concentration itself and in relation to  
217 compliance above and below the discharge point. In this case the question of what action to  
218 take is more difficult to address. Upstream sources appear to be the immediate issue, there  
219 remains the question that having addressed these upstream issues, will downstream sources  
220 have then to be dealt with as well?

221 It appears that the position relating to riverine concentrations of the fluorocarbons PFOS and PFOA is  
222 one of the relatively unusual instances where case c) applies. This could be interpreted as an instance  
223 where WwTW effluents appear to have a small impact on riverine concentrations, despite rivers and  
224 effluents being near to universally non-compliant themselves. Two further questions arise as  
225 consequence of these findings.

226

227 It might be assumed that in locations regarded as pristine/unspoiled environments fluorocarbon  
228 concentrations would be low. Unfortunately, this is not the case. PFAS have been recently detected  
229 (Muir et al., 2019) in seawater and sea ice in the European arctic at remarkably high concentrations.  
230 Concentrations of PFOA in sea ice have been reported as being in the range 20-100 pg/l (the marine  
231 annual average EQS is 130 pg/l). Freshwater (annual average EQS 650 pg/l) studies at high latitudes  
232 indicate a wide range of values presumably arising from variations in proximity to local sources, but  
233 concentrations of several thousand pg/l of PFOA have been determined (Lescord et al., 2015).

234

235 With respect to UK rivers, the concern is that WwTW discharges in an upper catchment might serve to  
236 elevate fluorocarbon concentrations to levels of concern and that sewage effluent discharges lower in  
237 the catchment serve to maintain these concentrations further downstream. The data presented here

238 neither proves nor disproves this theory. There were sites considered to be at the top of catchments  
239 where fluorocarbon concentrations were lower than elsewhere but in other locations this appeared not  
240 to be the case. However, it should be noted that the sampling programme's objectives were chosen  
241 based on higher risk locations that predominantly were not in the category of "pristine". Indeed, given  
242 the arctic data noted above, even the concept of a pristine environment in the UK might be questionable.

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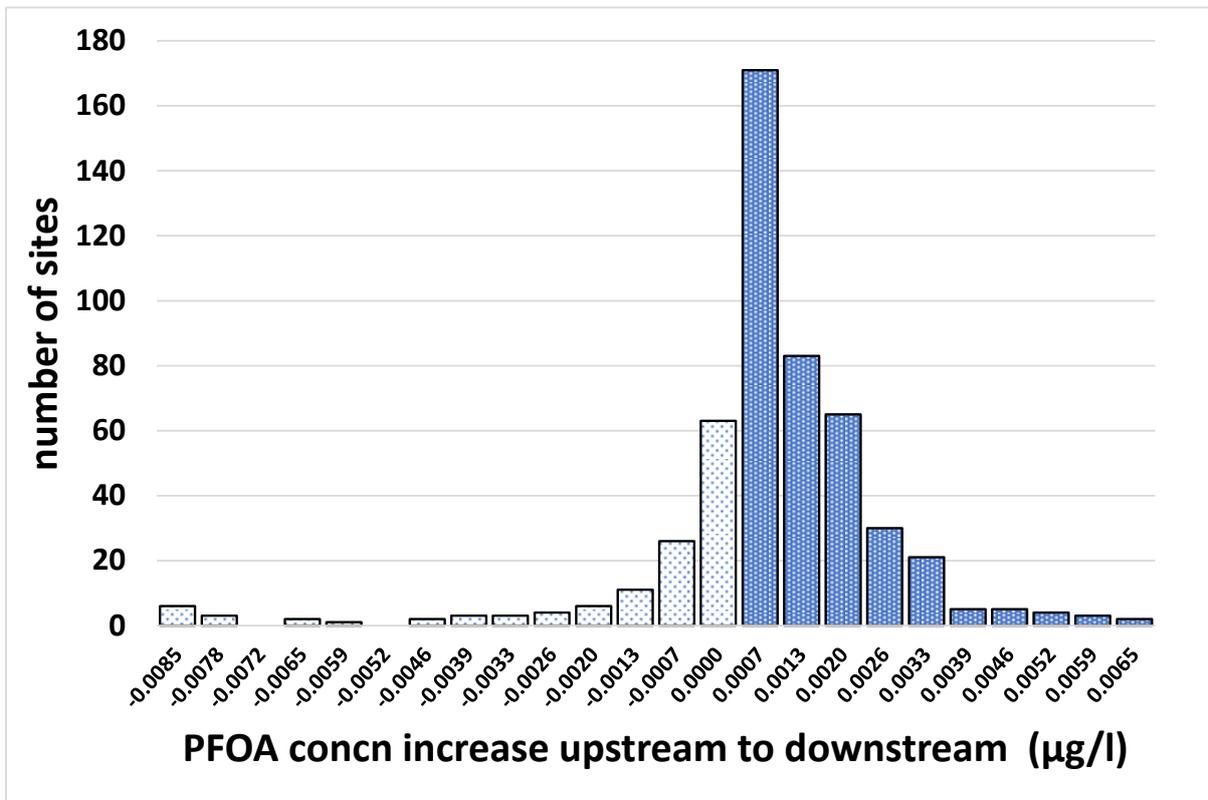
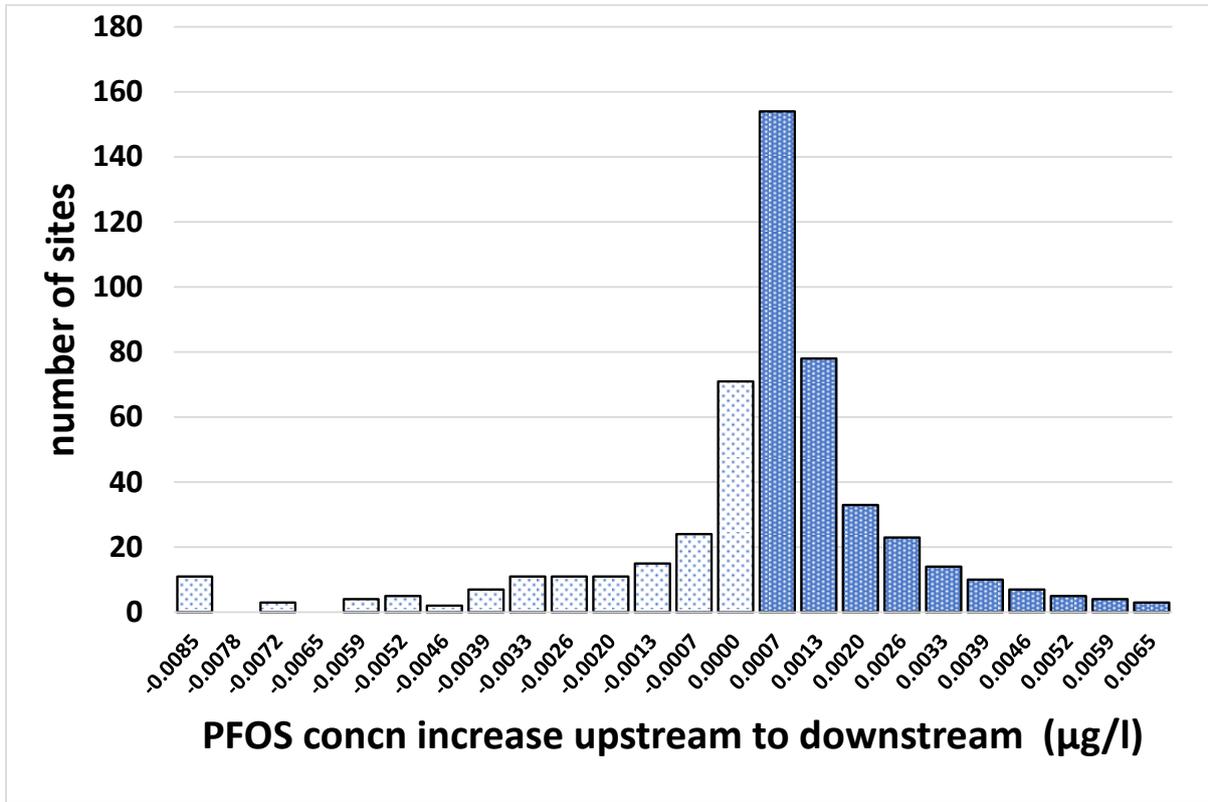
244 The data set also provides reasonable circumstantial evidence of the association between aviation and  
245 markedly higher fluorocarbon concentrations in surface water. However, out of the 600 sites only a  
246 handful of locations can be associated with plausible fluorocarbon sources such as airfields, airports or  
247 facilities where PFOS might be used in the context of fire prevention. This, of course, is a consequence  
248 of the site selection process which did not factor in the investigation of specific types of sites, other than  
249 those primarily where WwTW effluent were subject to relatively low dilution in the respective receiving  
250 water.

251

### 252 **3.2 Site by site analysis**

253 Further analysis was undertaken to examine the changes in fluorocarbon concentrations from upstream  
254 of the local WwTW discharge to downstream on a site-by-site basis in order to determine the extent to  
255 which individual WwTW discharges have a clear impact on downstream concentrations (Figure 3). The  
256 data show that both positive differences (downstream higher than upstream) and negative differences  
257 occur. In the case of PFOS, negative changes occur in 175 out of 527 comparisons (1/3<sup>rd</sup>), for PFOA  
258 this figure is 130 out of 527 (1/4). This is a demonstration of the complexity of the picture presented by  
259 PFAS compounds.

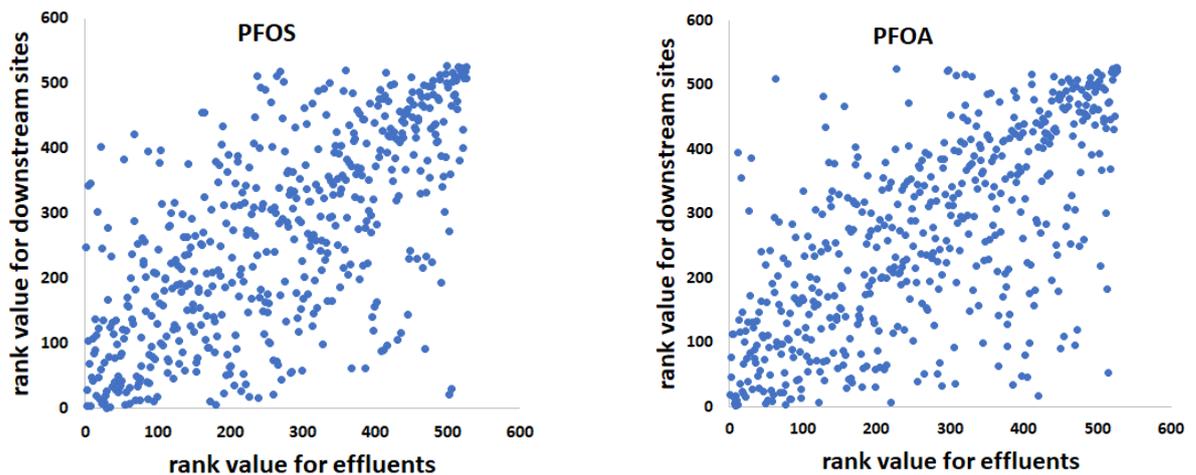
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**Figure 3** Histograms of upstream to downstream changes in concentrations at WwTW sites  
*Note: Each bar of the histogram shows the number of sites where the concentration is between the value shown on the x axis and the next category down.*

268 The interplay between upstream and effluent concentrations is complicated, such that the highest  
269 effluent concentrations do not necessarily correspond to the highest downstream concentrations. This  
270 is illustrated in the diagrams in Figure 4, in which the concentrations of the PFAS compounds in the  
271 effluent and downstream were ranked for all of the effluents, then plotted against each other. Owing to  
272 the persistence of PFOS and PFOA it can be assumed that there is little likelihood of any  
273 biotransformation between the upstream and downstream sites for the samples taken on each  
274 occasion. The rank values of each axis are the numerical order from lowest to highest concentration for  
275 effluents and downstream concentration values, respectively. Whilst there is a weak tendency for high  
276 concentration effluents to correspond to high concentrations downstream, there are many instances  
277 where low concentration effluents are associated with high concentrations downstream, and vice versa.  
278 Observed downstream concentrations are a function of effluent concentration and flow relative to that  
279 in the river upstream, however, it may be concluded that effluent concentration alone, is a poor guide  
280 to downstream water quality, with the importance of upstream PFAS contributions being far greater in  
281 many cases.

282



283

284 **Figure 4 Comparison of rank values for downstream and effluent concentrations**

285

286

287 **3.3 Fate in Wastewater Treatment**

288 An intensive survey of 20 Scottish WwTW over 28 sampling occasions provides a dataset with which  
289 to assess the impact of wastewater treatment on PFOS and PFOA (Figure 5). There are some key  
290 differences between the results for the two substances as summarised in Table 1.

291

292 **Table 1 Summary of changes in concentration from influent to effluent**

Percentage concentration - change influent to effluent (negative values indicate a reduction from influent to effluent)		
	PFOS	PFOA
10%ile	-67	-43
25%ile	-48	-2
50%ile	-39	15
75%ile	-20	35
90%ile	29	106

293

294 In summary, this dataset indicates removal of PFOS between 20% to 50% (interquartile range),  
295 whereas the change from influent to effluent for PFOA was on the whole an increase that was spread  
296 over an IQR of -2 to 35%. Other studies on the removal of PFAS during wastewater treatment suggest  
297 per fluorinated compounds are not consistently removed and that effluent concentrations can be higher  
298 than influent levels owing to their formation via biodegradation of precursor compounds (Arvaniti and  
299 Stasinkis, 2015). PFOA has been reported to be the main transformation product of 8:2 Fluorotelomer  
300 alcohol (8:2 FTOH) (Wang et al., 2005), this highlights that PFOA and PFOS are not the only fluorinated  
301 chemicals likely to be entering WwTW and that the pathways and breakdown products are likely to be  
302 complex. The controls on PFOS and PFOA use would be expected to be beginning to have an impact  
303 on observed concentrations and loads from sources such as WwTW, although there are only limited  
304 temporal datasets available and they tend to note that time periods have not been sufficient to provide  
305 significant statistical power (Nguyen et al., 2019).

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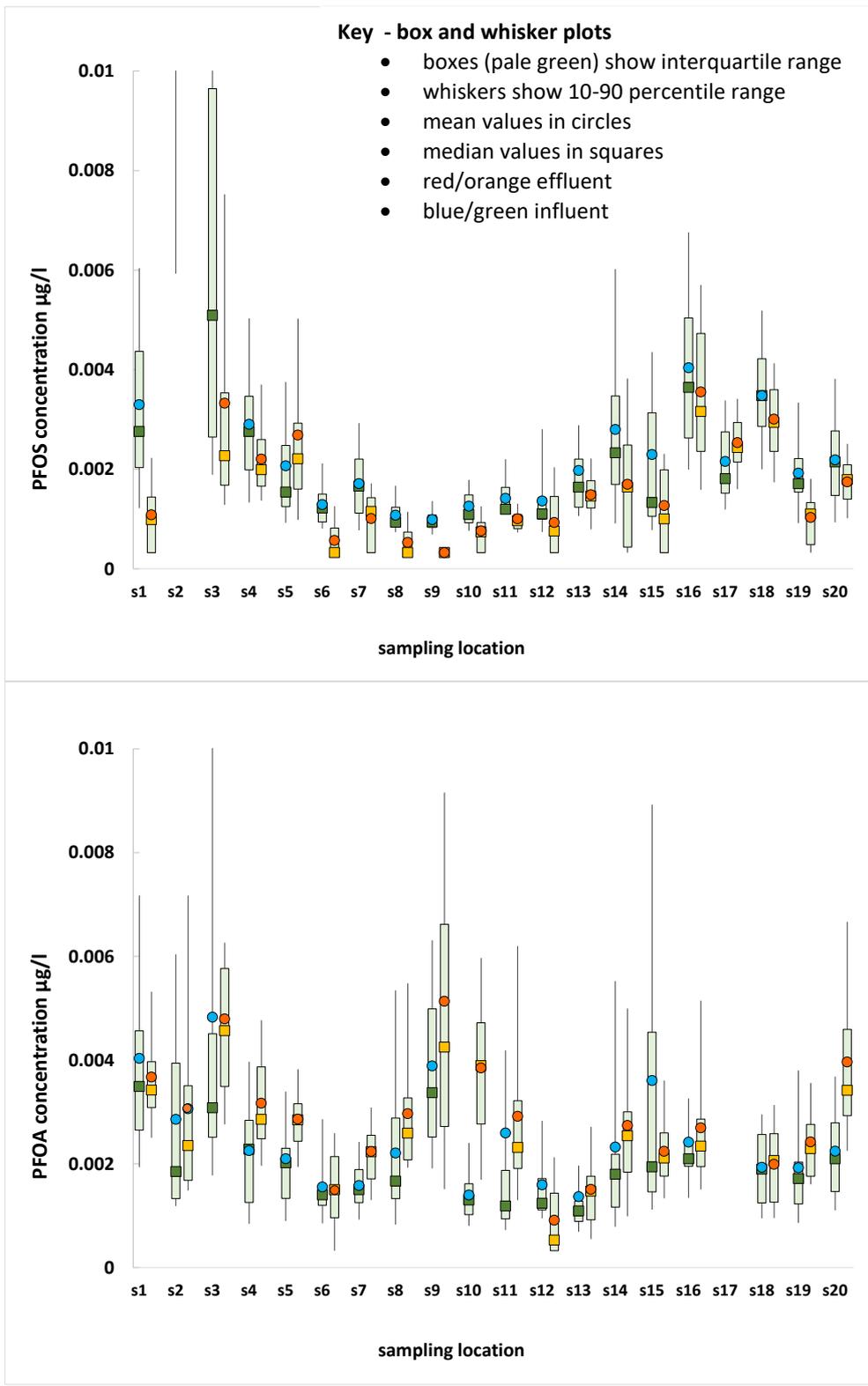
307 These data suggest that conventional wastewater treatment has little impact on PFAS concentrations  
308 reflecting their relatively low sorption potential, and so limited loss to sludge and high persistence which  
309 reflects their lack of biodegradation during secondary biological treatment. Advanced treatment  
310 techniques have been shown to be successful in removing a greater quantity of PFAS either to sludge  
311 or through aggressive degradation methodologies, however, it has been noted that there is a paucity of  
312 quantitative assessments taking account of economic and technical aspects (Arvaniti and Stasinkis,  
313 2015). Consequently, it is important to take account of the impacts of PFAS on receiving waters.

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**Figure 5 PFOS and PFOA concentrations in influent (green/blue) and effluent (red/yellow) of 20 UK WwTW**



399 than the LOD to 77 ng/L across Europe (SCHER, 2011). The estimated in-river concentrations are  
400 greater than those detected either upstream or downstream of WwTW in this study, where median  
401 concentrations were 2.6 and 3.2 ng/L for PFOS and 2.5 and 4.7 ng/L for PFOA respectively.

402

403 Acute toxicity of PFOS in freshwaters is typically in the mg/L range with fish appearing slightly more  
404 sensitive to PFOS compared with algae and invertebrates (SCHER, 2011). Chronic toxicity data  
405 reported No Effect Concentrations down to less than 2.3 µg/L range for chironomus (MacDonald et al.,  
406 2004). To generate an EQS a factor of 10 was applied to derive the 230 ng/L aquatic standard. The  
407 secondary poisoning standard for aquatic predators was based on a Cynomologus monkey study  
408 (Seacat et al., 2002). A No Observed Adverse Effect Level of 0.03 mg/kg was observed for hormone  
409 changes and was subjected to a 90 times safety factor (= 0.033 mg/kg bw). By applying observed worst  
410 case bioconcentration factors (worst case BCF = 2796) and biomagnification factors (mean = 5) a value  
411 of 2 ng/L for freshwater secondary poisoning. For human health a tolerable daily intake of 150 ng/kg  
412 has been derived and assuming 115g of fish eaten per day by a 70kg human being and that a maximum  
413 of 10% of the TDI may be used consuming fish, then a 9.1 µg/kg for biota (as wet weight) is derived.  
414 Dividing this value by a combination of the BCF and BMF above generates an equivalent water EQS of  
415 0.65 ng/L. This being the most conservative estimate is used as the overall EQS for water. As can be  
416 seen in Figure 2, the ubiquitous nature of PFOS and PFOA throughout the UK river system where the  
417 mean upstream concentrations of PFOS and PFOA are 2.6 and 2.5 ng/L respectively, means there is  
418 only 13% and 11% compliance for upstream samples for the PFOS and PFOA EQS respectively for  
419 data from over 600 sites generated as part of this study. This, of course, is not to absolve WwTW  
420 discharges from any implied responsibilities with respect to compliance, it merely illustrates that,  
421 currently, high upstream values mean that at a sizable proportion of CIP sites WwTWs do not cause  
422 non-compliance. Downstream compliance drops to only 5% and 2% for PFOS and PFOA, respectively.  
423 However, if all upstream concentrations were reduced to zero, it is clear that current inputs from WwTWs  
424 would be sufficient to result in widespread non-compliance with EQS values. Hence the implication is  
425 that for successful compliance both sources upstream of WwTWs and in nearly all WwTW effluents  
426 would require substantial reductions in PFAs inputs.

427

428 The question has been raised how mutually consistent these EQS values are (ie do compliance  
429 assessments made against both tend to agree?). This issue is addressed by a comparison of modelled  
430 biota data with observed water column results (Valentine et al., 2018) (Figure 7). A separate more direct  
431 study (Valantine et al., 2018) involving matched sampling and analysis of water column samples versus  
432 analysis of co-located biota (fish) also has indicated a degree of inconsistency between the two  
433 regulatory values. This set of duplicate data comparison offers the possibility of estimating a water  
434 column EQS value that is constant with the current biota EQS.

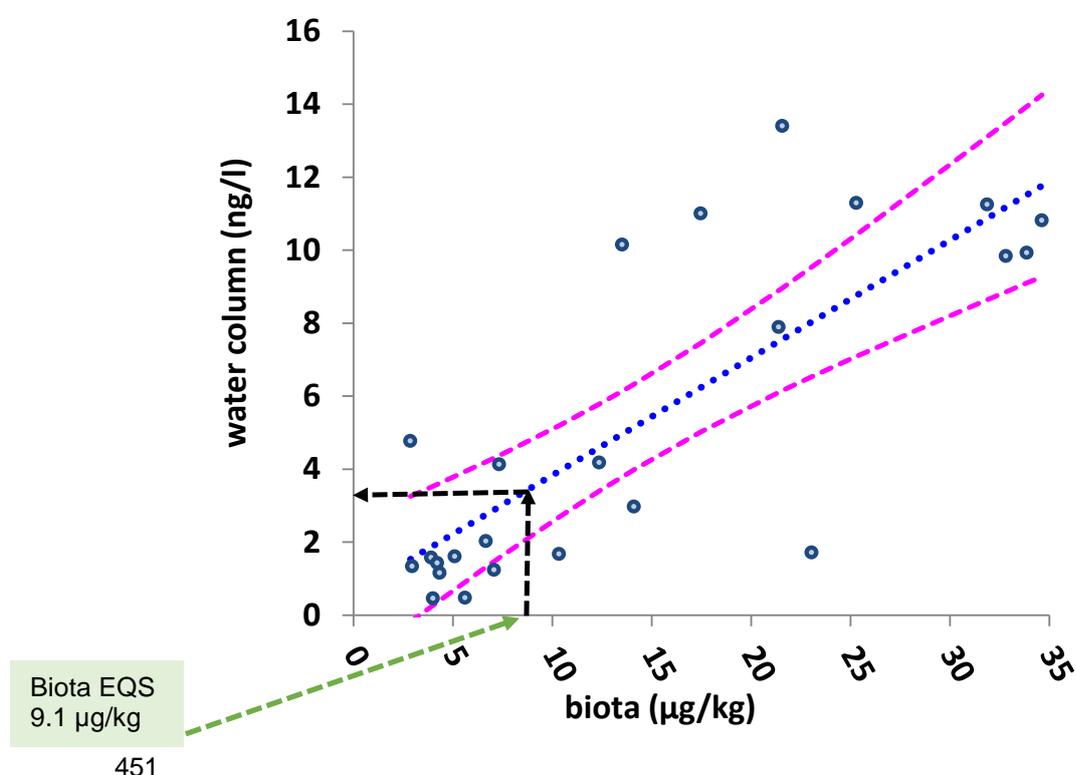
435

436 Applying a linear regression between observed biota and water column PFOS data, the water column  
437 concentration that is found to be consistent with the biota standard of 9.1 µg/kg is nearer to 3 ng/l than  
438 to 0.65 ng/l (Figure 7). The alternative approach is to regress water column data as “x” on biota data as

439 “y”. This approach (not shown) leads to an estimate of a biota EQS of 5 µg/kg, rather than 9.1 µg/kg,  
 440 as compatible with the water EQS value of 0.65 ng/l. A third simpler possibility is to use a non-parametric  
 441 ranking approach to assess compatible EQS values. This indicates that the current biota EQS might be  
 442 consistent with a water column value of approximately 2 ng/l. At this level, compliance increases to 29%  
 443 and 22% for PFOS and PFOA downstream of WWTW respectively (41% compliance for both based on  
 444 upstream samples).

445  
 446 The key point to note here is that these data do not support the claim that the two current EQS values  
 447 are compatible (EU, 2011). Essentially the “derivation” of the water column EQS from the more  
 448 important biota value appears to be biased (more stringent) by a factor of 3-5-fold.

449



452 **Figure 7 PFOS – “matched sample” comparison of biota and water column data (redrawn**  
 453 **from Valentine et al., 2018)**

454  
 455  
 456 Furthermore, a previous EQS derived for PFOA using the methodology set out under the Water  
 457 Framework Directive generated a value of 48 ng/L, which was considered protective for lifetime  
 458 consumption of fish by birds, humans and other mammals as well as for direct ecotoxicity to aquatic  
 459 organisms (Verbruggen et al., 2017). This value would result in 100% compliance for the UK based on  
 460 the available water quality data. The variations in bioaccumulation rates were identified as a key variable  
 461 in determining water standards from ecotoxicological endpoints. The decisions in choosing  
 462 accumulation and magnification factors as well as the reliability of toxicological endpoints can make  
 463 orders of magnitude difference in the final EQS. In view of the importance of confidence in the EQS

464 values to compliance assessment and the potential need to justify highly costly remedial measures,  
465 further comparative testing is indicated in order to establish improved consistency in regulatory values.

466

467 Based on previous estimates of persistent chemical die away in the aquatic environment (Comber et  
468 al., 2021) where rates of decline in concentration of contaminants in biota were predicted based on  
469 control measures of specified performance (i.e. nominal reduction in inputs), an assessment of the  
470 likelihood of achieving compliance in biota within a desired timescale was undertaken. Furthermore, a  
471 comparative assessment of likely success for different substances of current concern was carried out.  
472 In the case of PFOS, the estimated time to compliance in biota (for the current EQS) and given a 10%  
473 year on year reduction in emissions, was only 3 years. It is stressed that this figure is purely indicative  
474 and bears little relation to what might happen in any given real-life situation. Its significance is that it  
475 constitutes a measure of the likely difficulty in achieving compliance with a biota EQS for PFOS in  
476 relation to other substances of interest when all are assessed on the same basis against identical  
477 criteria. Thus, for PFOS, it might be concluded that a) a 10% annual percentage rate of reduction is not  
478 completely out of the question and b) relative to many other contaminants of concern, the prospects of  
479 progress for PFOS are encouraging (i.e. the timescale is relatively short). This assessment encourages  
480 the view that the PFOS biota standard (presuming it is ecologically well founded) appears to form the  
481 basis of a practicable future strategy, whereas the feasibility of meeting the water column standard, as  
482 noted above, is less certain.

483

#### 484 **4. Conclusions**

485 This study comprises a detailed analysis of a large dataset on the concentrations of PFOS and PFOA  
486 in WwTW effluents as well as samples upstream and downstream of the receiving waterbodies. This  
487 has made possible an investigation not only of implications for compliance with the EQS set for PFOS  
488 under the WFD but also the effectiveness of removal of the PFAS compounds. The following  
489 conclusions may be drawn from the study:

490

491 1. WwTW effluents contain concentrations of PFOS that exceed the annual average EQS by a  
492 factor between 1.1-fold and 40-fold. The corresponding factors for PFOA are between 2-fold  
493 and 22-fold. The ratios of upstream riverine concentrations to the EQS value are between 0.2  
494 and 80 fold (PFOS) and between 0.3 and 50 fold (PFOA). These ratios downstream are  
495 between 0.3 and 65.

496 2. The highest effluent concentrations do not necessarily correspond to the highest downstream  
497 concentrations – dilution being an obviously important factor. However, given selection of the  
498 CIP sites focused on sites with a relatively limited range of dilutions, the correspondence  
499 between effluent and downstream concentrations is very poor. Whilst there is a weak tendency  
500 for high concentration effluents to correspond to high concentrations downstream, there are  
501 many instances where low concentration effluents are associated with high concentrations

502 downstream, and vice versa. Thus, effluent concentration is a poor guide to downstream water  
503 quality.

504 3. Between a quarter and a third of individual effluent discharges are found to reduce the  
505 concentration of fluorocarbons in the river downstream of the discharge point.

506 4. Elevated concentrations occur upstream of the studied WwTW suggesting inputs of these  
507 PFAS compounds into the aquatic environment are ubiquitous and therefore difficult to address  
508 simply by setting permit conditions for individual WwTWs.

509 5. The derivation of EQS values in surface waters and biota for PFOS are apparently not entirely  
510 mutually consistent. The process of derivation involves the use of accumulation coefficients and  
511 large safety factors, the combination of which leads to a sub ng/L EQS for the water column.  
512 The usual practice of EU legislation, where multiple standards are involved, is to favour the  
513 standard devised for the protection of biota – with the use of an equivalent water column  
514 standard where this has greater practical applicability. In the case of PFOS this required  
515 equivalence is, at present, not necessarily demonstrable.

516

#### 517 **Conflicts of interest**

518 There are no conflicts of interest to declare.

519

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526

#### 527 **References**

528 Arvaniti O.S. and Stasinakis S. Review on the occurrence, fate and removal of perfluorinated  
529 compounds during wastewater treatment. *Sci of the Tot. Environ.*, 2015, 524-525, 81-92.

530

531 Canada.ca. Factsheet: Prohibition Of Certain Toxic Substances Regulations - Canada.Ca. 2019,  
532 [online] Available at: [https://www.canada.ca/en/environment-climate-change/services/canadian-  
533 environmental-protection-act-registry/factsheet-prohibition-toxic-substances-regulations.html](https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/factsheet-prohibition-toxic-substances-regulations.html)  
534 [Accessed 16 January 2021].

535

536 Christensen, K., Raymond, M., Blackowicz, M., Liu, Y., Thompson, B., Anderson, H. and Turyk, M.  
537 Perfluoroalkyl substances and fish consumption. *Environ. Res.*, 2017, 154, pp.145-151.

538

539 Cleveland W.S. and Devlin S.J., Locally Weighted Regression: An Approach to Regression Analysis by  
540 Local Fitting, *J. Am. Stat. Ass.*, 1988, 83, 596-610.  
541

542 Comber, S.D.W., Gardner M.J., Constantino C., Hargreaves A.J., Firth S. and Davies R.. Modelling  
543 scenarios of environmental recovery after implementation of controls on emissions of persistent organic  
544 pollutants. *Environ. Sci.: Processes Impacts*, 2021, **22**, 1865-1876 2020, DOI: 10.1039/D0EM00137F  
545

546 EA, Environment Agency. Investigation of PFOS and other perfluorochemicals in groundwater and  
547 surface water in England and Wales. Environment Agency, Bristol, 2007.  
548

549 EC, European Commission, Technical Specifications for Chemical Analysis and Monitoring of Water  
550 Status. Directive 2009/90/EC, 2009.  
551

552 EC, COMMISSION REGULATION (EU) No 757/2010 of 24 August 2010 amending Regulation (EC) No  
553 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards  
554 Annexes I and III. 2010.

555 EC, Commission Regulation (EU) 2017/1000 of 13 June 2017 amending Annex XVII to Regulation (EC)  
556 No 1907/2006, 2017.  
557

558 ECHA, Annex xv restriction report proposal for a restriction substance name: Perfluorooctanoic acid  
559 (PFOA), PFOA salts and PFOA-related substances. 2014.  
560

561 ECHA, Committee for Risk Assessment (RAC) Opinion on an Annex XV dossier proposing restrictions  
562 on Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances. ECHA/RAC/RES-O-  
563 0000006229-70-02/F. 2015.  
564

565 ECHA. Perfluoroalkyl Chemicals (PFAS) - ECHA. 2020, [online] Available at:  
566 <https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas> [Accessed 8 January 2021].  
567

568 EU, European Union, Water Framework Directive (2000/60/EC) of the European Parliament and of the  
569 Council establishing a framework for the Community action in the field of water policy, 2000.  
570

571 EU. European Union, PFOS EQS Dossier, prepared by the sub-group on the Review of the Priority  
572 Substances List, Under Working Group E of the Common Implementation Strategy for the Water  
573 Framework Directive. 2011.  
574

575 European Chemicals Agency. ECHA Perfluoroalkyl chemicals (PFAS). 2020, [Online] Available at:  
576 <https://echa.europa.eu/hot-topics/perfluoroalkyl-chemicals-pfas> [Accessed 20 December 2020].  
577

578 Gardner M.J., Comber S.D.W., Leverett D., Gravell A. Sample Stability of Trace Priority Substances

579 in Wastewater. *Analytical Letters* 2012;45(12):1686–94.  
580  
581 Guillette, T., McCord, J., Guillette, M., Polera, M., Rachels, K., Morgeson, C., Kotlarz, N., Knappe, D.,  
582 Reading, B., Strynar, M. and Belcher, S. Elevated levels of per- and polyfluoroalkyl substances in Cape  
583 Fear River Striped Bass (*Morone saxatilis*) are associated with biomarkers of altered immune and liver  
584 function. *Environ. Int.*, 2020, 136, 105358.  
585  
586 Hansen K.J., Johnson, H.O., Eldridge J.S., Butenhoff J.L. and Dick L.A., Quantitative Characterization  
587 of Trace Levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.*, 2002, 36, 1681-  
588 1685.  
589  
590 Land, M., de Wit, C.A., Bignert, A., Cousins I.T., Herzke D., Johansson J.H., Martin J.W. What is the  
591 effect of phasing out long-chain per- and polyfluoroalkyl substances on the concentrations of  
592 perfluoroalkyl acids and their precursors in the environment? A systematic review. *Environ Evid.*, 2018,  
593 7, 4. <https://doi.org/10.1186/s13750-017-0114-y>.  
594  
595 Lassen, C., Jensen, A., Warming, M. Alternatives to perfluoroalkyl and polyfluoroalkyl substances  
596 (PFAS) in textiles. LOUS Survey of chemical substances in consumer products. Danish Environmental  
597 Protection Agency, 2015.  
598  
599 Lescord G.L., Kidd K.A., De Silva A., Spencer C., Williamson W., Wang X., Muir D.C.G., Perfluorinated  
600 and polyfluorinated compounds in lake food webs in the Canadian high arctic, *Environ. Sci. Technol.*  
601 2015, 49, 2694-2702.  
602  
603 Lien N.P.H., Fujii, S., Tanaka S., Nozoe N. and Tanaka H. Contamination of perfluorooctane sulfonate  
604 (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo River basin (Japan). *Desalination*,  
605 2008, 226, 338-347.  
606  
607 Lindim C., Cousins I.T. and vanGils J. Estimating emissions of PFOS and PFOA to the Danube River  
608 catchment and evaluating them using a catchment-scale chemical transport and fate model. *Environ.*  
609 *Poll.*, 2015, 207, 97-106.  
610  
611 Muir D., Bossi R., Carlsson P., Evans M., De Silva A., Halsall C., Rauert C., Herzke D., Hung H., Letcher  
612 R., Rig F. and Roos A. Levels and trends of poly- and perfluoroalkyl substances in the Arctic  
613 environment - An update. *Emerging Contam.*, 2019, 5, 240-271.  
614  
615 McDonald M.M., Warne A.L., Stock N.L, Mabury S.A., Solomon K.R. and Sibley P.K. Toxicity of  
616 perfluorooctane sulfonic acid and perfluorooctanoic acid to *Chironomus tentans*. *Environ. Toxicol. and*  
617 *Chem.*, 2004, 23, 2116-2123.  
618

619 NIST. The median absolute deviation method - NIST/SEMATECH e-Handbook of Statistical Methods,  
620 2011. <http://www.itl.nist.gov/div898/handbook/>, May 2011.  
621

622 OECD. Toward A New Comprehensive Global Database Of Per- And Polyfluoroalkyl Substances  
623 (PFASs): Summary Report On Updating The OECD 2007 List Of Per- And Polyfluoroalkyl Substances  
624 (PFASs). Series on Risk Management No. 39. Organisation for Economic Co-operation and  
625 Development, 2018.  
626

627 Public Health England. PFOS and PFOA General Information. 2009, [online] Available at:  
628 [https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment\\_data/file/33](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/338258/PFOS___PFOA_General_Information_phe_v1.pdf)  
629 [8258/PFOS\\_\\_\\_PFOA\\_General\\_Information\\_phe\\_v1.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/338258/PFOS___PFOA_General_Information_phe_v1.pdf) [Accessed 14 January 2021].  
630

631 Ross, I., Hurst, J. & Miles, J. A. L. Poly- and Perfluoroalkyl Substances (PFAS), a new class of Emerging  
632 Contaminants.. The Chemical Industries Association (CIA) Matters, 2016, October, 15-18.  
633

634 Seacat A.M., Thomford P.J., Hansen K.J., Clemen L.A., Eldridge S.R., Elcombe C.R., Butenhoff J.L.  
635 Subchronic dietary toxicity of potassium perfluorooctanesulfonate in rats. *Toxicology*, 2003, 183, 117-  
636 131.  
637

638 SCHER. Scientific Committee on Health and Environmental Risks, Perfluorooctane sulphonate, PFOS  
639 EQS Dossier 2011.  
640

641 Soloff, A., Wolf, B., White, N., Muir, D., Courtney, S., Hardiman, G., Bossart, G., Fair, P. Environmental  
642 perfluorooctane sulfonate exposure drives T cell activation in bottlenose dolphins. *J. Appl. Toxicol.*,  
643 2017, 37(9), 1108-1116.  
644

645 Thompson M. and Ellison S.L.R. Towards an uncertainty paradigm of detection capability. *Analyt.*  
646 *Methods*, 2013, 5, 5857-61.  
647

648 UKWIR. The Chemical Investigations Programme Phase 2, 2015-2020 – Initial Findings, 2018,  
649 Volumes 1-4, ISBN 1 84057 851 3.  
650

651 UKWIR. The Chemical Investigations Programme Phase 2, 2015-2020.  
652 [https://ukwir.org/the-national-chemical-investigations-programme-2015-2020-volume-4-catchment-](https://ukwir.org/the-national-chemical-investigations-programme-2015-2020-volume-4-catchment-investigations)  
653 [investigations](https://ukwir.org/the-national-chemical-investigations-programme-2015-2020-volume-4-catchment-investigations)  
654  
655

656 US EPA. Basic Information On PFAS | US EPA. 2020a [online] Available at:  
657 <https://www.epa.gov/pfas/basic-information-pfas> [Accessed 12 January 2021].  
658

659 US EPA. EPA PFAS Action Plan: Program Update February 2020. 2020b, [online] Available at:  
660 [https://www.epa.gov/sites/production/files/2020-01/documents/pfas\\_action\\_plan\\_feb2020.pdf](https://www.epa.gov/sites/production/files/2020-01/documents/pfas_action_plan_feb2020.pdf)  
661 [Accessed 16 January 2021].

662  
663 Valantine E., Bradford B., Whitehouse P. Curtis-Jackson P. and Gardner M. Assessing risks from PBT  
664 substances in surface waters: possible alternatives to biota monitoring? Poster presented at SETAC  
665 Rome, May 2018.  
666  
667 Verbruggen E.M.J., Wassenaar P.N.H. and Smit C.E. Water quality standards for PFOA  
668 A proposal in accordance with the methodology of the Water Framework Directive. RIVM Letter report  
669 2017-0044, 2017.  
670  
671 Wang, N., Szostek, B., Folsom, P.W., Sulecki, L.M., Capka, V., Buck, R.C., Berti, W.R., Gannon,  
672 J.T. Aerobic biotransformation of <sup>14</sup>C-labeled 8-2 telomer B alcohol by activated sludge from a domestic  
673 sewage treatment plant. *Environ. Sci. Technol.* 2005, 38, 531–538.  
674  
675 Yeung, LWY., Dassuncao, C., Mabury, S., Sunderland, EM., Zhang, X., Lohmann, R. Vertical Profiles,  
676 Sources, and Transport of PFASs in the Arctic Ocean. *Environ Sci Technol.*, 2017, 51, 12, 6735-6744.  
677  
678 Zanolli, L. Why you need to know about PFAS, the chemicals in pizza boxes and rainwear. 2019,  
679 [online] Available at: [https://www.theguardian.com/us-news/2019/may/23/pfas-everyday-products-](https://www.theguardian.com/us-news/2019/may/23/pfas-everyday-products-toxics-guide)  
680 [toxics-guide](https://www.theguardian.com/us-news/2019/may/23/pfas-everyday-products-toxics-guide) [Accessed 16 January 2021].  
681  
682 Zushi Y., Takeda T. and Masunaga S. Existence of nonpoint source of perfluorinated compounds and  
683 their loads in the Tsurumi River basin, Japan. *Chemosphere*, 2008, 71, 1566-1573.