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Declines in the dissolved organic carbon (DOC) concentration and flux from the UK

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Abstract

Increased concentrations of dissolved organic carbon (DOC) have been reported for many catchments across the northern hemisphere. Hypotheses to explain the increase have varied (eg. increasing air temperature or recovery from acidification) but one test of alternative hypotheses is the trend over the recent decade, with the competing hypotheses predicting: continuing increase; the rate of increase declining with time; and even decrease in concentration. In this study, records of DOC concentration in non-tidal rivers across the UK were examined for the period 2003 to 2012. The study found that:

i) Of the 62 decade-long concentration trends that could be examined, 3 showed a significant increase, 17 experienced no significant change and 42 showed a significant decrease; in 28 of the 42 significant decreases, a significant step change was apparent with step changes being a decrease in concentration in every case.

ii) Of the 118 sites where annual flux and concentration records were available from 1974, 28 showed a significant step change down in flux and 52 showed a step down

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in concentration. The modal year of the step changes was 2000 with no step changes observed before 1982.

iii) At the UK national scale, DOC flux peaked in 2005 at 1354 ktonnes C/yr (5.55 tonnes C/km^2/yr) but has declined since.

The study suggests that there is a disconnection between DOC records from large catchments at their tidal limits and complementary records from headwater catchments, which means that mechanisms believed to be driving increases in DOC concentrations in headwaters will not necessarily be those controlling trends in DOC concentration further downstream. We propose that the changes identified here have been driven by changes in in-stream processing and changes brought about by the Urban Waste Water Treatment Directive. Therefore, signals identified in headwater catchments may bear little relation to those observed in large rivers much further downstream and *vice versa*.

Keywords: DOM; Urban wastewater; uplands; peat.

1. Introduction

The flux of dissolved organic carbon (DOC) from the terrestrial biosphere to the world's oceans has become a focus of attention for several reasons. First, DOC has multiple and diverse roles in freshwater systems: it contributes to the emission of carbon dioxide to the atmosphere (Moody et al., 2013); transports metals and organic micro-pollutants (Worrall et al., 1997); acts as an energy source (Hynes, 1983); affects light penetration (Schindler et al., 1996); plays a role in pH buffering (Kerekes et al., 1986); controls the partition of components between the water and sediment (Worrall et al., 1999); is a source of nutrients (Qualls et al.,1991); and, represents a major issue in the treatment of drinking water (Naden and McDonald, 1989;

Bieroza et al., 2009). Second, fluvial DOC is now widely recognised as an important component of terrestrial carbon budgets, in particular as a flux from organic-rich soils (Aitkenhead et al., 1999). Short-term observations of DOC concentrations and flux are widely available (e.g. for the UK, Worrall et al., 2012) and, even if long records (i.e. > 20 years) are not commonly available, records of DOC represent the most extensively observed component of the terrestrial carbon cycle in both space and time. If we can improve the understanding of DOC's role in the terrestrial carbon cycle and its relationship to other carbon flux pathways, this will enable the extensive resource of fluvial DOC records to support wider conclusions about the status of the terrestrial carbon cycle. Thirdly, rising DOC concentrations have been observed in many catchments across many countries across the Northern Hemisphere (Monteith et al., 2007, Bragee et al., 2014), leading to concerns about the terrestrial biosphere switching from a sink to a source of carbon.

The causes of the observed increases in surface water DOC concentrations are still debated. In their review, Monteith et al. (2007) explained the observed changes in terms of changing atmospheric deposition, with specific reference to sulphur (S). Sulphur deposition has led to changes in soil water acidity that has caused changes in DOC solubility (Evans et al., 2012). Clark et al. (2005) observed changes in DOC release from a peat soil due to acidification of the soil water after a drought. The action of a severe drought itself has been proposed as a mechanism for driving increases in DOC (Worrall and Burt, 2008) either through changes in flow or flow path (Holden and Burt, 2002) or changes in carbon turnover mechanisms as a result of the drought (Freeman et al., 2001a). Other explanations of observed increases in DOC concentrations have included: increasing atmospheric CO_2 (Freeman et al., 2004); changes in precipitation and runoff (Tranvik and Jansson, 2001; Hongve et al., 2004); increasing air temperature (Freeman et al., 2001b); eutrophication (Findlay, 2005); and changes in land management (Yallop and Clutterbuck, 2009). There is no reason to believe that any one of these explanations will work to the exclusion of others and indeed several studies have shown that some of these explanations are not sufficient because they are not acting alone (Chapman et al., 2010). Further, there is no reason to believe that every explanation would work in every catchment. For many of the explanations given above, studies have been published that show them not to be true for another study catchment: for example, for recovery from S deposition (Eimers et al., 2008); impact of drought (Worrall et al., 2008a); eutrophication (Worrall et al., 2008b); and, land management (Clay et al., 2009). Studies are often difficult to compare because of differences in scale, land management, or the time period over which analysis was performed. With respect to catchment scale, Monteith et al. (2007) generally considered small (several km^2), headwater catchments used to study the effects of acidification whilst Worrall et al. (2008a) considered catchments of more than 100 km^2 used for water supply. With respect to time scale, Worrall and Burt (2007a) studied the trend in non-tidal river DOC time from 198 catchments but all such trend analyses are sensitive to the start date such that trends identified from a short record may not be significant over a longer time scale (Howden et al., 2011). Worrall and Burt (2007a) documented DOC trends for 198 catchments across the UK and considered trends relative to certain consistent time windows which ended in 2002. There is now the opportunity to consider the same data set, but extended over a subsequent decade (2003 – 2012). Monteith et al. (2014) have extended their analysis of DOC trends for acid water monitoring network sites in the UK (now called Upland Water Monitoring Network) and for the period 1988 to 2008 at 22 sites there were no significant decreases in DOC concentration over that time period and 20 out of the 22 sites showed a significant increase in DOC concentration. The mechanisms proposed to explain the observed trends in DOC concentration would predict different trends over the decade. Recovery from acidification (Monteith et al., 2007) would predict ongoing increases in surface water DOC concentration as long as there was ongoing recovery from acidification but a flattening out if recovery were slowing; Air temperatures and atmospheric CO_2 have continued to increase over the last decade so if they were the drivers of DOC concentration change we would expect continued increases in DOC concentration to be observed. Changes in precipitation and occurrence of severe drought could lead to either increases or decreases in the observed DOC concentration depending upon the nature or timing of the change, e.g. if a severe drought had occurred at the national scale during the period of interest or not. Changes driven by land management could give rise to both increases or decreases but would be expected to be more spatially heterogeneous as land management changes in both time and space between catchments. Therefore, the aim of this study was to assess recent change in DOC concentration and flux from the UK as a test of what is driving change.

2. Methodology

The approach used to test these hypotheses was to consider the time series of both DOC concentration and flux from multiple sites across the UK. The data set analysed was compared to decadal trends up to 2002 as identified in Worrall and Burt (2007a). Not only were trends in concentration considered but also changes in DOC flux, both within each catchment, and for the UK as a whole. The approach was to consider first the available DOC concentration from the time series of the national averages and then the trends for individual catchments. Second, the DOC flux data are considered by national averages and trends for individual catchment records. The test of the central hypothesis of this study is that increases, or at least no change, are expected of both concentration and flux over the period 2003 – 2012. In response to these results, change point analysis was undertaken.

2.1. Study sites

The study used data from the Harmonised Monitoring Scheme (HMS - Bellamy and Wilkinson, 2001). There are 56 HMS sites in Scotland and 214 sites in England and Wales; the sites that had sufficient data (defined below) are shown in Figure 1 and regional details given in Table 1. HMS monitoring sites were selected for inclusion into the original monitoring programme if they were the tidal limit of rivers with an average annual discharge greater than 2 m^3s^{-1}, or any tributaries with a mean annual discharge above 2 m^3s^{-1} (Bellamy and Wilkinson, 2001). These criteria provided good spatial coverage of the coast of England and Wales, but in Scotland many of the west-coast rivers are too small to warrant inclusion in the HMS. No HMS data were available from Northern Ireland. Within the database maintained as part of the HMS programme, four determinands were of particular interest to this study: dissolved organic carbon concentration (DOC – mg C/l); water colour (degrees Hazen); instantaneous flow (m^3s^{-1}) and daily average flow (m^3s^{-1}). Among the monitoring agencies, water quality sampling frequencies (f) vary, ranging from sub-weekly to monthly or even less frequently. Annual data were rejected at any site where for any individual year there were fewer than 12 samples with the samples in separate months (i.e. f<12); in this way it was assumed that a range of flow conditions would be sampled. Although the main study period for this study was the decade 2003 – 2012, the records of DOC concentration were considered up to the end of 2015 and for flux to the end of 2014. The extension beyond the decade 2003 - 2012 was to ensure the maximum amount of information was reported: the latest complete year of DOC concentration data for these sites was 2015 and riverflow data was 2014.

Samples from the HMS sites were not always available for DOC concentration for all sites but in a number of cases, data were available for the related variable: water colour. The lack of DOC concentration was particularly noted for Scotland prior to 2007 and so for this region and only in this period the water colour data were used to calculate DOC concentration using the calibration approach of Worrall and Burt (2007b)

Since the publication of Worrall and Burt (2007a & b), it has become apparent that there was a data quality issue with some of the DOC concentration values in the HMS database – for some time series there was a transcription error from the Environment Agency database (covering England and Wales at the time and referred to as WIMS) to the HMS database which resulted in incorrect values of DOC concentration in the HMS database. Data after 2003 were not affected by these transcription issues; for data prior to 2003 DOC time series from the HMS and the Environment Agency databases were compared. When there was a discrepancy the Environment Agency data were taken as in all cases the transcription error had resulted in DOC concentrations in the HMS database that were distinctly too large. This transcription did not affect the majority of HMS sites but was largely concentrated into certain regions and in certain years. Of the 214 records examined for this problem 114 had records prior to 2003 for which a trend had been reported and 38 of them showed no sign of a transcription error while 76 sites were judged to have been impacted by a transcription error.

2.2. DOC concentrations

Analysis of variance (ANOVA) was used to consider all DOC concentration data from all sites, for all calendar years for which the frequency of sampling (f) was 12 or more per year. In the ANOVA three factors in relation to the DOC concentration were considered: (1) the difference between years with factor levels, one for each year between 1974 and 2015 – henceforth referred to as the *year factor*; (2) the month of sampling with 12 factor levels, one for each calendar month - henceforth referred to as the *month factor*; and, (3) the differences between sampling sites – henceforth referred to as the *site factor*. The analysis was considered with and without the covariate of instantaneous river discharge at the time of sampling. The covariate was log-transformed to ensure the greatest proportion of the original variance in the dataset was explained. Prior to applying ANOVA, the DOC concentration data were Box-Cox transformed to remove outliers and tested for normality using the Anderson-Darling test (Anderson and Darling, 1952). If the data were not normally distributed, the data were log-transformed and re-tested using the Anderson-Darling test; no further transformation was found to be necessary. *Post hoc* assessment of factors was carried out using the Tukey test. Results of the ANOVA are expressed as least squares means (also called marginal means) as these are the means controlled for the factors and covariates. Only DOC concentration data were considered in this analysis and no concentration data derived from calibration with water colour was included.

2.3. Trend Analysis

Trend analysis was performed using the seasonal Kendall test was performed on the DOC concentration data for the decade 2003 – 2012 (Hirsch et al., 1982) to match the approach used in Worrall and Burt (2007a). The seasonal Kendall test was used to assess the significance of any trend in the data sets and used to estimate the slope of any trend expressed as median annual change in the DOC concentration. The seasonal Kendall test is robust against departures from normality and resistant to outliers (Esterby, 1997).

Given that the hypothesis of this paper was that trends in DOC concentration or flux had changed since the last decade of assessment (1993 – 2002) as analysed in Worrall and Burt (2007a), it was important to confirm that the trends for that period were free from the identified transcription error and so each HMS was revisited and its trend re-examined for the period 1993 to 2002, using the same criteria and approach as described above.

2.4. DOC Flux

Multiple techniques were used to develop the best possible flux estimate for each catchment for each year. Cassidy and Jordan (2011) considered bias and precision in the calculation of fluvial fluxes of phosphorus from high-frequency measurements and showed increasing bias with decreasing sampling frequency, with bias of up to 60% on monthly sampling, and large uncertainty for all sampling frequencies except for near-continuous monitoring. Alternatively, Worrall et al. (2013) considered a three-year long, high-frequency (f = 1 per hour) time series of DOC concentrations and, by considering a range of extrapolation and interpolation methods and by considering the sources of variation (Goodman, 1960), showed that the best method

(Equation (i)) was a very simple method that had a very high precision (±8% for f = 1 per month) compared to some previous methods and a high accuracy (-2% at f = 1 per month):

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

where: Q_{total} = the total flow in a year (m^3a^{-1}); $E(C_i)$ = the expected value of the sampled concentrations (mgl^{-1}); and K = unit conversion constant (0.000001 for flux in tonnes). For the best results (highest precision and accuracy), the expected value of the sampled concentrations was based upon fitting a gamma distribution to the available concentration data and using the expected value of that fitted gamma distribution. This method was applied to every site-year combination in the HMS data where 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).

The flux estimates for all possible site-year combinations from across the entire record were assessed by ANOVA with two factors (year and site, as defined above). As previously, the data were Box-Cox transformed in order to assess for and remove any outliers and assessed for normality and transformed where required.

For those sites where a continuous DOC flux record was present for 2003 to 2012, then a trend analysis was performed as for the concentration records from the same period. Obviously, in the case of flux records for the decade 2003 to 2012, n=10 and any trend analysis will be less sensitive compared too much longer records.

2.5. National-scale DOC flux

From the flux estimate for each year for each monitored site, the export was calculated as the flux per unit catchment area per year. The flux from the UK was then calculated using an area-weighted average of exports using the method of Worrall and Burt (2007b). However, the approach of Worrall and Burt (2007b) 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 given year. However, this 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; however, there would be a problem if a severe drought existed in that year. Thus, this study examined all the region-year combinations where there was a flux result using ANOVA. The ANOVA was performed, as described above, with two factors: the difference between years and the difference between regions. The proportion of variance explained by each factor 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 that the dominant source of variation was within region, within year and the best possible combination of those two factors given the result of ANOVA. Furthermore, there were no DOC concentration data for Scotland prior to 2007 and so for years pre-2007, data from Worrall and Burt (2007a) calibrated from colour data were used. It should be noted that there were no reported or observed disparities between different national-scale water quality databases in Scotland. It should also be noted that no HMS data were available for Northern Ireland. However, the land area of Northern Ireland is 13843 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 upscaled to give an estimate of the flux from the whole of the UK.

2.6. Change point analysis

Visual inspection of the flux and concentration time series suggested that step changes might be present and could be controlling the observed trends and, therefore, the Pettitt test (Pettitt,

1979) for step changes was applied. The Pettitt test uses the same approach as the Mann-Whitney U test but is applied sequentially across the entire time series to find the maximum value of U. The use of a Mann-Whitney U statistic means that no assumption of normality is made about a time series that contains a suspected step change within it. Where the time series of length T years is divided into two samples, with x_1 to x_t being one set before year t and the other sample being x_{t+1} to x_j, the series of U statistics are calculated as:

$$U_t = \sum_{i=1}^{t} \sum_{j=1}^{T} \left[X_I - x_j\right] \qquad \text{(ii)}$$

The most likely point of change is where:

$$K_T = \max_{1<t<T} U_t \qquad \text{(iii)}$$

The probability of the step change is then:

$$p = 1 - \, exp\left(\frac{-6K_T^2}{T^3+T^2}\right) \qquad \text{(iv)}$$

As pointed out by Wilks (2006), the Pettitt test will suffer from family-wise error (false detection rate – Ventura et al., 2008) and so an enhanced significance level was estimated and adopted. The enhanced significance level was calculated using the Sidak correction. Given the approach above, N Mann-Whitney U tests are being performed and thus for a significance level of $\alpha = 0.05$ (95% probability of there being a step change), then the enhanced α at which the test must be performed is:

$$\alpha_{new} = 1 - (1-\alpha)^{\frac{1}{N}} \qquad \text{(v)}$$

where: α = the significance level or probability of being zero (in this study $\alpha = 0.05$); new= the equivalent significance level that should be examined for a test at a probability equivalent to α; and N = the number of repeated tests.

Many studies that have used the Pettitt test have not made a correction for the family-wise error (e.g. Xu et al., 2014). However, if the Sidak correction corrects for the enhanced probability of false positives in repeated significance tests, then we should also consider the probability of false negatives, i.e. perform a statistical power analysis; again, this is lacking in many applications of the Pettitt test (e.g. Zhang et al., 2014). The power analysis was performed to estimate the probability of a false negative (β). The power analysis was performed assuming effect sizes of 0.2, 0.5 and 0.8 with samples from 10 to 50 and assuming ratio of group sizes of 0.5, 0.66 and 0.75. The approach was to use the asymptotic relative efficiency compared to a t-test based on Lehman's method (Lehman, 1975). *A priori* the acceptable power was set at 0.8 (a false negative probability $\beta = 0.2$).

The effect size of the Pettitt test was first assessed using the common language effect size method (McGraw and Wong, 1992), where all possible pairs of data across the step change are compared and the percentage that are correct with respect to the purported step change is the effect size, i.e. where all possible pairs across the step change have the same sense as the step change, then the effect size is 1.0 or 100%. The common language effect size represents a measure of the clarity of the step change but not its magnitude. Therefore, for the monthly time series of DOC concentration for the period 2003 to 2012, the mean DOC concentration for the year prior to the step change was compared to the mean for the year after the step change for those time series where a significant step change was observed. This measure of the step change was only attempted for the monthly time series from 2003 to 2012 as this study did not consider monthly records prior to 2003. The quality control applied to the HMS data meant that only those sites with 12 samples per year were included for analysis.

The Pettitt test was applied to both the *annual* average concentration and flux time series for each catchment for the entire period of the study record (1974 – 2012), wherever there were at least 10 years of data (Figure 1c); and it was also applied to the *monthly* concentration time series for those sites where there were sufficient data for the decade 2003 – 2012 (Figure 1b).

3. Results

3.1. DOC concentrations

There were 49372 data observations for which both DOC and flow could be paired from 1974 to 2012, 54809 when extended to 2015. The median DOC concentration for the period 1974 to 2015 was 5.5 mg C/l with a 5th percentile of 1.5 mg/l and a 95th percentile of 15.4 mg C/l. There were 26426 observations for which both water colour and flow could be paired from 1974 to 2007; no water colour measurements were made after 2007. The median water colour was 18.1 Hazen with a 5th percentile of 7.4 Hazen and a 95th percentile of 90 Hazen.

The Anderson-Darling test showed that the concentration data should be log-transformed before analysis. The ANOVA of the log-transformed DOC concentration data showed that all three factors were significant at $p < 0.05$. The most important factor was the site factor (difference between catchments explains 64% of the variance in the original dataset); the second most important factor was the difference between years (explaining 5% of the variance in the original dataset); and the least important was the month factor (1% of the original variance explained). Because of the size of the dataset, the *post hoc* comparisons show significant differences between most years. The time series show that DOC concentrations at the national scale peaked in 1974, then declined after that to peak again in 1994; since 1994 concentrations have declined, although this has not been a monotonic trend (Figure 2).

Although Figure 2 represents a main effects plot, it is possible that differences between years represent differences in sampling, i.e. insufficient or no DOC sampling may have occurred in a particular year for a particular site or region. Overall, after Box-Cox transformation had removed outliers, there were 53809 data points in the analysis; the year with the lowest number of samples was 1975 (42 samples), the highest was 2012 (2718 samples) and the median was 1195 samples per year. Therefore, individual records were analysed. Figure 2 shows that DOC concentrations from the UK, when differences between sites and months are accounted for, have decreased by 43% from a peak in 1994 to 2012.

3.2, DOC concentration trends

It was possible to assess the 10-year trend (2003 to 2012) for 62 sites (Figure 1b). Of these sites, 17 sites showed no significant trend, 3 showed significant positive trends and the remaining 42 showed significant negative trends (Figure 3a). Given the hypotheses proposed to explain *increases* in stream water DOC concentration (e.g. increased frequency of drought) have been predicated on the basis that peat and organic soils are the major source of DOC, and therefore, we might expect that any significant increases would be in catchments with organic soils: this would appear not to be the case (Figure 3). All three catchments where a significant increase was observed between 2003 and 2012 were in catchments without any organic soils. Sites in northern and western England where peat and other organic soils dominate the headwaters showed significant declines. Significant declines are incompatible with hypotheses of DOC concentration change based upon increasing air temperature, atmospheric CO_2 and if there is ongoing recovery from acidification. The site with the largest significant decline and showing a significant step change was the River Stour (Worcestershire) at Stour footbridge (National Grid Reference SO814709; N52:20:11 W2:16:25) and shows a decline prior to a step change in the summer of 2007 (Figure 4). There were 36 sites where a trend from the preceding decade (based only on the WIMS database, 1993-2002: Worrall and Burt, 2007a) could be compared to the trend for the period 2003-2012 as calculated in this study. The three-way contingency table (Table 2) shows that for the 36 sites where comparison was possible, 17 showed no change of significant (downward) gradient. Of the 19 transitions that showed a change in significant gradient between the two decades, the most frequent change was from no significant change to a negative change. There were no records that changed from a significant decrease to a significant increase or *vice versa*. The comparison in Table 2 supports the view that some downturns in the DOC concentration occurred in the mid-1990s and have continued since while for others the decline has occurred since 2002.

3.3. DOC flux

There were 3193 year-site combinations where there were sufficient DOC and flow data to calculate a flux (i.e. sample frequency > 11 per year). The median flux was 1683 tonnes C/yr with a 5th percentile of 190 tonnes C/yr and a 95th percentile of 16067 tonnes C/yr.

Like the ANOVA for DOC concentration, the flux data were log-transformed to normalise the data for subsequent analysis. For the ANOVA without flow as a covariate, then both site and year factors were found to be significant with the most important factor being the difference between sites explaining 93% of the variance in the original dataset while the year factor explained 4% of the original variance. When the log-transformed water yield was included as a covariate, the site factor became even more important (98% of the original variance) and the year factor became less important (1% of the original variance). The main effects plot of the year factor shows that other than for the year 1975 when high values of least squares mean may be distorted by the low samples size in that year, then there is perhaps a decline in DOC flux from 2000 but the variation after 2001 is largely within the variation observed prior to 2001 (Figure 5), suggesting again that individual time series should be examined. Inclusion of covariates may no obvious difference to the main effects plot of Figure 5.

3.3. DOC flux trends

Of the 62 records where there were sufficient data to conduct a flux calculation for each year from 2003 to 2012, the trend analysis showed that there were eight trends significant at least at the 95% probability of which seven have significant negative trends over the ten-year period (Figure 6). The one trend showing a significant increase was in south-east England; its catchment does not contain peat or organic soils (River Chelmer - Figure 3b).

3.4. National-scale DOC flux

The annual flux of DOC from the UK is area-weighted and so should be less prone to a lack of sampling at any individual site as each region will always be represented. 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 7). The extrapolation methods that do use calibrated water colour data from Scotland are higher than those methods that did not use Scottish data until 1997. Over the course of the study the extrapolation within regions, as opposed to extrapolation within years, created a less variable result with the use of ANOVA making little difference. The different extrapolation methods show very little difference over the last decade of the data available, with the annual average DOC flux over that decade varying only 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 values ranged from 812 in 1975 to 3875 ktonnes C in 2004, i.e. far higher than found here but that study did not use the WIMS database. 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. The values used by Finlay et al. (2016) were 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 estimates the average annual DOC flux at the tidal limit for the period of 2005 to 2014 as 859 ktonnes C/yr. The national-scale flux results complement those reported above for DOC concentrations, which are also now declining and have been doing so for the last decade of the study; however, and despite the national scale flux showing an average decline independent of the extrapolation method used, none of the flux records, no matter how calculated, showed a significant trend ($P< 0.05$) over the decade.

3.4. Change point analysis

The power analysis shows that the probability of a false negative could be approximated as:

$$(1 - \beta) = \underset{(0.002)}{0.008}T + \underset{(0.06)}{0.06}d + \underset{(0.14)}{0.51}\frac{t}{T} - \underset{(0.08)}{0.45} \qquad r^2 = 0.899, n = 35 \qquad \text{(vi)}$$

where: d= the effect size (0.0 to 1.0). Only those variables found to be significant at least at the 95% level are included and the values in brackets beneath the equation are the standard errors in the coefficients and the constant term. Equation (vi) shows that, for the power analysis of annual records considered here where the maximum value of T is 42, then for the statistical power to reach the acceptable threshold of 0.8 (80%), this would only occur for the largest T (longest time series) where the step change was in the middle of the record ($\frac{t}{T} = 0.5$) and the effect size was large ($d = 0.9$). Therefore, we can conclude that, although we can eliminate false positives from the Pettitt test, there will remain a high chance of false negatives. For the monthly time series where T is 120, then, even for a step change after one year, a power of 80% would be achieved for all values of d observed.

For the annual average concentration time series, where there were 118 records of 10 or more years in length, 93 showed a significant step change when initially assessed at 95% probability, but when the Sidak correction was applied, then only 52 sites were found to have significant step changes. For the annual flux series, 63 of 118 showed a significant step change at 95% probability which decreased to 28 when the Sidak correction was applied. The number of significant step changes in the annual average concentration time series was larger than that for the annual flux series and suggests that flow variation obscures any step change in the concentration of DOC.

When the effect size for DOC concentration was considered, the range was 0.25 to 1 with a geometric mean of 0.79, but when only those step changes which were significant after the Sidak correction were considered, then the effect size ranged from 0.55 to 1 with a geometric mean of 0.95. In all cases the step change was to lower DOC concentrations; none represented an increase in DOC. The spatial distribution of the step changes (Figure 8) shows that sites without a step change dominate in the north and west of England and Wales. Significant step changes appear to cluster near major urban areas in England, e.g. Manchester and Birmingham. For the annual concentration time series, both the median and modal year of change was 2000 and the spatial distribution shows no obvious pattern (Figure 9). Of the 118 DOC concentration records only 8 showed a step change before 1992 but when significant step changes were considered then only 3 showed a step change before 1992.

For the sites where it was possible to perform a trend analysis on the DOC concentration data between 2003 and 2012, the change point analysis showed a significant step change in 28 out of the 62 catchments. In 24 of these cases, the step change was in 2004 with two in 2006 and one each in 2007 and 2008. Of those which showed a significant step change, the median value of the common language effect size was 0.96 with a range of 0.76 to 1, i.e. far larger than that previously observed. When the percentage change in concentration across the step change was measured, then the median was 41% with a range between 21 and 83%. The spatial distribution is shown in Figure 10. The median change was a decrease in the annual average DOC concentration of 2.9 mg C/l. The magnitude of the step change can be compared to the change predicted by the measured gradient at each site: the step change represents a median of 107% of the expected gradient, i.e. on average, the step change at each site explained more than the change predicted by the gradient. The apparent size of the step change in comparison to the gradient could suggest that the step change is in opposition to a background upward trend. The median year of the step change was 2004 with no significant step change found after 2008.

5. Discussion

All the sites and records included here were either at the tidal limit of catchments or for tributaries where the average discharge was greater than 2 m^3s^{-1}, i.e. the dataset is for sites on higher-order rivers; this is in contrast to studies such as Monteith et al. (2007) or Evans et al. (2005) where the results were all for low-order headwater catchments. In previous discussions of the causes of rising DOC concentration, there has often been a tacit assumption that effects will be independent of scale and, therefore, that it is reasonable to compare results across scales. For example, Worrall and Burt (2008) used records from an 818 km^2 catchment with 21% peat coverage to compare to a record from one of its headwater catchments (11.4 km^2) 80 km upstream with 90% peat cover. Subsequently, Moody et al. (2013) have shown that for the same catchment (the same catchment where the 818 km^2 scale and the 11.4 km^2 scale were compared) as considered by Worrall et al. (2008a), there was between 48 and 68% removal of DOC, i.e. the in-stream processing along an 80 km length was sufficient to remove the majority of the DOC. In-stream processing would here include photo- and biodegradation (Jones et al., 2016); flocculation (McKnight et al., 1992); and release from particulate organic matter (Evans et al., 2012). However, such an estimate of the net removal rate belies the possible in-stream processing potential: Worrall and Moody (2014), modelling the complete TOC processing of a stream, showed that, whilst there was 52 and 63% net removal of TOC, between 10 and 44% of the DOC left was produced from turnover of POM within the stream. Therefore, streams have very large capacity to process DOM and any trend observed for sites in the lower course of a river will in large part reflect the in-stream processing potential. If in-stream processing potential is controlling the trend in DOC concentration and flux, then a number of additional drivers should be considered. Increased water temperature, increased stream residence time (eg. drought leading to persistent low flows), decreased supply of organic particles, or a change in the supply of nutrients (e.g. a change in inputs from farmland or wastewater treatment works) could all lead to increased turnover of DOC and so drive a decrease in DOC concentration at a downstream site. It should be remembered that the best available evidence would suggest that DOC concentrations in UK upland waters, i.e. the headwaters of the catchments for the sites used in this study, were still rising, at least to 2008 (Monteith et al., 2014).

With respect to river water temperature, Hannah and Garner (2015) have reviewed changes across the UK and shown an increase in river water temperature over the latter half of the 20th century and into the 21st century. Such an observed increase in stream temperature would be expected to lead to increased turnover and thus decreased DOC concentrations downstream. However, Worrall and Moody (2014) modelled Q_{10} values for the net in-stream processing of POC and DOC (i.e. both production and degradation of POC and DOC by both photic and biotic processes) of between 1.02 and 1.08 and so a 1^{o} K rise in stream temperature would lead to a maximum increase of approximately 1%, i.e. too small to be identified in this study. Of course, stream temperature will also be dependent on stream residence time.

Increasing in-stream residence time, i.e. drought, could lead to decreased DOC concentration as there would be more time for stream processes to turn over the DOM. Huntington (2006) has proposed that climate change would bring about an intensification of the water cycle that would lead to increased average river flows and reduced in-stream residence times. Marsh and Dixon (2012) showed that outflows increased from the UK for the period 1961-2011, although it was only statistically significant for Scotland. Hannaford and Marsh (2006) for two study periods (1963-2002 and 1973-2002) found increases in western and northern Britain (especially Scotland), in contrast to southern and eastern England where no trend was apparent. Increases in annual runoff reported by Marsh and Dixon (2012) were as high as 22.2% in Scotland but only 1.7% in England. If stream discharge were driving DOC concentration changes at the tidal limit, then increases in DOC would be observed and they would be focused in Scotland – this is not apparent in the data reported here. There might be merit in repeating the analyses of Marsh and Dixon (2012) for different seasons so that the possible effects of higher winter flows and lower summer flows could be considered.

The impacts of drought on stream residence time would lead to changes in DOC concentration that mimic those already ascribed to the general impact of droughts. That is, increased stream residence time during the drought, and quite probably increased str temperatures, would lead to declines in downstream DOC concentration but, once the drought had abated, an increase in flow would reduce the in-stream residence time and lead to an increased DOC concentration at downstream sites. Worrall et al. (2006) have suggested increased frequency of severe droughts would impact DOC release from UK peatlands. Pärn and Munder (2012) have ascribed increases in DOC concentration in river catchments of up to 47815 km^2 in Estonia to increased drought but those records did not contain step changes. Hannaford (2015) listed the severe droughts that affected the UK including 1990-1992 and 1995-1997 but none in the 2000s. In other words, the timing of major droughts has not been consistent with the step changes observed in this study.

Particulate organic matter turnover within a river could produce DOC, and indeed, Worrall and Moody (2014) noted times in an English catchment when DOC would increase due to relative turnover rates of POM and DOM, therefore a decrease in supply of POM could lead to lower DOC concentrations in rivers. For the UK, the flux of particulate organic matter at the tidal limit has declined since a peak flux in 1996 (Worrall et al., 2014) and so, if organic particles (POM) are a source of DOC, then declines in particles could be driving changes in DOC concentration. As with DOC, it will be peat and organic soils that will be the biggest sources of organic particles. In the degraded and heavily impacted peat-covered upland catchments of northern and western England, POC fluxes can be as high as 195 tonnes C/km^2 /yr (Evans et al., 2006); but, there is no evidence that soil sources such as peat have been changing significantly. Worrall et al. (2014) showed that changes in POM were being driven by improvements in waste water treatment after the implementation of the Urban Waste Water Treatment Directive (European Commission, 1991).

What is observed here is a more mixed picture with many of the records showing step changes, but what could be driving the step changes? Step changes could not be ascribed to linear drivers unless there are demonstrable threshold responses. Within the temporal resolution of the data available, it is possible that a drought could appear as step change. However, the influence of a drought would cause a step down in concentration followed by a recovery and so the common language effect size would be low. The step changes observed in this study have larger effect sizes but many step changes were in the opposite direction to the gradient and could therefore represent a "saw-tooth" response. Therefore, we propose that the step changes observed here on large rivers have resulted from the implementation of the Urban Waste Water Treatment Directive (UWWTD). The step changes are mainly found in the latter half of many records with most occurring in the late 1990s and only a fifth showing step changes prior to 1992, i.e. most step changes occurred after the implementation of the UWWTD. Furthermore, in relation to the spatial differences observed in Figure 8, there is a contrast between sites around urban areas, where many significant step changes were observed, compared to more rural areas further north and west where far fewer significant step changes were observed.

The UWWTD required secondary treatment (meaning at least biological treatment of waste water, e.g. activated sludge process) for treatment works greater than 15000 population equivalent (p.e.) by 31 December 2000. Indeed, this study can show that after the implementation of the UWWTD in 1992, the modal year for change was in 2000 and as noted above there were only 3 significant step changes observed before 1992. At that date the UK was 90% compliant with the requirement: by the end of 2007 it was 99.9% compliant (Defra, 2012). For treatment works between 2000 and 15000 p.e. the Directive required provision of secondary treatment by end of 2005; by then the UK was over 99% compliant, and indeed, this study showed that within the decade 2003 to 2012, 24 out of the 28 significant changes occurred prior to 2005, but four occurred after 2005. Finally, designated sensitive areas require tertiary treatment (e.g. phosphorus stripping). The UK currently has 588 sensitive areas totalling 19,466 km of river channel with a total catchment area of 2737 km^2.

Implementation of the UWWTD can include interventions to remove nutrients but can also include measures to lower the organic matter discharged, and indeed it has already been noted that declines in POM concentration and flux from the UK have been driven by the changes implemented by the UWWTD (Worrall et al., 2014). Therefore, a decline in DOC as a result of implementing improved waste water treatment could be either because a source of DOM has been removed or because a source of nutrient has been removed. We have speculated above that decreased nutrient supply would lead to increased DOC concentration at downstream sites; however, it is also possible that the nutrient source was enhancing the activity of river flora and fauna and so enhancing the autochthonous source of DOM. Therefore, it is plausible that diminishing a point source of nutrients (e.g. enhanced wastewater treatment) would lead to removal of nutrient and so cause declines in DOM concentration. Noacco et al. (2017) studied a 130-year long 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 and a long-term trend due to temperature, the most important driver of change was increasing discharge from sewage works as the population of the catchment increased, i.e. even with advances in sewage treatment, the increased amount of water coming into the catchment via sewage works caused increased DOC concentration in the river.

The time series of DOC relative to key periods would provide a test of the many of the mechanisms proposed for the observed increases in DOC concentration such as those reported in Monteith et al. (2007) and has been proposed as a test for such mechanisms (Helliwell et al., 2014). Indeed, the long-term records, or at least sections of them used within this study, have been used to test what mechanisms are driving changes in DOC concentration in predominantly upland and peat-covered soils (e.g. Worrall et al., 2008a). However, this study shows that comparisons between records, no matter how long, from large, downstream catchments with small, headwater catchments is illegitimate. Such comparisons, including by authors of this study (e.g. Worrall and Burt, 2008), will be wrong for two reasons: firstly, DOC concentrations in large, downstream catchments reflect in-stream processing as well as sources in their headwaters; and secondly, urban sources, in particular waste water treatments works, are important, even dominant sources of DOM to downstream reaches of large rivers. Therefore, this study cannot comment on the mechanisms that are controlling release of DOC from peat soils and especially in small catchments. Furthermore, larger catchments will integrate multiple drivers more than small ones, and indeed Lepistö et al. (2008) showed this for a 3160 km^2 boreal catchment, and therefore larger catchments will naturally be poor sites for understanding controls upon release from soils into headwaters. The question then for future research is: to what extent does a large river retain the signal of changes generated in the headwaters?

6. Conclusions

This study has shown that recent trends in DOC concentrations and flux in large catchments are not consistent with the range of current hypotheses proposed to explain trends in DOC concentration and flux. Over the decade 2003 to 2012, of the 62 (large river) sites that could be assessed, 42 showed significant decline in concentration, seven showed significant decline in annual DOC flux, but only three showed significant increase in concentration and only one a significant increase in DOC flux. At the UK national scale, DOC concentrations peaked in 1994 and DOC flux peaked in 2000. Over the period since 1974, 28 of the 118 sites for which flux records were available showed a significant step change. When DOC concentration time series were considered, 52 out of 118 showed a significant step decrease with a median decrease of 84% over the step; the modal year of the step change was 2000. In all cases it was a step decline with a geometric mean effect size of 79% over the step. We conclude that in these large catchments, there is not necessarily a link with carbon release in headwaters and what is observed much further downstream. Downstream, observed trends and step changes are dominated by changes in in-stream processing and the supply of nutrients, especially those brought about by the Urban Waste Water Treatment Directive.

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Figure 1. The location of the study sites used in this catchment: a) all sites with DOC records available to this study; b) sites with sufficient data for trend and change point analysis of monthly concentration DOC data between 2003 – 2012; and c) sites where a change point analysis could be conducted on the annual average concentration and flux time series.

Figure 2. The main effects plot of DOC concentration data across the entire study period. The 95% confidence interval in the least squares means was ±2.3%. The difference between main effects with and without flow as a covariate is slight but both are plotted.

Figure 3. a) The spatial distribution of trends in the DOC concentration time series from 2003 to 2012. The gradient is expressed as mg C/l/month and significance was judged at a 95% probability of the gradient being different from zero. b) The distribution of organic soils in Great Britain as defined by Hodgson (1997).

Figure 4. The monthly time series of DOC concentration from River Stour at Stourport footbridge.

Figure 5. The main effects plot of DOC flux across the entire time period. The error is given as the 95% confidence interval in the least squares means - approximately ± 3.0%. The difference between the least squares means with and without covariates is within the range of the plotted symbol.

Figure 6. The spatial distribution of significant trends in the annual DOC flux over the period 2003 – 2012. Only those records with trends significant at 95% probability are shown. The Frome and Piddle catchments (*) are too close to appear separately.

Figure 7. The national flux of DOC at the tidal limit for the UK from 1974. Different time series represent the different approaches to interpolation and extrapolation.

Figure 8. The spatial distribution of the step change in the annual DOC concentration time series. Manchester and Birmingham are illustrated for reference to the text.

Figure 9. The spatial distribution of the year before a significant step change in the annual DOC concentration time series.

Figure 10. The spatial distribution of the step change in the monthly DOC concentration time series between 2003 and 2012.

Table 1. The distribution and spatial coverage of catchments from the UK for which DOC flux or concentration was available for this study. Regions refers to those illustrated in Figure 1.

Region	No. of study catchments	Area of region (km^2)	Area of study catchments (km^2)	Percentage of total area sampled
NW England	18	14165	10847	77
NE England[†]	5	13320	11807	89
Severn-Trent	11	21600	18328	85
Ouse	10	14362	4692	33
East Anglia	8	26816	10803	40
Thames Basin	15	12900	12017	93
SE England	11	10979	4850	44
Hampshire Basin	7	6422	4163	65
SW England	17	14298	6366	45
Wales	39	20779	9272	45
Scotland[‡]	50	74087	21307	29
N Ireland	0	13843	0	0
Total	228	243564	114452	47

[†] The NE England includes 4300 km^2 of the River Tweed which is in Scotland but which has a tidal limit in England.

[‡] The values for Scotland exclude 4300 km^2 of the River Tweed which is within the country of Scotland but discharges to the sea in England.

Table 2. The contingency table for the comparison of the trends from the decade 1993-2002 (Worrall and Burt, 2007a) and those estimated by the same method for the same site for the period 2003-2012. Significance is judged as > 95% probability of a trend greater, or less, than zero.

	DOC trend 2003-2012		
DOC trend 1993-2002	Significant +ve trend	No significant trend	Significant -ve trend
Significant +ve trend	0	1	4
No significant trend	1	5	11
Significant -ve trend	0	3	12