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Perfluorinated Alkyl Substances: Sewage treatment and implications for receiving waters.

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Abstract

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

Key words: PFAS; wastewater treatment works; removal; PFOS; PFOA; rivers.
1. Introduction

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

PFAS tend to be mobile, when released either into the atmosphere or surface water/groundwater. Loads of as much as 25-850 kg/year of PFAS have been reported to be transported to polar regions (Yeung et al., 2017). Consequently, with respect to bioaccumulation, PFAS in the oceans and freshwater bodies can enter the food chain and bioaccumulate and biomagnify across all trophic levels. Risks to human health thus arise via contaminated drinking water, consumption of fish and shellfish or foods that are grown in contaminated soil (Christensen et al., 2017). Toxicity has been reported for fish and dolphins (Guillette et al., 2020; Soloff et al., 2017); and human exposure to PFAS is of concern as illustrated by effects in animals on reproductive, developmental, liver, kidney, and endocrine systems (US EPA, 2020a). Phasing out of production and implementation of action plans were initially instigated in the USA (Zanolfi, 2019; US EPA, 2020b). Other countries such as Canada have implemented bans on manufacture, sales and imports (Canada.ca, 2019). Within Europe PFOS and PFOA are restricted under the EU POPs Regulation (Regulation (EU) 2019/1021) and some short chain PFAS controlled under the REACH EU chemical legislation (ECHA, 2020). Most significantly, globally PFOA and PFOS have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs). There are some exemptions for use under specified circumstances such as within photoresists or anti reflective coatings for photolithography processes and photographic coatings (EC, 2017). Use of PFOA appears to have been slightly less than PFOS (ECHA, 2014, 2015). Controls imposed on the production and use of these fluorcarbons means that concentrations should be declining in the environment. Specific high risk uses such as the use in firefighting foams can result in direct release of PFASs into the environment, as was reported for a major fire in the UK in 2005 (EA, 2007).
Concerns regarding the environmental impacts of PFAS chemicals have led to PFOS being categorised as a Priority Hazardous Substance with a freshwater Environmental Quality standard of \(6.5 \times 10^{-4} \mu g/L\) (0.65 ng/L), as an annual average (EU, 2000). There is no equivalent value for PFOA. PFOS and PFOA have been reported in river samples downstream of WwTW in countries such as Japan and USA where concentrations range from low ng/l up to 1000's of ng/l (Hansen et al., 2002; Lien et al., 2008; Zushi et al., 2008). Further data are required on the occurrence, sources, routes of transport and removal of PFAS in wastewater treatment.

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

2. **Methodology**

2.1 **Sampling**

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

Samples were collected as grab samples taken at approximately evenly spaced intervals over (for each site) a two-year sampling period, rather than as composite sampling. This latter approach was precluded by concerns about sample stability raised in tests prior to the commencement of the programme (Gardner et al., 2012). Taking randomly scheduled discrete samples is a guarantee of an
unbiased estimator of the variables of interest, such as mean, median and variance etc. Alternative approaches such as composite sampling, whilst it does provide a nominally more precise estimate of mean etc (for a given sampling effort) is not a sound approach to generate a ready appreciation of variance. A minimum of 15% of sampling was undertaken in non-working hours (evenings and weekends) and included in the data analysis to account for any possible systematic effects in the sample collection process.

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

2.2 Sample treatment and analysis

Samples were collected in stainless steel samplers, stored in glass containers and transported at 4°C to the analytical laboratories. The maximum sample storage period was determined for key determinands prior to the beginning of the programme by undertaking tests of sample stability. A period of 3 to 5 days storage for trace determinands (depending on substance) was shown not to lead to more than a 20% change in concentration. Detailed sampling, filtration and preservation requirements are provided in S1 of the Electronic Supporting Information (ESI). Analytical work was commissioned from
contracted laboratories, who used their own in-house analytical methodologies, which were not standardised but had to meet minimum and exacting performance criteria. Given the variety of potential methods used and allowing for commercial sensitivities it is not possible to detail specific Gas and/or Liquid Chromatographic-Mass Spectrometry techniques employed by the laboratories. However, to ensure analytical quality was paramount the programme management team specified analytical performance characteristics for laboratories to meet before participating. This included ISO17025 accreditation, the requirement to undertake tests of analytical performance to demonstrate that they met the stated programme requirements for limit of detection (LOD), precision and recovery in relevant sample matrices at relevant concentrations. The required LOD values for PFOS and PFOA was 0.00065 (in effluents) and 0.00009 (in river waters) µg/L. LOD was defined as 3.3x the standard deviation of blank-corrected results of determinations made on a sample containing essentially no determinand (where possible in a relevant sample matrix) (Thompson and Ellison, 2013). In some cases, it was not possible to find effluent samples free from determinands in which case a synthetic sample was used. The full dataset for PFOS showed that <2%, <2% and <0.5% of samples were <LOD for the effluent, upstream and downstream river samples respectively. The equivalent data for PFOA were <1%, <2% and <0.5% of samples were <LOD for the effluent, upstream and downstream river samples respectively. See section S1 and Table S1 of the electronic supporting information for more detail.

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

3.1 PFOS and PFOA in UK rivers, upstream and downstream of WwTW effluent discharges

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

The plots illustrate the widespread EQS exceedances at upstream sites as well as the influence of the WwTW discharge on downstream water quality. This impact is shown by the degree to which the downstream curve is displaced to the right (to higher values of x) with respect to the upstream curve. The occurrence of a large displacement rightwards, should it occur, indicates that downstream concentrations are increased. There are some clear conclusions to be drawn; namely that for PFOS in particular the increase in concentration downstream is small and that concentrations of PFOS and PFOA upstream of WwTW discharges predominantly exceed EQSs by a large margin. The mean increase for both substances is 10% of the upstream value and the median increase for PFOS is 19% and for PFOA 35%. This is a consequence of the upstream concentrations being already markedly elevated, such that the percentage of EQS non-compliance only changes from the high eighties to the mid to high nineties for both substances. The UK situation reflects similar reports for developed countries with similar concentration profiles between PFOS and PFOA and elevated concentrations in WwTW effluents (Lein et al., 2008). Other studies have showed an increasing concentration of PFAS compounds down a catchment owing to their persistence combined with increasingly urban populations in the lower parts of the catchment. The Danube for example exhibits concentrations up to 30 ng/L for PFOS and PFOA (Lindim et al., 2015). However, a recent review noted the positive effect of phase-outs and regulations but noted the impacts on the environment have not always been well studied and longer-term surveillance monitoring is required to increase the power of the trend analysis (Land et al., 2018).
Figure 2  CDF plots for concentrations in WwTW effluents and in rivers and upstream and downstream of effluent discharges
A fundamental issue relating to the implementation of pollution control measures is the extent to which changes in riverine contaminant concentrations are apparently brought about by specific effluent discharges. For instance, it is possible to envisage at least three different categories of situation:

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

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

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

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

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

With respect to UK rivers, the concern is that WwTW discharges in an upper catchment might serve to elevate fluorocarbon concentrations to levels of concern and that sewage effluent discharges lower in the catchment serve to maintain these concentrations further downstream. The data presented here
neither proves nor disproves this theory. There were sites considered to be at the top of catchments where fluorocarbon concentrations were lower than elsewhere but in other locations this appeared not to be the case. However, it should be noted that the sampling programme’s objectives were chosen based on higher risk locations that predominantly were not in the category of “pristine”. Indeed, given the arctic data noted above, even the concept of a pristine environment in the UK might be questionable.

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

### 3.2 Site by site analysis

Further analysis was undertaken to examine the changes in fluorocarbon concentrations from upstream of the local WwTW discharge to downstream on a site-by-site basis in order to determine the extent to which individual WwTW discharges have a clear impact on downstream concentrations (Figure 3). The data show that both positive differences (downstream higher than upstream) and negative differences occur. In the case of PFOS, negative changes occur in 175 out of 527 comparisons ($1/3^{rd}$), for PFOA this figure is 130 out of 527 ($1/4$). This is a demonstration of the complexity of the picture presented by PFAS compounds.
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.
The interplay between upstream and effluent concentrations is complicated, such that the highest effluent concentrations do not necessarily correspond to the highest downstream concentrations. This is illustrated in the diagrams in Figure 4, in which the concentrations of the PFAS compounds in the effluent and downstream were ranked for all of the effluents, then plotted against each other. Owing to the persistence of PFOS and PFOA it can be assumed that there is little likelihood of any biotransformation between the upstream and downstream sites for the samples taken on each occasion. The rank values of each axis are the numerical order from lowest to highest concentration for effluents and downstream concentration values, respectively. Whilst there is a weak tendency for high concentration effluents to correspond to high concentrations downstream, there are many instances where low concentration effluents are associated with high concentrations downstream, and vice versa. Observed downstream concentrations are a function of effluent concentration and flow relative to that in the river upstream, however, it may be concluded that effluent concentration alone, is a poor guide to downstream water quality, with the importance of upstream PFAS contributions being far greater in many cases.

Figure 4  Comparison of rank values for downstream and effluent concentrations
3.3 Fate in Wastewater Treatment

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

### Table 1 Summary of changes in concentration from influent to effluent

<table>
<thead>
<tr>
<th></th>
<th>Percentage concentration - change influent to effluent (negative values indicate a reduction from influent to effluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFOS</td>
</tr>
<tr>
<td>10%ile</td>
<td>-67</td>
</tr>
<tr>
<td>25%ile</td>
<td>-48</td>
</tr>
<tr>
<td>50%ile</td>
<td>-39</td>
</tr>
<tr>
<td>75%ile</td>
<td>-20</td>
</tr>
<tr>
<td>90%ile</td>
<td>29</td>
</tr>
</tbody>
</table>

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

These data suggest that conventional wastewater treatment has little impact on PFAS concentrations reflecting their relatively low sorption potential, and so limited loss to sludge and high persistence which reflects their lack of biodegradation during secondary biological treatment. Advanced treatment techniques have been shown to be successful in removing a greater quantity of PFAS either to sludge or through aggressive degradation methodologies, however, it has been noted that there is a paucity of quantitative assessments taking account of economic and technical aspects (Arvaniti and Stasinkis, 2015). Consequently, it is important to take account of the impacts of PFAS on receiving waters.
Figure 5  PFOS and PFOA concentrations in influent (green/blue) and effluent (red/yellow) of 20 UK WwTW
3.4 Seasonality

Figure 6 illustrates a breakdown of the data by month of sampling over the five-year programme (bearing in mind that for logistical reasons the sampling programme was staggered such that any given location was only sampled for 24 consecutive months).

![PFOS time series plot](image.png)

Figure 6  PFOS time series plot. Note “LOESS” – local optimised scatterplot smoother (Cleveland and Devlin, 1988)

The pattern evident here is of marginal seasonal variation corresponding to lower in-river dilution in the summer months compared with the winter, with possibly a suggestion of a general fall in concentration at the start of the series. This fall, if it is such, is not apparently sustained in subsequent years.

3.5 Regulation and Compliance

Assessments of compliance made in relation to the parallel Water Framework Directive EQSs in the water column and in biota do not necessarily agree to the extent that might be expected. The surface water annual average EQS concentrations for PFOS is 0.65 ng/L with a Maximum Admissible Concentration of 36 µg/L. The corresponding biota-based EQS is 9.1 µg/kg (i.e. a tissue-based concentration) as an annual average.

The derivation of the EQS for PFOS (SCHER 2011) shows that the 0.65 ng/L EQS is derived as the lowest value for all receptors and is designed to protect human health via consumption of fishery products. An EQS of 230 ng/L and 2 ng/L were derived for protection of freshwater pelagic communities and secondary poisoning of predators respectively. Estimated environmental concentrations were calculated as 88 ng/L as a regional worst case. Reported concentrations in river water range from less...
than the LOD to 77 ng/L across Europe (SCHER, 2011). The estimated in-river concentrations are greater than those detected either upstream or downstream of WwTW in this study, where median concentrations were 2.6 and 3.2 ng/L for PFOS and 2.5 and 4.7 ng/L for PFOA respectively.

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

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

Applying a linear regression between observed biota and water column PFOS data, the water column concentration that is found to be consistent with the biota standard of 9.1 µg/kg is nearer to 3 ng/l than to 0.65 ng/l (Figure 7). The alternative approach is to regress water column data as “x” on biota data as
“y”. This approach (not shown) leads to an estimate of a biota EQS of 5 µg/kg, rather than 9.1 µg/kg, as compatible with the water EQS value of 0.65 ng/l. A third simpler possibility is to use a non-parametric ranking approach to assess compatible EQS values. This indicates that the current biota EQS might be consistent with a water column value of approximately 2 ng/l. At this level, compliance increases to 29% and 22% for PFOS and PFOA downstream of WWTW respectively (41% compliance for both based on upstream samples).

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

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

Furthermore, a previous EQS derived for PFOA using the methodology set out under the Water Framework Directive generated a value of 48 ng/L, which was considered protective for lifetime consumption of fish by birds, humans and other mammals as well as for direct ecotoxicity to aquatic organisms (Verbruggen et al., 2017). This value would result in 100% compliance for the UK based on the available water quality data. The variations in bioaccumulation rates were identified as a key variable in determining water standards from ecotoxicological endpoints. The decisions in choosing accumulation and magnification factors as well as the reliability of toxicological endpoints can make orders of magnitude difference in the final EQS. In view of the importance of confidence in the EQS
values to compliance assessment and the potential need to justify highly costly remedial measures, further comparative testing is indicated in order to establish improved consistency in regulatory values.

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

4. Conclusions

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

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

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

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

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

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

Conflicts of interest
There are no conflicts of interest to declare.

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