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THE IMPORTANCE OF SEWAGE EFFLUENT DISCHARGE IN THE EXPORT OF DISSOLVED ORGANIC CARBON FROM UNITED KINGDOM RIVERS

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Abstract

The flux of fluvial carbon from the terrestrial biosphere to the world's oceans is known to be an important component of the global carbon cycle but within this pathway the flux and return of carbon to the river network via sewage effluent has not been quantified. In this study monitoring data from 2000 to 2016 for the dissolved organic carbon (DOC) concentration, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the final effluent of sewage treatment works from across England were examined to assess the amount of DOC contributing to national-scale fluvial fluxes of carbon. The study shows that the median concentration of DOC in final effluent was 9.4 mg C/l compared to 4.8 mg C/l for all surface waters for the UK over the study period, and the DOC in final effluent significantly declined over the study period from 11.0 to 6.4 mg C/l. Rivers receiving sewage effluent showed a significant, on average 19%, increase in DOC concentration downstream of sewage discharges. At the scale of the UK, the flux of DOC in final effluent was 31 ktonnes C/yr with a *per capita* export of 0.55 kg C/yr and compared to an average annual flux of DOC from the UK of 859 ktonnes C/yr, i.e. only 3.6% of national-scale flux. The lability of this DOC was limited, with only 7.4% loss of final effluent DOC concentration over in-stream residence times of up to 5 days. The direct decline in DOC concentration from sewage treatment works was not large enough on its own to explain the declines observed in DOC concentration in UK rivers at their tidal limit.

Keywords: greenhouse gases; water treatment; carbon budget.

1. INTRODUCTION

The fate of organic matter transported into and through river basins has been shown to be an important component of the global carbon cycle (Regnier et al., 2013); in-stream processes in rivers can rapidly transfer carbon from the terrestrial biosphere to the atmosphere (Moody et al., 2013). A source of carbon to rivers that is yet to be quantified is discharge from sewage treatment works. The discharge from sewage treatment works will add to the amount of carbon in rivers but, furthermore, it represents a source of carbon to rivers that can be readily managed and diverted to reduce carbon flows in rivers. Biomarkers have been used to demonstrate the presence of sewage-derived substances in rivers (e.g. dos Santos et al., 2016). Further, studies have demonstrated that discharges from sewage treatment works impact downstream environmental compartments. Heibati et al. (2017) have used fluorescence spectroscopy to detect sewage-derived DOC in domestic tap water while Tedetti et al. (2011) have used fluorescence spectroscopy to show that sewage DOC could be detected on a coral reef.

Alongside being an important component of the global carbon cycle, organic matter in rivers acts as an energy source (Hynes, 1983); transports metals and organic micro-pollutants (Worrall et al., 1997); plays a role in pH buffering (Kerekes et al., 1986); affects light penetration (Schindler et al., 1996); controls the partition of components between the water and sediment (Worrall et al., 1999); leads to mobilisation of arsenic in groundwater (Mladanov et al., 2015); is a source of nutrients (Qualls et al.,1991); and, represents a major issue in the treatment of drinking water (Bieroza et al., 2009). Studies have focused on nutrients (e.g. phosphorus – Jarvie et al., (2006); nitrogen – Jordan and Smith, (2005)), but also suspended sediments (Carter et al., 2003), metals (Chou et al., 2012), non-metals (Neal et al., 2002); and micropollutants (Johnson et al., 2008). With regard to carbon, Eatherall et al. (2000) considered the impact of sewage discharges on the DOC concentration in the Yorkshire Ouse catchment, but did not actually sample final effluent from sewage treatment works and so the study could

not quantify the flux of DOC from sewage treatment works relative to other fluvial carbon fluxes. Naden et al. (2016) did include organic carbon in their model of historical fluxes of nutrients from sewage treatment plants but their numbers were based on loads to the treatment plants and the efficiency of the plant but they had no observations relative to organic carbon. Therefore, this plausibly large, and controllable, source of labile carbon has not been examined in the context of its contribution to fluvial carbon and also to atmospheric greenhouse gases.

Initial attempts to quantify the flux of carbon from rivers focused on the flux from the mouth of the rivers to the continental shelf as the point where rivers passed through the tidal limit. Meybeck (1993) estimated the flux of carbon (dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC)) from the world's rivers to the oceans was around 542 Mtonnes C/yr in proportions 37:18:45 for DOC:POC:DIC, respectively. Ludwig et al. (1996) estimated total fluvial carbon fluxes of 800 Mtonnes C/yr with a split of 50:25:25 for DOC:POC:DIC, respectively. Such early estimates did not attempt to quantify the loss of carbon during transport within rivers between the terrestrial biosphere and the continental shelf and so such values could not account for the losses of carbon from the terrestrial biosphere, perhaps most importantly the amount of carbon transferred to the atmosphere. The 2007 Intergovernmental Panel on Climate Change (IPCC - Solomon et al., 2007) did not consider the effect of in-stream losses of any form of carbon, inorganic or organic. For the global scale, Cole et al. (2007) estimated that 1900 Mtonnes C/yr enter rivers of which 800 Mtonnes C/yr (42% of the input) is returned to the atmosphere. Battin et al. (2008) used a 21% removal rate for DOC from global rivers, implying that, in comparison to the values suggested by Cole et al. (2007), there must be considerable contributions from the loss of POC and DIC. Regnier et al. (2013) have estimated that the total global carbon flux (inorganic and organic carbon) into freshwaters was 2800 Mtonnes C/yr of which 1000 Mtonnes C/yr was exported from the tidal limit (i.e. a 64% removal rate). These studies have made the connection

between carbon loss from rivers and impact on the atmosphere but did not consider the speciation of the carbon or the organic matter and so these estimates could not be used to give an estimate of the greenhouse gas impact of the losses from rivers. Worrall et al. (2016) extended the assessment of fluvial carbon loss to consider loss of organic matter and the speciation of that loss as CO_2 or as CH_4 , and also the potential for the release of N_2O to the atmosphere – both CH_4 and N_2O are more powerful greenhouse gases than CO_2 (Houghton et al., 1995). Several studies have shown that areas receiving urban drainage and especially sewage treatment discharge have higher greenhouse gas fluxes to the atmosphere than those without urban influence and more natural land uses – from China (Wang et al., 2017), and from USA (Aitkenhead-Peterson and Steele, 2016).

Finlay et al. (2016) considered the role of drinking water abstraction from rivers and groundwater in diverting organic matter from rivers. Water abstraction for drinking water supply will remove particles (which would include particulate organic matter - POM) and then flocculate dissolved organic matter (DOM) to remove DOC. Finlay et al. (2016) found that the removal of TOC (POC + DOC) by water abstraction in the UK represented 1.5% of the total removal rate of fluvial carbon across UK watersheds – more important than the role of floodplains at removing carbon. If water abstraction for drinking water is removing fluvial organic matter and represents a sink of organic matter, then the return flow of this abstracted water and its organic matter content must also be considered. The return flow of abstracted water is via wastewater, or sewage, treatment.

Recently, Noacco et al. (2017) have ascribed a long-term trend (130 years, 1884 to 2005) in DOC concentrations for the River Thames to increases in sewage discharges as the population of the catchment rose from 900,000 to 3,200,000. Further, Worrall et al. (2018) have shown that there have been recent declines (the period 2003 to 2015) in the DOC

concentration of UK rivers at their tidal limits. The declines were dominated by significant step decreases that could be associated with the implementation of the Urban Wastewater Treatment Directive (UWWTD – European Commission, 1991), i.e. step declines in the DOC concentration time series could be ascribed to changes in discharges from sewage treatment works. Neither study directly considered the discharges from sewage treatment works. Rodriguez-Murillo et al. (2015) showed that for four large Swiss rivers the temporal trends in DOC concentration between 1974 and 2010 could in part be explained by changes fluxes of sewage discharges. Therefore, the aim of this study was to directly assess the proportion of the flux of fluvial organic matter that is due to discharges from sewage treatment works; to assess changes to the reactivity of fluvial organic matter as a result of this added material as means of considering whether it will disproportionately be lost to the atmosphere; and, whether step changes observed at tidal limits can be observed at the proposed sources.

2. APPROACH & METHODOLOGY

This study used several lines of evidence to assess the impact of sewage effluent on the fluvial flux of dissolved organic matter. Direct measures of organic matter concentration (e.g. DOC and POC) are not routinely taken for discharges from wastewater or sewage treatment plants in the UK as most analytical effort is focused on requirements of Statutory Water Quality Standards, typically nutrients (especially ammonium and species of phosphorus), suspended solids, and measures of oxygen demand (e.g. chemical oxygen demand). However, DOC concentration has, on occasion, been measured in the final effluent of sewage treatment works and these data were collated and analysed within the context of the DOC flux from UK rivers. Therefore, the first approach used by this study was to use the available DOC concentration data to assess the importance of this source to rivers in comparison to national-scale fluxes of DOC from rivers.

Although, DOC is not routinely measured in the discharges from sewage treatment works, chemical oxygen demand (COD) is routinely measured in the final effluent of sewage treatment works and the COD will be related to amount of organic matter and its composition (varying with the oxidation state of the organic matter – Masiello et al., 2008). Therefore, the second approach taken by this study examined whether COD in final effluent could be used as a proxy for DOC in the final effluent and to apply the proxy accordingly to understand the magnitude and changes in the DOC concentration in the discharges from sewage treatment works.

The third approach taken by this study was to consider DOC concentration measured in the rivers receiving discharges from sewage treatment works. The concentration of DOC concentration is commonly measured in rivers at sites close to the discharge points of sewage treatment works and these data were considered to attest the impact of sewage discharges on the river network.

A priori we hypothesize that DOC from sewage treatments works may be highly labile and this could be one reason why it has not been quantified previously, i.e. the effect of sewage-derived DOC on the flux measured at downstream sites is minimal as the DOM has already been decomposed and lost to the atmosphere. Conversely, our hypothesis that sewage discharge DOC is highly labile will mean that the impact of rivers on atmospheric greenhouse gas levels has been underestimated. The biochemical oxygen demand (BOD) is commonly measured in the final effluent from sewage which is a measure of the rate of turnover in a water sample and thus related to the lability of the organic matter in the sample. Therefore, as a fourth approach used in this study, the relationship between organic matter in the final effluent from sewage treatment plants and BOD in that effluent was explored as a means of assessing organic matter lability in this source to rivers.

As shown by the previous studies of Finlay et al. (2016), Noacco et al. (2017) and Worrall et al. (2018), the extensive monitoring records maintained in the UK over time and space mean that the UK is the ideal location for considering sewage treatment works as a source of DOC to rivers.

2.1 DOC concentration in sewage treatment discharge

Records of DOC concentration in the final effluent of sewage treatment works were sought from the UK's national environmental monitoring agencies (Environment Agency; Natural Resources Wales; Scottish Environmental Protection Agency; Northern Ireland Environment Agency) for the period 2000 to 2016; however, there were only results for final effluent from England. Only samples listed as being from routine sampling of final effluent were included and this rule excluded any samples listed as being from known pollution incidents as these latter samples could, *a priori*, be expected to have higher values. Furthermore, pollution incidents may also represent a higher frequency of sampling than would be routine and as such would distort the estimate of the distribution of DOC concentration in final effluent.

DOC concentration data were subjected to analysis of variance (ANOVA). The distribution of the DOC data was tested using the Anderson-Darling test (Anderson and Darling, 1952) and if necessary log-transformed and re-tested. A Box-Cox transformation was used to identify and remove outliers. The relatively high value of DOC concentration in final effluent means that the distribution of DOC in sewage discharges was not distorted by many values below a limit of detection. The ANOVA was performed with three factors: month of sampling; year of sampling; and site of sampling. The month of sampling factor had 12 levels, one for each calendar month. The year of sampling had up to 17 levels, one for each year between 2000 and 2016. The number of sites of sampling was limited to only those sites with 10 or more measurements of DOC in final effluent. For the majority of sites which had 10 or

more analyses it was possible to include the consented dry weather flow as a covariate. Dry weather flow can be taken as indicative of the size of the sewage treatment works. *Post hoc* analysis for testing between levels was performed using a Tukey test. The magnitude of the effects of each significant factor and interaction was calculated using the generalised ω^2 (Olejnik and Algina, 2003) and values were presented as least squares means (otherwise known as marginal means).

2.2 The national-scale flux of DOC from sewage discharges

The results of the ANOVA for the available DOC records in the final effluent discharged from English sewage treatment works were compared to the declared volume of sewage discharged each year by each UK water company. Total volume of sewage treated and the number of customers supplied for each UK water company for the period 2008 to 2014 were available from industry reported values (http://www.water.org.uk/**)**. The values of sewage discharge are reported without uncertainty and were used as such within this study. Although the monitoring data could be associated with individual sewage treatment works (STWs), there were not data for all sites for either discharge DOC concentration or annual discharge concentration. The summary of DOC concentration data was guided by the results of the ANOVA. Given the range of DOC concentrations that could be expected, the amount of DOC that was then being released from STWs would be the stochastic combination of the sewage discharge for each company and its respective DOC concentration range. For this study, 100 realisations were performed for the annual amount of DOC released to rivers.

The importance of DOC flux from sewage discharges will be viewed in the context of the flux of DOC through the entire fluvial network. Multiple techniques and attempts have been used to assess flux of determinands through river networks and indeed the flux of DOC from nation states. In this study we updated the UK national DOC flux based upon the method of

Worrall et al. (2013). There are a number of advantages of this approach. Firstly, given the result for high-frequency data of Cassidy and Jordan (2011), Worrall et al. (2013) showed that the best method of flux calculation from low-frequency data such as that typically available from national monitoring agencies was:

$$F = KE(C_i)Q_{total} \quad \text{(i)}$$

where: Q_{total} = the total flow in a year (m^3/yr); $E(C_i)$ = the expected value of the sampled concentrations (mg/l) and K = unit conversion constant (0.000001 for flux in tonnes). For the best results (highest precision and accuracy), the expected value of sampled concentration was based upon fitting a gamma distribution to the available concentration data and using the expected value of that fitted gamma distribution. Worrall et al. (2013) showed that for monthly sampling, the accuracy of this method is an underestimation of the flux of 2%. This approach was only applied to sites within the UK Harmonised Monitoring scheme (HMS - Bellamy and Wilkinson, 2001) where DOC concentration had been measured for more than 11 times in any year. In previous estimates (e.g. Worrall and Burt, 2007) data on DOC calibrated from water colour data were used – this was not done here but for one exception: for Scotland where there were no DOC concentration data prior to 2007; only water colour data were recorded. Furthermore, after the study of Worrall and Burt (2007), it has been subsequently observed that for some site-year combinations within the HMS database there had been a transcription error and the DOC values recorded were too high; therefore, in this study the original Environment Agency database of DOC values was used. This approach of Equation (i) was applied to every site-year combination in the HMS data where there were both sufficient DOC concentration data and the total flow per year could be calculated from daily flow measurements. Values of Q_{total} were calculated from the National River Flow Archive (https://nrfa.ceh.ac.uk).

From the flux estimate for each year for each HMS site, the export was calculated as the flux per unit catchment area per year. The flux from the UK was then calculated using a region-weighted average of exports using the method of Worrall and Burt (2007) where the UK is divided into 12 regions based on the regional offices of the respective national environmental agencies. However, the approach of Worrall and Burt (2007) assumed that, if the flux result for a region were missing for any one year, then the best estimate would be the average of all the regions for which a flux result existed for that year. Such an approach could mean that results for southern England (with a very small area of organic soils and thus a low DOC flux from its rivers) could in some years be being used to predict the flux from Scotland where there are extensive organic soils. An alternative assumption would be to extrapolate between years within the same region, then, for example, a year without data from Scotland would be estimated from data for a year on either side. However, there would be a problem if a severe drought existed in the missing year. Thus, this study examined all the region-year combinations where there was a flux result using ANOVA. The ANOVA was performed with two factors: the difference between years and the difference between regions. The proportion of variance explained by each factor (years or region) was used to weight the national-scale flux based upon extrapolation between regions and the national-scale result based upon extrapolation between years. So, in this study the national-scale flux was calculated assuming the dominant source of variation was within region, within year and the best possible combination of those two factors given the result of ANOVA (henceforward referred to as the general linear model – GLM) and each of these approximations was considered with and without the pre-2007 data from Scottish sites where calibration from water colour had been used. It should also be noted that no HMS data were available for Northern Ireland; the land area of Northern Ireland is 13,843 km^2 (6% of total UK land area) and so the results for Great Britain (the countries of England, Wales and Scotland, i.e. the UK without Northern Ireland)

were up-scaled to give an estimate of the flux from the whole of the UK. The estimated flux from sewage treatment works was compared to this national scale flux for DOC.

2.3 COD as a proxy record of DOC in sewage discharges

This study used COD as a proxy for DOC in the final effluent from sewage treatment works. The measurement of COD can also be related to and interfered with by the presence of two important inorganic constituents of many waters – chloride and nitrite ions. Therefore, for all the samples of final effluent where the DOC had been measured, the DOC, nitrite and chloride concentrations were compared to the measured COD in the same final effluent sample. Because of the small sample size that resulted from these requirements, then records from the HMS database were also considered and in a separate analysis all those samples in the HMS database where COD, DOC, nitrite and chloride were measured were considered. In both cases data for the final effluents and data from the HMS database, multiple regression was used with variables selected by the term being significantly different from zero at least at a 95% probability.

Given the analysis above, all COD measurements in routine sampling of final effluent from sewage treatment work discharges between 2000 and 2016 were selected, i.e. as for DOC concentration; samples listed as being in response to pollution incidents were removed. The COD data were analysed by ANOVA. As above, the data were subjected to the Anderson-Darling test and log-transformed if necessary; furthermore, the data were subject to Box-Cox transformation to remove outliers. The ANOVA was performed with three factors: month of sampling, year of sampling, and site of sampling. The month of sampling factor had 12 levels, one for each calendar month. The year of sampling had up to 17 levels, one for each year between 2000 and 2016. Unlike for the DOC concentration of the final effluent, there were too many sites with sufficient data to include as a factor and so no sampling site factor was included in this ANOVA.

2.4 DOC concentration in rivers receiving discharges

Although DOC is not commonly measured in the final effluent of sewage treatment works, the DOC concentration of river waters is. Within the monitoring of English river waters sites have often been explicitly chosen to test the impact of a sewage discharge upon the receiving river and, although not of the final effluent themselves, were deliberately chosen to be either above or below a named sewage treatment work discharge. For each monitoring site designated as being located with respect to a sewage discharge, those where DOC had been measured were selected. For each of these designated and selected monitoring points, its corresponding partner site was chosen as long as DOC concentration was also measured at that site; this site may be either below or above the sewage discharge. The hypothesis proposed was that, if a sewage discharge were having a significant impact on DOC concentration, then the DOC concentration of the river would be higher downstream of the discharge. However, with every catchment having a different background concentration of DOC, the comparison between monitoring sites above and below a sewage discharge was performed as the relative change in the DOC concentration between the upstream and downstream sites: henceforward these reaches are referred to as sewage discharge reaches. Further, it could be expected that DOC concentration would change downstream anyway and that any two sampling sites upon a river would be different. Therefore, the relative difference between sampling sites above and below a known sewage discharge were compared to the relative difference between pairs of sites on river reaches where there was no sewage discharge; these relative differences would be considered as control for normal river reach behaviour. Henceforth, these are referred to as control reaches; these control reaches were selected from the same rivers as the sewage discharge reaches and, where possible, were taken from both above and below the sewage discharge reach. In each case the control reach was chosen such that it did not have a common monitoring site with the sewage discharge reach. Reaches, whether control or sewage discharge reaches, were only

selected if they were indeed a river reach and no tributary entered the river between the monitoring points.

The relative data from both sewage discharge reaches and control reaches were analysed as part of two-way ANOVA as described above. The ANOVA used two factors, firstly, a reach factor with two levels: sewage discharge reach and control reach. Because control and sewage discharge reaches were taken from the same river, the second factor was the river from which the reaches came. Otherwise ANOVA was performed as above.

2.5 Lability of final effluent DOC from BOD

To assess the lability of the DOC sourced from sewage treatment works and to give an estimate of the loss of this flux to the atmosphere, the BOD records for final effluents in which DOC had been measured were considered. The BOD is a measure of the degradation of the organic matter in a sample of final effluent but this is not just the degradation of DOM but also of POM. However, POM is not measured in the final effluent of any English sewage treatment works but suspended solids is very frequently measured and, therefore, for samples of final effluent where DOC had been measured, the BOD measured was compared to both the DOC and suspended solids concentration. It must be emphasized that suspended solids concentration is not itself a measure of particulate organic carbon but we are proposing that:

$$[BOD]_t = f(t)[DOC]_t + g(t)h(t)[SS]_t \qquad \text{(ii)}$$

where: [X] = concentration of X in sample at time t where X is BOD, DOC or SS (suspended solids); f(t) represents the function over time of the proportion of DOC that contributes to the BOD; g(t) represents the function over time of the proportion of particulate organic carbon that contributes to the BOD; and h(t) represents the function over the time of the proportion of the

suspended solids that is particulate organic carbon. Normally, $[BOD]_t$ would be expressed as mg O_2/l but, if it is assumed that all oxygen consumption results in the production of CO_2, then BOD can simply be expressed as mg C/l given a conversion factor of 32/12. Thus, for Equation (ii), $[BOD]_t$ and $[DOC]_t$ can be expressed as mg C/l while $[SS]_t$ is expressed as mg/l, as h(t) represents the proportion of the mg/l that is C. The functions f(t), g(t), and h(t) could vary between different STWs, but there would be insufficient data from this dataset to warrant such an approach and Equation (ii) was fitted to all samples from all sites for which DOC was measured. The functions f(t), g(t) and h(t) were assumed to follow a seasonal cycle based upon the month of sampling and were fitted assuming:

$$X(t) = A\left(sin\left(\frac{m\pi}{6}\right) + cos\left(\frac{m\pi}{6}\right)\right) \quad \text{(iii)}$$

where: m = month number with January as 1 to December as 12; and A is a fitted constant. The form of Equation (iii) means that annual average of the functional X(t) is seasonally adjusted.

Knowing what proportion of any BOD measurement in final effluent is constituted by the turnover of DOC or POC does not directly resolve how much of the DOC sourced from sewage discharges will degrade and be lost from the river to the atmosphere. BOD represents a rate of the process of interest but not the time over which the process would have to occur. Measurement of BOD is over a fixed 5-day period which historically was set to be the in-stream residence time of water in the River Thames at low flow; however, Worrall et al. (2014) have shown that the median in-stream residence time of UK rivers was only 26.7 hours. Therefore, the actual impact of the turnover of DOC discharged from sewage works will be considered across a range of plausible in-stream residence times.

3. RESULTS

3.1 DOC concentration in sewage treatment discharge

Between 2000 and 2016 there were 3,569 routine measurements of DOC in the final effluent from 146 sewage treatment works (Figure 1). The median concentration was 9.4 mg C/l with the 95th percentile range being 4.8 to 28.5 mg C/l. Finlay et al. (2016) reported all DOC measurements in fresh surface waters (including lakes and reservoirs) with 145,320 samples (42788 from Scotland) and data coming from 4326 locations (1151 from Scotland) that between 2005 and 2015 DOC had a median concentration 4.4 mg C/l (5th to 95th percentile range – 1.1 to 13.0 mg C/l). It is therefore clear that final effluent has a higher DOC concentration than the receiving waters.

The distribution of final effluent DOC concentration data was log-normalised and after Box-Cox transformation and removing data for sites with less than 10 samples then 3358 data points remained from 72 sewage treatment works. Although the three factors were considered (month, year and site), estimation of interaction terms proved impossible as there was insufficient cross-classification between sites and years of sampling with many sites only ever being sampled in one year. The most important factors were the month and the site of sampling with ANOVA explaining 41% of the original variance, but most of this variance is explained by differences between sewage treatment works. The least squares means of the sites shows the biggest contrast being between Hull sewage treatment works with least squares mean DOC discharge concentrations of 12.9 mg C/l and 6.5 mg C/l for Mildenhall sewage treatment works. There was a significant difference between months of sampling with the peak in DOC concentration final effluent in June (June average = 11.0 mg C/l) and a minimum in February (February average = 8.4 mg C/l). The year factor shows a decline in DOC in final effluent with a peak value in 2001 of 11.0 mg C/l and a minimum in 2008 of 6.8 mg C/l: a 41% decline over the available years (Figure 2). However, the lack of data in the later years of the study means

there are only data between 2000 and 2011 with data missing for 2006 and 2009. The *post hoc* analysis shows that there was no significant difference between the years after 2005, although there was a significant difference between year 2001 and 2011, i.e. there is no evidence here that DOC declined after 2005. The median least squares mean across all years from the ANOVA was 8.9 mg C/l which compares closely to the median calculated from all data of 9.4 mg C/l. For 38 of the 72 sites it was possible to include the consented dry weather flow as a covariate; however, this covariate did not prove significant.

The longest record for any individual site was for Derby sewage treatment works (Fig 3). The time series for the Derby works shows that at the start of the record the annual average DOC concentration in final effluent was 13.2 mg C/l while in 2005 the annual average was 6.5 mg C/l. Most of the decline occurred in 2002 where a 51% decline in average DOC concentration occurred. The records of discharge consents for the Derby works show that discharge consents were changed during this period but it is unclear whether the required changes would have affected the DOC of the final effluent. However, it does imply that at individual works sharp changes can occur. Worrall et al. (2018) found that the median step change in DOC concentration, for those river records where a significant step decrease was observed, was 41% decline.

3.2 The national-scale flux of DOC from sewage discharges

The volumes of waste water processed annually by UK water companies are given in Table 1. The average sewage production was 227 l/day/capita which is larger than the average water consumption per capita (ca) per day for the UK; this could be for a number of reasons including that the volume of sewage being treated includes storm runoff and industrial waste water. The total population from the reported number of sewage customers is lower than the total population of the UK and this can be ascribed to the remaining population that is not connected

to mains sewerage and that relies on septic tanks. Given the volume of sewage processed annually in the UK, then the flux of DOC from UK sewage treatment would have a median flux of 31 ktonnes C/yr (5^{th} to 95^{th} percentile – 0.5 to 135 ktonnes C/yr). Given the population this serves, then the flux of DOC *per capita* would be 0.55 kg C/yr/ca. (5^{th} to 95^{th} percentile range of 0.01 to 2.36 kg C/yr/ca). Given the results of the ANOVA, then this value of flux would be expected to be the median and, given the range across the study period, then the expected flux would be 36.2 ktonnes C/yr in 2000 decreasing to 22.4 ktonnes C/yr in 2011. Similarly, the per capita export would be 0.63 kg C/ca in 2000 and 0.4 kg C/ca in 2011.

The annual flux from the UK varied from 326 ktonnes C/yr in 1978 to a peak of 1354 ktonnes C/yr in 2005 (Figure 4). The extrapolation methods that did not use calibrated water colour data from Scotland are higher than those methods that did use Scottish data until 1997. Over the course of the study period, extrapolation within regions, as opposed to extrapolation within years, created a smoother result with the use of ANOVA making little difference. Use of the different extrapolation methods made very little difference over the last decade for which data were available, with the annual average DOC flux over that decade varying between 857 and 859 ktonnes C/yr between the extrapolation methods. Worrall et al. (2013) attempted to correct the previous estimates of DOC flux and found the range 812 in 1975 to 3875 ktonnes C in 2004, i.e. far higher than found here but that study used the HMS data that contained the transcription error and also used data calibrated from water colour. Finlay et al. (2016), when considering the fluvial flux of carbon from the UK, used a value of 904 ktonnes C/yr for DOC flux at the tidal limit for the period 2005 to 2015 based upon values from Worrall et al. (2012) as updated in Worrall et al. (2014) but not using the same interpolation methods as in this study – this study would give the average annual DOC flux at the tidal limit for the period of 2005 to 2014 as 859 ktonnes C/yr. Given the flux from sewage treatment works, it can be concluded that, at maximum, sewage effluent would comprise 3.6% of the DOC flux at the tidal limit of

the UK. Aitkenhead-Peterson and Steele (2016) found that permitted effluent discharge contributed between 1 and 35% of DOC flux above and below the Dallas-Fort Worth metropolis. Alternatively, Sousa et al. (2011) showed that the DOC in the Acre river of the Amazon basin did not significantly change across urban areas with the seasonality being the dominant driver of DOC changes.

3.3 COD as a proxy record of DOC in sewage discharges

For final effluent samples there were only 47 samples where DOC, COD, nitrite and chloride were all measured: the best-fit equation was:

$$[COD]_t = \underset{(0.05)}{1.30}[DOC]_t \qquad n = 47,\ r^2 = 92\% \qquad \text{(iv)}$$

where only those terms found to be significant at better than 95% probability of not being zero were included. The value in the brackets below Equation (iv) is the standard error in the coefficient. Within this dataset no significant role was found for nitrite or chloride, nor is there a significant constant term found for Equation (iv). There is clearly a strong relationship between COD and DOC in final effluent; however, the coefficient is significantly larger than 1. If DOC alone were responsible for COD, then the coefficient would be expected to be 1.0, and a value larger than 1 suggests that either some other component in the final effluent is contributing, but that would have been represented by a constant term in Equation (iv). Alternatively, the DOM in final effluent could have a high concentration of other oxidisible elements such as N and that DOM final effluent had a low C/N ratio.

When the data from the HMS database were considered, there were 18,277 samples were COD, DOC, nitrite and chloride and the best fit equation was:

$$[COD]_t = 1.44[DOC]_t + 28.8[NO_2^-] + 0.006[Cl^-] \qquad \text{n= 18277, } r^2 = 67.8\% \quad \text{(v)}$$

(0.008) (5) (0.0002)

Only those terms found to be significantly different from zero at a 95% probability were included and the values in brackets are the standard error in the coefficients. The average values of COD, DOC, nitrate and chloride were 8.1, 4.7, 0.002, 58.1; at these concentrations 94% of the variation in COD was due to DOC. As further evidence, a partial regression analysis showed that the terms in nitrite and chloride together explained 3.5% of the variance explained. Therefore, there is good reason to support correlating COD records with DOC. As for Equation (v) the coefficient for the term in [DOC] is significantly greater than 1.

For the COD in final effluent there were 245877 samples from 3992 distinct sewage treatment works (Figure 5), The data required log-normalisation and Box-Cox transformation removed 136 data (0.05% of the original dataset). The two factors were both significant with the most important being the year factor which explained 80% of the variance explained by the ANOVA while the month factor explained 19% of the explained variance. *Post hoc* testing showed there were significant differences between every month and that COD peaked in final effluent in April with a minimum in November, i.e. different to the seasonal cycle observed for DOC concentration in final effluent. *Post hoc* testing of the levels of the Year factor showed significant differences between every year and the least squares means show that has been close to a monotonic decline in COD in final effluent with the maximum value observed at the start of the study period in 2000 and the minimum in 2016 (Figure 6). If the least mean squares of the COD in final effluent were converted to DOC concentration via Equation (iv), then the DOC in final effluent decreased from an average of 16.7 mg C/l in 2000 to 11.7 mg C/l in 2016 – a 30% decline from 2000.

3.4 DOC concentration in rivers receiving discharges

The reach data required log-transformation and after Box-Cox transformation, there were 3084 reach data with 1525 reach data from sewage discharge reach and 1559 from control reaches; these data came from 43 separate rivers (Figure 7). The ANOVA showed that both reach and river factors were significant at a probability of 95% and together explained 40% of the original variance. The river factor was the more important factor explaining 35% of the original variance while 5% of the original variance was explained the by the reach factor. The least square mean value for the sewage discharge reaches was 1.15 (± 0.04) and for control reaches 0.96 (±0.04) where the error is given as the 95% confidence interval, i.e. there is a significant difference between the sewage discharge and control reaches. The relative change across control reaches shows that on average DOC concentration decreases downstream, an average decline of 4% and that this was significantly less than no change downstream, i.e. significantly lower than 1 at a probability of 95%. For the sewage discharge reaches there is an average 15% increase downstream of the discharge compared to the upstream values. The least squares mean difference between sewage discharge and control reaches was 0.19 (±0.04) and this would mean that a sewage discharge increases the downstream DOC concentration of the receiving river water by 19%. Therefore, if the entire source of DOC from the sewage discharge were shut off, then the concentration observed in the river downstream of a sewage treatment works would decrease by 16%, far lower than the average 41% observed for step changes at tidal limit sites as measured in Worrall et al. (2018).

3.5 Lability of final effluent DOC from BOD

There were 395 occasions where BOD, DOC and suspended solids were measured in the same sample of final effluent. Fitting Equations (ii) and (iii) to the available data showed that there

was no significant role for seasonal adjustment within the dataset and that the best-fit equation was:

$$[BOD]_t = \underset{(0.02)}{0.23}[DOC]_t + \underset{(0.02)}{0.06}[SS]_t \quad \text{n= 395, } R^2 = 66.5\% \quad \text{(vi)}$$

where the terms are as defined above. Only those variables found to be significant at least at 95% probability of being different from zero were included and the values in the brackets below the equation are the standard errors in the coefficients. Equation (vi) shows that over the 5-day fixed time period that BOD is measured, that BOD is made up of 23% of the initial DOC concentration and 6% of the initial suspended solid concentration. Moody and Worrall (2016) showed that for DOC in a first-order peat stream, the average rate of DOC loss over 70 hours was 1.25 mg C/l/hour which gave an average of 64% loss over approximately 3 days, i.e. far faster and more extensive loss than for DOC in final effluent. In this sample set used to derive Equation (vi) the average $[BOD]_t, [DOC]_t$ and $[SS]_t$ were 3.1 mg C/l, 12.3 mg C/l and 12.6 mg/l respectively. It may appear that suspended solids made a smaller contribution or was less labile; however, it should be noted that, if the percentage of POC in the suspended solids was 25% or less, then the POC in the final effluent would in fact be proportionately more labile than the DOC in final effluent. At the average values recorded over the dataset, then only 0.7 mg C/l of DOC from the final effluent would be lost over a 5-day period. Knapik et al. (2015) measured amounts of biodegradable DOC as high as 4.2 mg C/l in a highly sewage-impacted river but this was measured over a 10-day period.

The median in-stream residence time for UK rivers is 26.7 hours and so, on the basis of a linear interpolation of the rate of turnover from the BOD values, only 0.22 mg C/l would be lost over 26.7 hours. However, as pointed out by Moody and Worrall (2016), most of the

DOC turnover in UK streams was in the first diurnal cycle and so it would be conservative to assume that 0.7 mg C/l is lost within the stream network, which would mean the average DOC concentration due to sewage final effluent at the tidal limit would be 8.7 mg C/l and thus a flux at the tidal limit of the UK due to sewage effluent was 29 ktonnes C/yr with a 5^{th} to 95^{th} percentile as 0.4 to 124.8 ktonnes C/yr.

4. DISCUSSION

This study has quantified the magnitude of DOC fluxes from sewage treatment works and the extent to which this has contributed to changes observed at the national-scale and to emissions of carbon to the atmosphere. The turnover of DOC from sewage treatment works' final effluent will contribute to the atmospheric emissions from rivers. Worrall et al. (2012) estimated a contribution of urban land use to carbon fluxes through rivers and gave an annual export of DOC from urban areas of 6.7 (±1.1 – standard error) tonnes C/km^2/yr and a flux of 234 ktonnes C/yr for the UK. Given the population connected to mains sewerage reported in this study, this would give a *per capita* figure of contribution of carbon from sewage effluent discharge of 4.1 kg C/ca/yr, i.e. considerably larger than the value found in this study. Noacco et al. (2017) studied a 130-year record of DOC concentration and flux from the River Thames and showed that, although there were short-term increases in DOC concentration due to land-use change, the most important driver of change was increasing discharge from sewage treatment works as the population of the catchment increased. Even with advances in sewage treatment, the increased amount of water coming into the catchment via sewage treatment works caused increased DOC concentration in the river. In the study period considered by Noacco et al. (2017), transient DOC concentrations from increasing population rose from 1.5 mg L^{-1} in 1884 to 4.1 mg L^{-1} in 2005, with 90% of the long-term trend in increased DOC concentrations being explained by the rise in C inputs from population growth and urban expansion ($p < 0.001$).

Over the same period the population of the Thames rose from 911,000 and 3.7 million, which indicates a change in per capita export from 3.46 to 2.28 kg organic C per person, per year, i.e. there was an increased rate of removal but this was not weighed by the increase in population using sewage treatment works. These studies do not quite measure the same thing as one is based upon urban runoff and the other upon direct measurement of sewage treatment plant final effluent; urban runoff will include other sources, combined storm overflows (CSOs) in particular. In contrast, Finlay et al. (2016) found that for water abstraction, i.e. taking water in from rivers for domestic supply, the per capita sink of DOC relative to rivers was 0.41 kg C/ca/yr (0.18 to 0.72 kg C/ca/yr), i.e. lower than the value predicted here for the return flow through STWs, suggesting that even for the lower values of DOC flux from sewage effluent discharge there is a net contribution of DOC to rivers from the water industry. Within this study we do not provide further independent verification of the presence or impact of DOC from sewage treatment discharges. Characterisation of the dissolved organic matter, such as excitation-emission matrix (EEM) fluorescence spectra (e.g. Ohno et al., 2008) in rivers could help apportion sources of that DOM and that could include sewage discharges. Indeed, Yang et al. (2018) showed that a protein-like component identified from PARAFAC analysis of EEM was correlated with urban DOM sources.

This study has only considered the importance of sewage treatment with respect to river carbon flows and the contribution of rivers to greenhouse gas emissions but not the contribution of sewage treatment itself. One population equivalent in the UK is 60 g of BOD in 200 litres of water per day and this is suggested to be up to 200 g COD (Henze et al., 2002). This equates to between 500 and 1200 mg O_2/l COD as load to the inlets of sewage treatment works; based upon Equations (iv) and (v) this COD load would be equivalent to up to 412 mg C/l but this would include both particulate and dissolved carbon. In comparison to these literature values, it was possible to examine records for crude sewage for many of the sewage treatments works

in 2015. For BOD the median was 220 mg O_2/l with an interquartile range (IQR) of 153 to 295 mg O_2/l (n= 4573 from 453 separate works). For COD the median was 543 mg O_2/l with an IQR of 382 to 734 mg O_2/l (n = 4573 from 444 separate works) and for suspended solids the median was 220 mg/l with IQR of 160 to 270 mg/l (n = 972 from 69 separate sites). Given Equation (iv), this equates to 153 mg C/l of DOC and POC and, even if all the suspended solids were organic matter, then the minimum median [DOC] at input would be 52 mg C/l. This value of 52 mg C/l should be compared to the median DOC concentration in the sewage treatment work discharges calculated in this study of 9.4 mg C/l, i.e. a removal rate of 82%.

Of course, sewage treatment works are designed to remove organic matter and therefore the real impact of sewage treatment is the removal of the organic matter and the energy required to do so. The Inter-governmental Panel on Climate Change (IPCC, 2014) and UK government (DECC, 2016) only use emissions factors for CH_4 and N_2O for domestic waste water handling (0.29 ktonnes CH_4/ per million people and 0.035 N_2O ktonnes/million people). Based on the above values, the TOC concentration of influent sewage would be 0.412 tonnes C/Ml of influent sewage which, given the volume of sewege reported to be treated per year (Table 1), means that approximately 19.5 Mtonnes C/yr are flowing into UK treatment works. The DOC in effluent discharge reported by this study is of the order of 30 ktonnes C/yr and, even if the flux of POC in sewage effluent discharge were a factor of 10 higher (i.e. ~300 ktonnes/yr), then the amount of influent sewage that must leave the sewage treatment works by other means is of the order of 19.0 Mtonnes C/yr, Defra (2012) reported that 1,412,836 tonnes dry solids/yr was produced as sewage sludge in the UK in 2010. If sludge were approximately 50% C in composition, then 18.3 Mtonnes C/yr must be lost to gaseous emissions: that is 0.39 tonnes C/Ml of influent sewage, or 1.41 tonnes CO_{2eq}/Ml of influent sewage if all the loss is as CO_2. Alternatively, Scottish Water (2012) has cited the greenhouse gas (GHG) footprint of 0.7 tonnes CO_{2eq}/Ml of sewage treated and that value includes the GHG consequences from the

energy consumption in sewage treatment works. Jones et al. (2016), using only the data for the GHG emissions due to production and chemical use from water treatment works and not the values for turnover of DOM and POM within works or removed in sludge, calculated that the GHG emissions varied from 11 to 133 tonnes CO_{2eq}/tonne fluvial C removed. By analogy therefore, we could expect a similar order of magnitude emissions for each tonne of influent C.

Worrall et al. (2018) found a median decline of 41% in DOC concentrations at the tidal limit that was coincident with improvements in sewage treatment work discharges. However, they could not ascribe an exact mechanism to this decline and proposed two possibilities. Firstly, that the sewage treatment works could be the source of the DOC and improved treatment has removed this source of DOC. Secondly, that the sewage treatment works are a source of nutrients that stimulated river flora and fauna resulting in an increased autochthonous production of DOC and so, when treatment is improved, then the source of nutrient declines and autochthonous production of DOC with it. Although here we could show that declines of 50% or more were observed at the outfall of individual sewage treatment works, it was clear that the average impact upon the rivers themselves would not be large enough on its own to cause the sorts of declines observed. Therefore, we should conclude that there is a role for nutrients from STW discharges in stimulating in-stream DOC production and so when treatment works are upgraded to remove nutrients they also limit subsequent DOC production in the receiving river.

5. CONCLUSIONS

This study has shown that the export of DOC from sewage treatment works significantly increases the DOC concentration of the receiving river. The median flux of sewage DOC for the UK was 31 ktonnes C/yr; this is equivalent to a median per capita export of DOC from sewage treatment works of 0.55 kg C/yr/ca. When compared to the national flux of DOC from

UK rivers to the tidal limit, the discharge of DOC from sewage treatment works represents a maximum of 3.6% of the total flux. In comparison to measured rates of BOD, it would appear that DOC in final effluent is relatively stable compared to fresh DOC from the terrestrial biosphere and that, at typical in-stream residence times, 7.4% of the final effluent DOC is lost to the atmosphere before discharging at the tidal limit. Over the study period, the available evidence suggests that DOC in final effluent had significantly declined; this is supported by evidence from COD which suggests that there had been at least a 30% decline between 2000 and 2016. The direct decline in DOC concentration from sewage treatment works was not large enough on its own to explain the decline observed in DOC concentration in UK rivers at their tidal limit.

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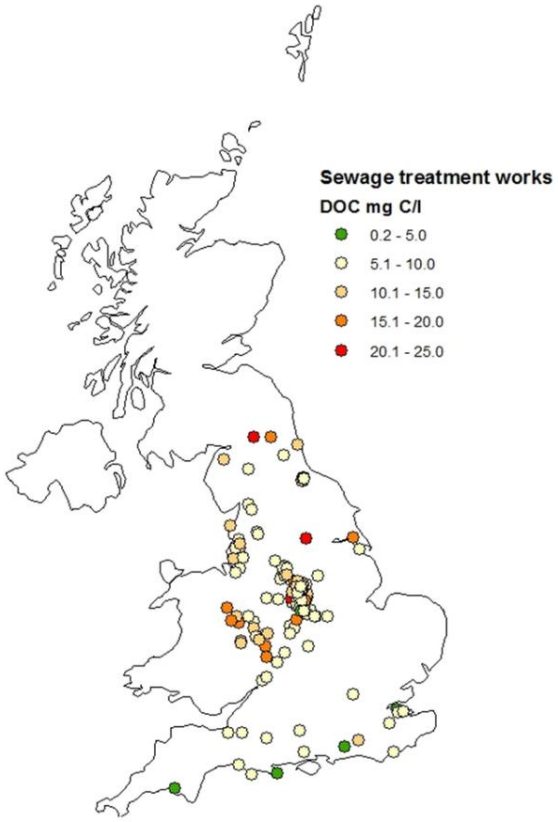

Fig. 1. The location of the sewage treatment works for which DOC concentration in final effluent data were available.

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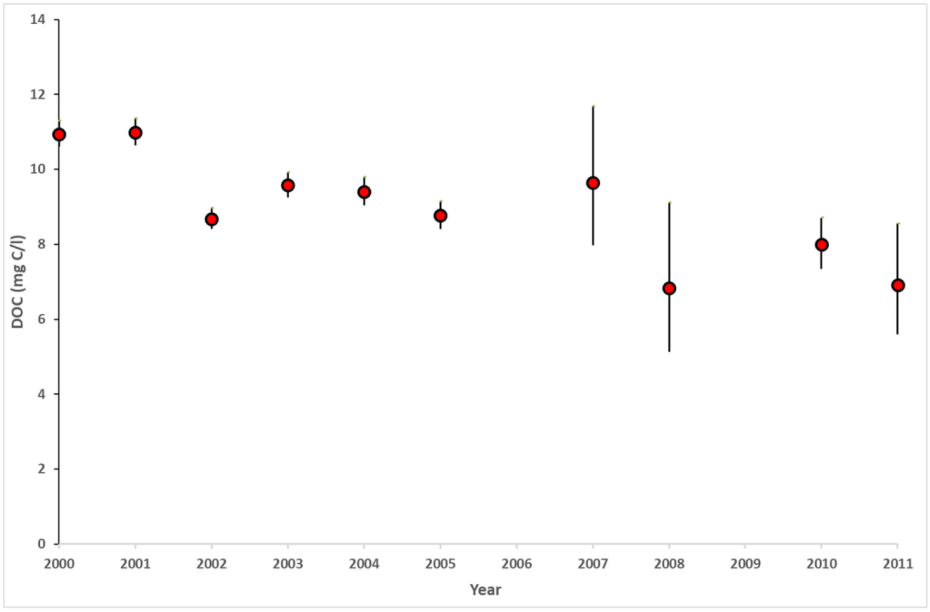

Fig. 2. The main effects plot of Year factor on DOC concentration of final effluent – error bars are given as the 95% confidence interval on the mean.

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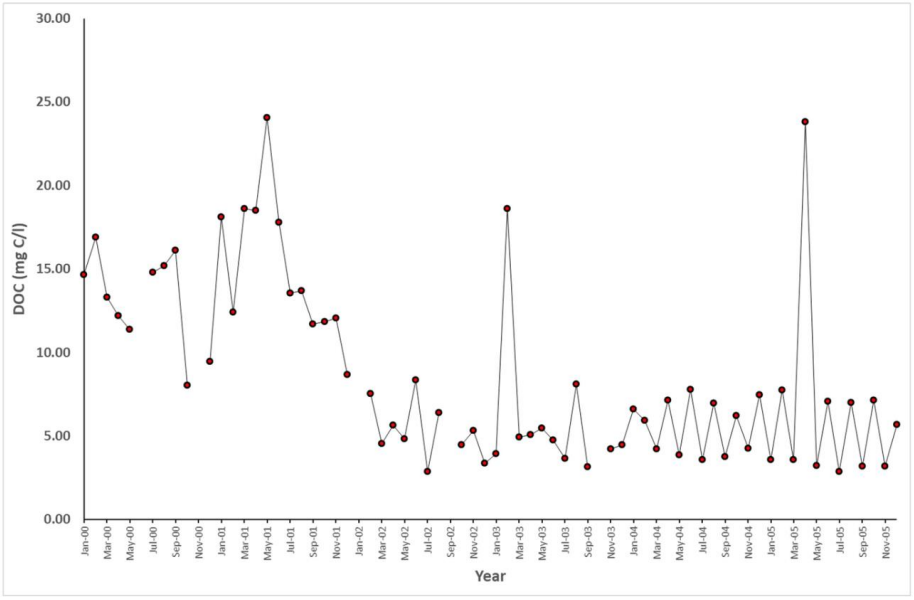

Fig. 3. The time series of the monthly average DOC concentration in the final effluent of the Derby sewage treatment works.

Figure 3. The time series of the monthly average DOC concentration in the final effluent of the Derby sewage treatment works.

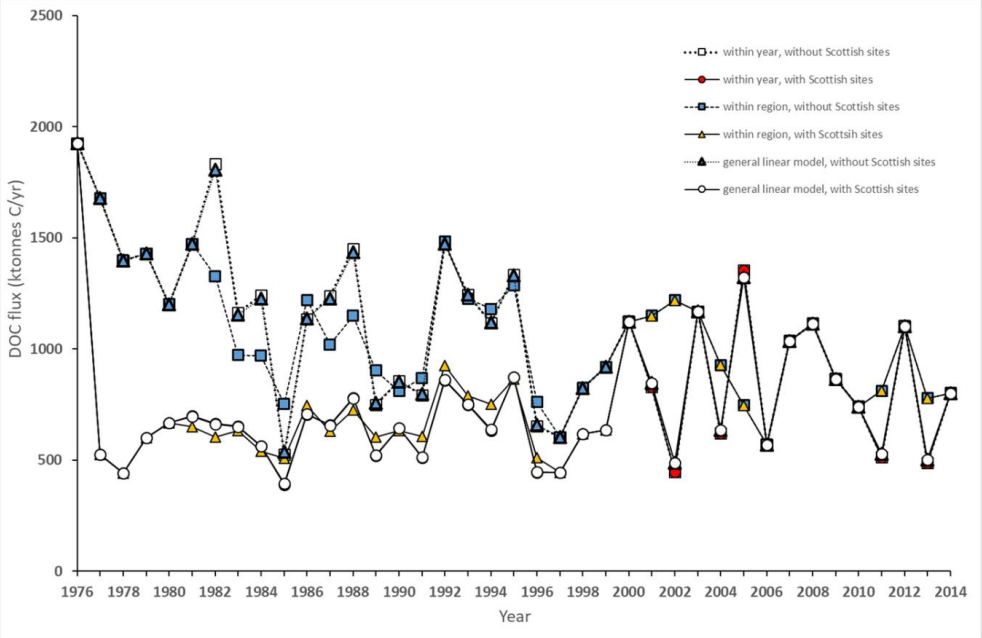

Fig. 4. The UK national flux of DOC at the tidal limit since 1977.

Figure 4. The UK national flux of DOC at the tidal limit since 1977.

Fig. 5. The sites of paired monitoring data.

Figure 5. The location of sewage works for which COD data were available over the course of the study.

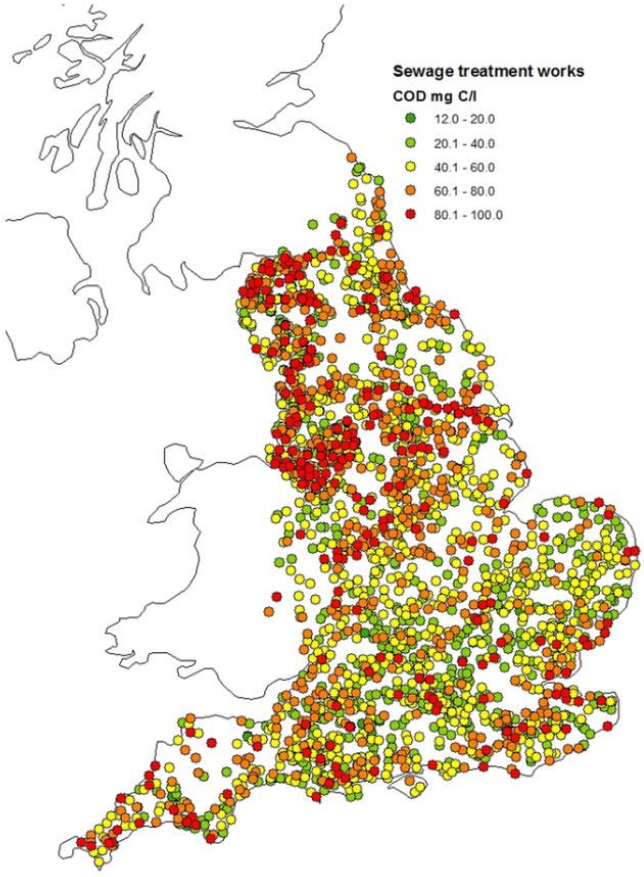

Fig. 6. The location of sewage works for which COD data were available over the course of the study.

Figure 6. The main effects plot of Year factor on COD concentration of final effluent – error bars are given as the 9% confidence interval on the mean.

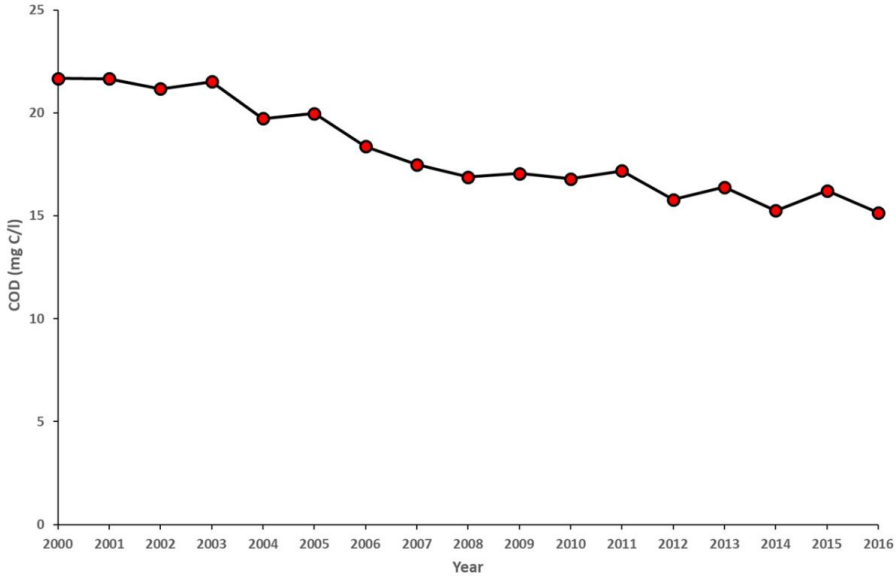

Fig. 7. The main effects plot of Year factor on COD concentration of final effluent – error bars are given as the 9% confidence interval on the mean.

Figure 7. The sites of paired monitoring data for assessing the DOC concentration in the rivers receiving discharges.

Table 1. The production of sewerage by water treatment companies in the UK.

Water company	Sewerage customers	Volume of sewerage (m^3/day)
Severn-Trent	7948000	1400000
Southern	9038000	718000
Thames	9162000	4600000
Yorkshire	4925000	1000000
United Utilities	7031000	1271000
Anglian	4416000	1002324
Welsh	3007000	682795
Northumbrian	1038000	235745
South West	2375000	539125
Wessex	1260000	286200
Scottish	5090000	921000
Northern Ireland	1870000	330000
Total	57161000	129861189