The fluvial flux of particulate organic matter from the UK: quantifying in-stream losses and carbon sinks.

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Abstract

This study considers records of fluvial suspended sediment concentration and its organic matter content from across the United Kingdom from 1974 to 2010. Suspended sediment, mineral concentration and river flow data were used to estimate the particulate organic matter (POM) concentration and flux. Median annual POM flux from the UK was 1596 ktonnes/yr. The POM concentration significantly declined after the European Commission’s Urban Wastewater Directive was adopted in 1991 although the POM flux after 1992 was significantly higher. Estimates of POM flux were compared to a range of catchment properties to estimate the flux of particulate organic carbon (POC) and particulate organic nitrogen (PON) as they entered rivers and thus estimate the net catchment losses. The total fluvial flux of N from the soil source to rivers was 2209 ktonnes N/yr with 814 ktonnes N lost at the tidal limit, and so leaving 1395 ktonnes N/yr loss to atmosphere from across UK catchments - equivalent to an N2O flux from UK rivers of between 33 and 154 ktonnes (N2O)/yr. The total fluvial flux of carbon from the soil source to rivers for the UK was 5020 ktonnes C/yr; the flux at the tidal limit was 1508 ktonnes C/yr, equivalent to 6.5 tonnes.

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C/km\(^2\)/yr. Assuming that all the net catchment loss goes into the atmosphere, then the impact of rivers on the atmosphere is 3512 ktonnes C/yr, equivalent to 15.2 tonnes C/km\(^2\)/yr. The loss of POM from the UK suggests that soil erosion in the UK prevents soil being a net sink of CO\(_2\) and is instead a small net source to the atmosphere.

**Keywords:** particulate organic carbon, POC, particulate organic nitrogen, PON, soil erosion, N\(_2\)O.

1. Introduction

Meybeck (1993) estimated the flux of carbon (dissolved organic carbon, particulate organic carbon, and dissolved inorganic carbon) from the world’s rivers to the oceans was around 542 Mtonnes C/yr in proportions respectively 37:18:45, i.e. global river flux of POC is about 98 Mtonnes C/yr. Ludwig et al. (1996) used a spatially-explicit model of global fluvial carbon fluxes to suggest fluxes of 800 Mtonnes C/yr with a split of approximately 50:25:25 for DOC:POC:DIC, i.e. a global POC of 200 Mtonnes C/yr. These figures provide useful estimates of fluvial POC losses from the land to the oceans at the tidal limit, but they do not account for in-stream losses along the length of the river, between the carbon sources (e.g. soils) and the ocean. Thus, to understand total carbon losses from catchments, it is also necessary to estimate in-stream losses.

Kempe (1982, 1984) recognised that many surface freshwater bodies were saturated with respect to CO\(_2\). Cole et al. (1994) showed, in a survey of 1835 lakes across the globe, that lakes, on average, were supersaturated with respect to the atmosphere by a factor of 3 and that, assuming this value, degassing of CO\(_2\) from global lakes would represent an additional 140 Mtonnes C to the atmosphere each year. This excess dissolved CO\(_2\) comes not only from the excess CO\(_2\) present in water entering a terrestrial water body from the
relatively closed system of soil and bedrock porosity, but also from the mineralisation of DOC and POC. Thus, rivers and lakes become sources of CO$_2$ because water entering them carries excess dissolved CO$_2$. For the global scale, Cole et al. (2007) estimated that 1900 Mtonnes C/yr enters rivers of which 800 Mtonnes C/yr (42% of the input) is returned to the atmosphere. Battin et al. (2009) considered the loss of DOC from rivers at a global scale and suggested 21% removal of DOC in-stream 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. The 2007 Intergovernmental Panel on Climate Change (IPCC) report included an estimate of global DOC flux from rivers (Solomon et al., 2007) but did not consider the effect of in-stream DOC losses, let alone the flux and loss of POC. In other words, the carbon fluxes to the atmosphere from in-stream losses have not yet been included in estimates of terrestrial greenhouse gas (GHG) emissions.

Analysis of the global river network’s contribution of fluvial carbon to GHG emissions has relied on relatively sparse data from very few rivers. Worrall et al. (2007) used nationally-collected monitoring data for biochemical oxygen demand (BOD) as a measure of fluvial carbon turnover (where turnover is considered as the biochemical reaction of fluvial carbon to form greenhouse gases) and estimated a loss equivalent to 31% of the DOC flux across the UK fluvial network – equivalent to an additional release to the atmosphere of 1 tonne C/km$^2$/yr across the entire UK land surface. However, their BOD approach assumes a fixed fluvial residence time of 5 days – a long residence time for the short, relatively-unimpounded rivers of the UK. In addition, BOD is usually measured downstream in the fluvial network, away from upstream sources of more readily degraded DOC. Alternatively, Worrall et al. (2012a) modelled the DOC export from over 194 catchments across the UK, over 7 years and assessed net watershed losses through comparisons to the soil, land-use and hydro-climatic characteristics of each catchment. They found a net watershed DOC loss of up
to 78%, equivalent to between 9.0 and 12.7 tonnes C/km$^2$ of UK land area/yr. These figures are large when compared to other studies on single catchments. Individual studies are often based on experimental studies of DOC turnover in the dark and not daylight (Wickland et al., 2007; del Georgio and Pace, 2008) or based on samples from systems with residence times far longer than most UK rivers, e.g. lakes - Jonsson et al. (2007). Dawson et al. (2001) studied a short river reach (2 km) in a peat-covered headwater catchment and estimated DOC removal of 12-18%. Wallin et al. (2013) considered a 67 km$^2$ boreal catchment and found that fluvial CO$_2$ evasion (loss of gas from the river surface to the atmosphere) was equivalent to 53% of the fluvial carbon flux; some of this CO$_2$ evasion would be due to rapid loss of DOC to the atmosphere from low-order streams. The estimated net DOC watershed loss from the UK river network (Worrall et al., 2012a) represents 3% of the UK’s greenhouse gas inventory (Cannell et al., 1999).

Further, the turnover of organic matter not only represents a release of carbon to the atmosphere but also a potential loss of nitrogen. Kroeze et al. (2003) found that fluvial N retention in surface waters is typically between 11 and 50% of N input and, by retention, this is the proportion of nitrogen not transferred out of the catchment via the river and includes losses to the atmosphere. Worrall et al. (2012b) compared fluxes of dissolved nitrogen species from different sized catchments and, by allowing for differences in catchment soil cover, land use and hydro-climatic properties, the net catchment loss of dissolved nitrogen was estimated as 63% of the flux entering the rivers at the soil source.

If loss of dissolved CO$_2$, DOC and DON have been considered, what about the turnover of POC or PON? The decline in suspended sediment export (often referred to as yield) through a catchment has often been expressed as a sediment delivery ratio (e.g. Walling, 1983). This decline in sediment yield has been associated with in-channel storage of suspended sediment (e.g. Collins and Walling, 2007) and on floodplains (e.g. Walling and
Owens, 2003). Studies have considered the concept of spiralling of organic matter (Newbold et al., 1982) where organic matter is cycled through the stream biota, but they have not considered loss by turnover (e.g. Young and Huryn, 1997, Griffiths et al., 2012). Furthermore, studies that have examined the fate of eroded soil have reported erosion as a net sink of carbon (e.g. Van Oost et al., 2007) but have not explicitly considered the possibility of CO₂ being released from the eroded soil organic matter as it is transported within the river network. Therefore, given the large potential impact that organic matter turnover in rivers has on atmospheric greenhouse gases, the aim of this study is to estimate the flux of particulate organic matter from soil source to UK rivers and from UK rivers to the tidal limit and so assess the loss of particulate carbon and nutrients in stream.

2. Methodology

The approach used to calculate fluvial fluxes for individual catchments was similar to that of Worrall et al. (2013a), and the approach used to assess net catchment losses followed that of Worrall et al. (2012a and b).

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 (Figure 1, Table 1). Note that one Scottish river (River Tweed) actually is included in the NE England dataset because, although most of its catchment is in Scotland, its tidal limit is in England. HMS monitoring sites were selected for the inclusion into the original monitoring programme if they were the tidal limit of rivers with an average annual discharge greater than 2 m³/s; in addition, any tributaries with a mean annual discharge above 2 m³/s were also included in the original monitoring programme. 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, three determinands were of particular interest to this study: suspended sediment concentration (mg/l); instantaneous river flow (m³/s); and ash content of the suspended sediment (mg/l). From these data the suspended sediment flux was estimated and, as the ash content represents the mineral proportion of the suspended sediment (particulate mineral matter – PMM), it was possible to calculate the particulate organic matter (POM) concentration of each sample by difference. From the calculated POM concentrations and river flow data, it was then possible to calculate the POM flux.

2.1. POM concentrations

Analysis of variance (ANOVA) was used to consider all data from all sites for which the frequency of sampling was more than 12 per year. In the ANOVA three factors in relation to the concentration and percentage of mineral matter (PMM) were considered: (1) the difference between years with 37 factor levels, one for each year between 1974 and 2010 – 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 covariates of suspended sediment concentration and instantaneous river discharge at the time of sampling. Both covariates were log-transformed to ensure the greatest proportion of the original variance in the dataset was explained. On the basis of the ANOVA, multiple regression was used to model PMM concentration, percentage PMM content and subsequently the POM concentration.

2.2. Flux calculation
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 there were fewer than 12 samples in that year with the samples in separate months (f<12); in this way a range of flow conditions would be sampled. In general, 12 monthly spot samples was the sampling scheme being followed within the HMS. An interpolation method was then applied to calculate the flux for any site-year combination that met this criterion:

\[ F_y = K \sum_{i=1}^{n_y} n_y C_i Q_i \]  

(i)

\[ n_x = \frac{A_x}{n_y} \]  

(ii)

where: \( F \) = the annual flux at the site; \( C_i \) = the measured concentration at the site at time \( i \); \( Q_i \) = the river discharge at time \( i \); \( K \) = a conversion factor which takes into account the units used; \( n_y \) = the number of samples at the site in that year; and \( A_y \) = the number of days in that year, i.e. this can vary with a leap year. This approach assumes that each sample taken at a site is equally likely to be representative of an equal proportion of the year as any other sample. Note that this method corresponds to “method 2” of Littlewood and Marsh (2005) modified for irregular sampling.

When considering suspended sediment, or indeed any particulates, Webb et al. (1997) considered 5 interpolation and 2 extrapolation methods and found that, for suspended sediment flux estimation, extrapolation methods gave the least biased results and that bias increased with decreased sample frequency. Several studies have recommended or considered adaptive strategies. Kronvang and Bruhn (1996) suggested taking samples “hydrologically” rather than on a regular basis and a number of studies (e.g. Cooper and Watts, 2002;
Skarbøvik et al., 2012) have suggested including flood samples alongside regular sampling. However, the use of extrapolation and adaptive strategies is impractical when considering a dataset from a monitoring scheme such as the HMS monitoring network in the UK where sampling is regular rather than adaptive and often infrequent (typically monthly).

The quality of methods and sampling frequencies used to calculate flux need to be considered in two ways. Firstly, the accuracy can be considered as the difference between the true load and estimated load and represents the systematic bias. Secondly, the precision of the method represents the spread of the load estimates about a central value, in other words the consistency of the load estimates. In many studies that discuss uncertainty in flux estimation due to changing method or sampling frequency, it is the precision that is described and not the bias or accuracy. An example of this is Littlewood et al., (1998) who could only trace precision with changing sampling frequency with “indicative” curves but could not discuss accuracy of methods because there was no “true” value available. Johnes (2007) considered 17 catchments where there was daily measurement of phosphorus but had no sub-daily data and chose to assume that “method 5” (Littlewood, 1995) was the true value and only considered precision but not bias. The lack of a “true” value with which to compare bedevils the assessment of both accuracy and precision of changing method of sampling frequencies. Cassidy and Jordan (2011), with sub-daily measurement of phosphorus, considered both bias and precision in their approach and thus 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. Worrall et al. (2013b) showed that “method 5”, often quoted as the preferred interpolation method, contained a curious bias because it corrected “method 2” by assuming that river discharge is normally distributed, which it is not, and this led to overestimation of fluxes at high sampling frequencies (f > 1 sample per 7 days) because the method overestimated the expected value of the river
discharge, i.e. it used an arithmetic mean when other estimates of the expected value of river discharge (e.g. geometric mean) would be more appropriate. Furthermore, Worrall et al. (2013b) showed that extrapolation methods were, because of large changes in the sample set used to derive rating curve, highly erratic for low-frequency sampling leading to poor accuracy and precision.

It is clear that for the type of low-frequency data available to this study, there could be considerable sampling bias, most likely leading to underestimation. However, Worrall et al. (2010a) tackled this issue for the low-frequency data typical of the HMS by application of analysis of covariance (ANCOVA) to establish and correct for sample frequency bias: the sampling frequency for all site-year combinations was compared to a flow-weighted flux estimate (i.e. $F_y \sum Q$), which is equivalent to the annual average flow-weighted concentration. In the ANCOVA, sampling frequency was considered as a factor with four levels (sampling frequency $\geq 1$ per week, $\geq 2$ weeks, $\geq 3$ weeks, and $\geq 1$ per month – note that sites with a sampling frequency of worse than $1$ per month had already been removed). The annual water yield for each site-year combination ($\sum Q$) was used as the covariate. The normality of the data was tested using the Anderson-Darling test (Anderson and Darling, 1952); if the test failed at a 5% probability of the data not being normally distributed, then the data were transformed and the distribution re-tested. The Tukey test was used to assess post hoc differences between factor levels. If there is a significant effect due to sampling frequency at the 95% probability, then ANCOVA demonstrates that a sampling bias exists with changing sampling frequency. Where significant differences were found, a correction factor for that sampling frequency was derived relative to the other factor levels, i.e. relative to other sampling frequencies. These correction factors were then applied to the flow-weighted flux for each site-year combination to adjust the interpolation method results. This was applied in such a way as to correct all flow-weighted fluxes to the average sampling bias for the highest
sampling frequency; thus, all results were adjusted as though each site had been sampled sub-
weekly. Worrall et al. (2013a) tested this method for correcting for sampling bias by applying
the extrapolation method of Ferguson (1986) to calculating suspended sediment flux for the
two sites in the HMS dataset with the largest contrast in baseflow index within the HMS
catchments (BFI – Gustard et al., 1992). The extrapolation method was applied based upon
all the available suspended sediment concentration and flow data for that catchment and
given that the data were made stationary over the time series of their sampling period. For the
River Test (the high BFI catchment) the 10-year average suspended sediment flux the results
were: 4820 tonnes/yr for extrapolation method; 3179 tonnes/yr for interpolation method; and
4705 tonnes/yr for the corrected interpolation method, i.e. the correction method used here
gave a result that was 98% of that from an extrapolation method. For the River Thurso (the
low BFI catchment) the 10-year average suspended sediment flux the results were: 1302
tonnes/yr for extrapolation method; 2427 tonnes/yr for interpolation method; and 5270
tonnes/yr for the corrected interpolation method. The reason for the low estimate from the
extrapolation method in this latter case is that rating curve for this catchment shows two
distinct trends even once it had been made stationary, i.e. extrapolation methods can be
unreliable because a single relationship is assumed but not always appropriate.

The bias-corrected flux for each HMS site in each year was then used to calculate the
export rate as the flux per unit catchment area per year. The flux from the UK was then
calculated using an area-weighted average of export rates. For each region of the UK for
which POM fluxes could be estimated, an average export was calculated for each year from
1974 to 2010 (Figure 1, Table 1). The regions are based upon UK Environment Agency’s
administrative areas that are bounded by watersheds. The flux from all the regions was
summed to give the national flux. This regional approach better represents regional
differences without biasing the national value due to uneven spatial distribution of available
records, while also using all site information to calculate national-scale flux. Errors due to upscaling from catchment export estimates to the regional and national scales was estimated as half the percentage difference between the values estimated from the 5th and 95th percentile exports for each region: this gives an estimated upscaling error of ±15%. It should be noted that no HMS data were available for Northern Ireland. However, the land area of Northern Ireland is 13843 km² and so the results for Great Britain (the countries of England, Wales and Scotland, i.e. the UK without Northern Ireland) could be scaled up to give an estimate of the flux from the whole of the UK.

Where a catchment PMM or POM flux could be calculated for the period 2001 to 2010, the average catchment flux over those years was compared to a range of catchment characteristics. The period 2001-2010 was chosen for three reasons: (1) it is the most recent decade; (2) a decadal average is less likely to be distorted by particularly wet or dry years; and, (3) the available land use data were collected for the middle year of this period. The land use for each 1 km² of Great Britain (i.e. the UK minus Northern Ireland) was classified into: arable, grass and urban from the June Agricultural Census for 2004 (Defra, 2005). In addition, the number of cattle and sheep in each 1 km² were recorded within this census. To provide a single measure for livestock, the equivalent sheep per hectare were calculated based on published nitrogen export values of the respective livestock (Johnes et al., 1996) which gives a ratio of 3.1 sheep per cow. The dominant soil-type of each 1 km² grid square in Great Britain was classified by this study into mineral, organo-mineral and organic soils based upon the classification system of Hodgson (1997), and used nationally-available data (Smith et al., 2007, Lilly et al., 2009). Note that, by this definition, peat soils are a subset of organic soils. The catchment area to each monitoring point was calculated from the CEH Wallingford digital terrain model which has a 50 m grid interval and a 0.1 m altitude interval (Morris and Flavin, 1994). The soil and land-use characteristics for each 1 km² were summed across each
catchment to the monitoring points with available flux information and, on each catchment, the relative proportion of different soil and land-use properties was determined in addition to a range of hydrological characteristics. For each of the catchments, for which the study could calculate a suspended sediment flux, the following hydrological characteristics were used: the base flow index, the average actual evaporation and the average annual rainfall. The hydrological characteristics for each catchment were available from the National River Flow Archive (www.ceh.ac.uk/data/nrfa/). The study did not include the average annual total river flow for each catchment within the hydrological characteristics considered. The average annual total river flow would simply be the difference between average annual rainfall and the average actual evaporation for each catchment: if total river flow were important it will be apparent from the importance of these two variables. Multiple linear regression was used to compare the average annual flux for the period 2001 to 2010 to catchment characteristics.

The multiple linear regression was performed with both explanatory variables and the response variable untransformed and log-transformed. Normality of transformed and untransformed variables was tested using the Anderson-Darling test and variables were only included in the model if they were statistically significant (probability of difference from zero at $p < 0.05$). Models were chosen both on the basis of model fit, as assessed by the correlation coefficient ($R^2$), and the physical interpretation of the model. Of particular interest were models which only included those soil and land-use characteristics that could be mapped across Great Britain, and models that identified a relationship between POM flux and catchment area. The latter were used because significant net watershed losses should be discernible from the relationship between total POM flux and catchment area. The best-fit significant model was obtained to judge this relationship. If the best-fit model included catchment area, the model was then recalculated excluding catchment area and the residuals of that model were compared to the catchment area. In using regression to filter the data for
effects other than that of catchment area, care was taken to consider information that was a proxy or co-linear with catchment area, e.g. area of arable land. An analysis of residuals was performed for statistically significant models, where a standardised residual (residual divided by its standard deviation) greater than 2 was considered an outlier and worthy of further investigation. As further analysis of fit of preferred models, the residuals after model fitting were tested for normality using the Anderson-Darling test.

### 3. Results

#### 3.1. Mineral and organic matter concentrations

For site-year combinations that met the criterion of f > 1 sample per month, there were 35490 mineral concentrations from 1974 to 2010. The median PMM concentration was 7.5 mg/l with a 5th percentile of 1 mg/l and a 95th percentile of 75 mg/l. When the percentage mineral content was considered, the median percentage was 66.7% with a 5th percentile of 25% and a 95th percentile of 94%. Given the percentage mineral content, the median POM concentration was 4.6 mg/l; with a 5th percentile of 0.5 mg/l and a 95th percentile of 23 mg/l. Assuming the carbon content of particulate organic matter was between 45 and 50% by mass (Moody et al., 2013), our results suggest that organic carbon content as a percentage was between 2.7% (5th percentile) and 38% (95% percentile) with a median value of 15.8%, which in turn yields a median POC concentration of 2.2 mg C/l varying between 0.2 mg C/l (5th percentile) and 11.5 mg C/l (95th percentile). For British rivers, Hope et al. (1997) gave a “preferred” value of 14% organic C content, while Hillier (2001) measured the carbon content of suspended sediment along the River Don in Scotland (catchment area = 1,320 km²) and showed values varied between 6.9 and 14.1%. Neal (2003) studied sediment from rivers with catchment areas from 373 to 8231 km² and found organic carbon contents varied from 5 to 17%.
The ANOVA of PMM concentration data showed that all three factors and one interaction were significant at $p < 0.05$ (Table 2). The most important factor was the site factor (difference between catchments) and the least important was the month factor (the difference between months, i.e. the seasonal cycle). However, once covariates were included, differences in the suspended sediment concentrations explained most of the differences between factor levels. The post hoc comparisons for the year and month factors showed the PMM time series was dominated by an increase in PMM concentration from the early 1990s (Figure 2). When covariates were included, then the apparent trend in the time series is largely suppressed although post hoc testing shows that the years 1992 through 1995 were still significantly higher than years before or after. Towards the end of the study period and certainly after 1992 there is some suggestion that sampling targeted places and times of high PMM concentration, so the analysis including covariates provides a more realistic picture of underlying trends as the ANCOVA takes account of flow conditions. The average seasonal cycle in the PMM concentrations, once covariates have been accounted for and so independent of flow change, shows a clear annual minimum in January (3.8 mg/l) with a maximum in July (4.4 mg/l).

When percentage PMM content was considered by ANOVA, all factors and one interaction were found to be significant at $p < 0.05$ (Table 2). Including covariates, the percentage variation explained by the covariates was smaller than that observed for the PMM concentration. With the inclusion of covariates the variation due to the month factor and the interaction between year and month factors were no longer significant, i.e. the covariates explained the importance of this factor and interaction. The annual trend in percentage PMM content shows that the proportion of PMM dramatically rose after 1991, although once covariates were included, then the dramatic rise is almost reversed by 2009. The changes observed in both the PMM concentration and the percentage PMM content in the first half of

The Directive required a minimum of secondary treatment for all sewage treatment works with a population equivalent greater than 2000 people and tertiary treatment for works with a population equivalent greater than 10,000 people. Therefore, the Directive aimed to remove suspended solids from sewage work outflows. If the PMM concentration and percentage PMM are considered after accounting for covariates, the change in POM concentration can be considered (Figure 3) which shows there was a significant change in average POM concentration around 1992: prior to 1992 mean annual POM concentration was 4.7 mg/l, while after 1992 it was 2.8 mg/l. However, this apparent success of the Urban Wastewater Directive may not be reflected in the fluxes of organic matter, as flows from sewage outfalls are more likely to be dominant at lower flows.

The ANOVA suggests a simple multiple regression for the PMM concentration could be derived:

\[
\ln[PMM] = 0.03\ln(flow) + 1.073\ln[sedt] + 0.0083Year + 0.023\sin\left(\frac{mn}{6}\right) + 0.044\cos\left(\frac{mn}{6}\right) - 17.4
\]

\[R^2 = 0.91 \ n= 35489 \quad (iii)\]

where: \([X]\) = concentration of X (mg/l, with PMM = PMM concentration, and [sedt] = concentration of suspended sediment); \(flow\) = instantaneous river discharge (m\(^3\)/s); \(Year\) = calendar year; \(m\) = month of the year with 1 = January and 12 = December. Only those variables significantly different from zero at \(p < 0.05\) are shown. Standard errors for each coefficient are given in brackets. Equation (iii) suggests a significant increase in the PMM concentration over the period of record with PMM concentration increasing on higher flows.
and, not surprisingly, the PMM concentration increases as suspended sediment concentration increases.

Similarly for the percentage PMM content the best-fit equation was:

\[
\ln[\%\text{PMM}] = 0.014\ln\text{flow} + 0.035\ln[\text{sedt}] + 0.004\text{Year} + 0.01\sin\left(\frac{m\pi}{6}\right) + 0.025\cos\left(\frac{m\pi}{6}\right) - 8.2
\]

\[
\begin{array}{cccccc}
\text{R}^2 = 0.14 & n= 35489 & (iv) \\
(0.0007) & (0.0009) & (0.004) & (0.001) & (0.001) & (0.3)
\end{array}
\]

The format of equation (iv) is as for equation (iii) with only variables significant at 95% probability included and standard errors given in the brackets. Equation (iv) explains only 14% of the original variance in the dataset but it still highlights that the proportion of PMM in suspended sediment concentrations increased over the study period and mineral matter was more important as both suspended sediment concentration and flow increased. The relatively poor fit of Equation (iv) is most likely because the equation makes no allowance for the differences between catchments.

For the POM concentration:

\[
\ln[\text{POM}] = 17.9 - 0.018\ln\text{flow} - 0.794\ln[\text{sedt}] - 0.009\text{Year} - 0.025\sin\left(\frac{m\pi}{6}\right) - 0.076\cos\left(\frac{m\pi}{6}\right)
\]

\[
\begin{array}{cccccc}
\text{R}^2 = 0.74 & n= 35489 & (v) \\
(0.7) & (0.002) & (0.001) & (0.0003) & (0.004) & (0.004)
\end{array}
\]

Only those variables significantly different from zero at p < 0.05 are shown. Standard errors for each coefficient are given in brackets. Equation (v) confirms a decline in particulate organic matter concentration since 1974 (p<0.05) and that organic matter concentration decreases both with increasing suspended sediment concentration and with increasing river
flow. It might be considered that equation (v) should be similar to equation (iii) as [POM] was calculated from [PMM]; however, the differences in fit between equations (iii) and (v) illustrate that the suspended sediment concentration and its composition can vary independently of each other.

Examining the individual sites means that it was possible to assess significant relationships with covariates at individual sites. For 156 sites it was possible to assess significant relationships with covariates; there was a significant relationship in POM concentration in 90 of them of which in only 3 was the POM concentration significantly increasing with time. For 92 study catchments there was a significant relationship with river flow and for all but 14 of these the POM concentration decreased with increasing flow.

The spatial distribution of the average POM concentrations is shown in Figure 4.

### 3.2. Mineral and organic matter flux

The annual suspended sediment flux could be calculated for all 270 sites in the HMS scheme but out of a possible 9472 site-year combinations over the monitoring period a flux calculation was possible for 6026 site–year combinations (66%) – the suspended sediment concentrations and fluxes are analysed in Worrall et al. (2013a). For the mineral matter, flux could be calculated for 111 sites and 2808 site-year combinations. Dividing the 2808 site-year combinations there were 62 with \( f > 1 \) per week, 1164 with \( f = 1 \) sample per 1-2 weeks, 639 with \( f = 1 \) sample per 2-3 weeks and 943 with \( f = 1 \) sample per 3 weeks - 1 month.

On the basis of the Anderson-Darling test, the flow-weighted annual PMM fluxes were log-transformed before ANCOVA. Both the sampling frequency and the water yield (defined above as the total discharge from a study catchment in a year – \( \Sigma Q \)) were found to be significant although they collectively only explained 11.5% of the original variance as no allowance was made for differences between catchments or changes over time. The post hoc
tests showed that within the sampling frequency factor there were significant differences between all the levels of sample frequency. Given the *post hoc* differences, the average for each class of sample frequency was compared to that for sampling frequency of less than 1 week to derive a correction factor such that samples from each class of sampling frequency could be bias-adjusted to the equivalent flux expected from a sample frequency of less than 1 week. The derived correction factors were: \( f > 1 \) sample per week = 1.00, 1 week > \( f \geq 2 \) weeks = 1.15, \( 2 > f \leq 3 \) weeks = 1.26, and 3 weeks > \( f \leq 1 \) per month = 1.31. The result suggests that for sampling frequencies of 12 per year (\( f > 1 \) month) the uncorrected result would be 69% of the true value. For phosphate, Cassidy and Jordan (2011) suggested for one site that monthly sampling (\( f = 12 \) per year) was 40% of the true value and Worrall et al. (2013b) found that for DOC monthly sampling gave a flux estimate was 48% of the true value. All the site-year combinations were then corrected according to the sampling frequency in each year.

The median POM export was 6.9 tonnes/km\(^2\)/yr, with a 5\(^{th}\) percentile of 1.9 tonnes/km\(^2\)/yr and a 95\(^{th}\) percentile as 44.4 tonnes/km\(^2\)/yr while the PMM exports have a median of 16.7 tonnes/km\(^2\)/yr with a 5\(^{th}\) percentile of 3.2 tonnes/km\(^2\)/yr and a 95\(^{th}\) percentile of 150.6 tonnes/km\(^2\)/yr. In comparison, the suspended sediment exports have a median of 22.2 tonnes/km\(^2\)/yr with a 5\(^{th}\) percentile of 5.4 tonnes/km\(^2\)/yr and a 95\(^{th}\) percentile of 107.7 tonnes/km\(^2\)/yr. The distribution of the POM flux as a proportion of suspended sediment flux for each of the study catchments is given in Figure 5. Given the values of the carbon content and C/N ratios outlined above, it is possible to estimate the range of POC flux of 3.2 tonnes C/km\(^2\)/yr (with the range between the 5\(^{th}\) and 95\(^{th}\) percentile of 0.9 to 22.2 tonnes C/km\(^2\)/yr) and for PON of 0.4 tonnes C/km\(^2\)/yr (with the range between the 5\(^{th}\) and 95\(^{th}\) percentile of 0.1 to 2.6 tonnes N/km\(^2\)/yr). For the UK, POC fluxes are commonly reported for peat-covered catchments where the extent of degradation and vegetation cover control the loss of POC and
fluxes can be as high as 195 tonnes C/km²/yr (Evans et al., 2006) but as low as 3.4 tonnes C/km²/yr (Worrall et al., 2011). Elsewhere in the world, Hilton et al. (2012) have proposed that the steep mountain forested catchments of Taiwan are a hot-spot for POC production and export to the continental shelf with average POC export of 21 tonnes C/km²/yr for catchments up to 2900 km². For PON, the high fluxes of particulate organic matter from organic soils is reflected in PON fluxes of between 0.2 to 0.7 tonnes N/km²/yr (Worrall et al., 2012c). Russell et al. (1998) estimated PON export of between 0.06 and 0.28 tonnes N/km²/yr for 4 UK catchments up to 6,500 km².

Upscaling the POM fluxes to the national level shows the median annual UK POM flux was 1596 ktonnes/yr, peaking in 1996 at 4585 ktonnes/yr with a minimum in 2003 of 656 ktonnes/yr; this is equivalent to an export of between 2.7 and 18.8 tonnes/km²/yr. The median flux of PMM from the UK was 8121 ktonnes/yr with a minimum of 1,543 ktonnes/yr in 1978. The flux of total suspended sediment from the UK also peaked at 27,550 ktonnes/yr in 1978 and had a minimum of 2,199 ktonnes/yr in 2003 (Figure 6); this is equivalent to an export range of between 9.6 and 119.8 tonnes/km²/yr. There was no significant trend with time, either for the suspended sediment flux or for the POM flux and so, although concentration of POM was declining (Equation (v), this has no impact on POM flux. This suggests the concentration decline was predominantly at low flow where the flux is minimal, indicating a decline in point, rather than diffuse sources. A one-way ANOVA was performed on the national-scale POM flux where the one factor was set as before or after 1992, i.e. the implementation of the Urban Wastewater Directive, with the national-scale suspended sediment flux and water yield as covariates. All variables were considered both untransformed and log-transformed and the result showed that there was a significant difference across the 1992 boundary; the average decrease was 553 ktonnes C/yr, i.e. over the 18 years since the implementation of the Urban Wastewater Directive had saved; diverted as
sludge to land; or emissions to the atmosphere of 9972 ktonnes C. Note that this change is not
due to a change in total river flow as that was a covariate though it might be due to change in
the timing or distribution of the river flows within the year.

The proportion of the suspended sediment flux that was POM varied from 5% in 1990
to 48% in 2004 with a median value of 18%. There was a significant increase of the
suspended sediment flux that is POM over time since 1974 ($r^2 = 0.21$, $n = 36$, $p = 0.00$) with
the average annual increase in the proportion being 0.3%/yr.

Between the years 2001 and 2010 it was possible to calculate an average flux for 80
catchments for which complete land use, hydroclimatic and soil characteristics could be
obtained (Figure 1), but note that during this time there was no POM concentration data
measured in Scotland (excluding the 4300 km$^2$ of the River Tweed which is monitored as part
of the NE England region). The best-fit multiple regression equation was:

$$POM_{\text{flux}} = 3827 + 6.7\text{Orgmin} + 8.1\text{Org} + 7.5\text{Grass} - 2.4\text{Area}$$

(842) (2.6) (2.2) (3.3) (1.4)

$R^2 = 0.5$, $n=80$ (vi)

where: $\text{Orgmin} = \text{the area of organo-mineral in the catchment (km}^2\); \text{Org} = \text{the area of}
organic soils in the catchment (km$^2$); $\text{Grass} = \text{the area of grazed land within the catchment}
(km$^2$); and $\text{Area} = \text{the area of the catchment (km}^2\). Equation (vi) can be interpreted as an
export coefficient model where each regression coefficient is interpreted as an export
coefficient, e.g. Equation (vi) predicts that 1 km$^2$ of organo-mineral soil would export 6.7 ±
2.6 tonnes/km$^2$/yr of POM where the range denotes the coefficient’s standard error. This
interpretation suggests the biggest source of POM was organic soils but also suggests there is
no significant flux of POM from a catchment with only arable or urban land use on mineral
soils. Equation (vi) includes a significant loss term with catchment area which implies that for every additional 1 km$^2$ of catchment area 2.4 tonnes/yr of POM are lost. It is this loss term with catchment area that has been used in previous studies to estimate dissolved C and N losses (Worrall et al., 2012a & b). In equation (vi) there is a non-zero y-intercept value, i.e. even at zero km$^2$ this equation would predict a POM flux of 3827 tonnes/yr. It is not certain what such a default flux might represent but all rivers would be expected to produce an organic particles with or without inputs from the terrestrial biosphere of the catchment.

When the export (total flux per unit area of the catchment) was considered, a significant relationship was found once two outliers were removed (the River Nant y Frendod at Llansamlet = 1540 tonnes POM/km$^2$; and the River Dearne at Pasture’s Bridge = 626.9 tonnes POM/km$^2$):

\[
\log_{10}(POM_{\text{export}}) = 2.5 - 0.54 \log_{10}(Area) - 0.19 \log_{10}(\%\text{Min}) + 0.14 \log_{10}(\%\text{Org})
\]

(842) (2.6) (2.2) (3.3) (1.4)

$R^2 = 0.5$, n=80 (vii)

where: $\%\text{Min}$ = the percentage of the catchment that is covered by mineral soils; and $\%\text{Org}$ = the percentage of the catchment area that is covered by organic soils. With respect to the proportion (not percentage) of POM in the total flux the best-fit equation was:

\[
\log_{10}(P_{\text{POM}}) = 0.4 - 0.3 \log_{10}(Area)
\]

(0.2) (0.06)

$R^2 = 0.24$, n=80 (viii)
By setting \( P_{\text{POM}} = 0 \), Equation (viii) predicts that the suspended sediment flux would be 100% mineral matter for catchments smaller than 21 km\(^2\) which is a consequence of the lack of small catchments in the dataset but it also predicts the greatest decline in the proportion of POM will be for catchments < 100 km\(^2\).

4. Discussion

Flux of POC and PON from the UK

Given that the organic carbon content of organic matter is between 45 and 50% and that the average C/N ratio of suspended sediment in the UK has been found to be \(8.1 \pm 5.2\) (n=13 – Hillier (2001)) which is within the range reported by Ittekkot and Zhang (1989) for rivers from across the globe of 6.2, then it is possible to estimate a time series for POC and PON (Figure 7). The POC flux would now be estimated as having varied between 2431 ktonnes C/yr in 1996 and 313 ktonnes C/yr in 2003. Note that when estimating budgets the study provides a best estimate to 4 significant figures. The PON flux would now be estimated as having varied between 24 ktonnes N/yr in 2003 and 796 ktonnes N/yr in 1996. Based on Equation (vi) the following equations was derived:

\[
P_{\text{OC}} = 1722 + 3.00_{\text{Org min}} + 3.60_{\text{Org}} + 3.4_{\text{Grass}} - 1.1\text{Area}
\]

\( R^2 = 0.5, n=80 \)

\[
P_{\text{ON}} = 213 + 0.4_{\text{Org min}} + 0.5_{\text{Org}} + 0.4_{\text{Grass}} - 0.13\text{Area}
\]

\( R^2 = 0.5, n=80 \)
Equations (ix and x) were used to map the export of POC and PON across Great Britain (Figures 8 and 9). The POC map of Great Britain (Figure 8) reflects the distribution of organic soils in Great Britain but the highest POC exports are predicted for the uplands of England and Wales as opposed to the Highlands of Scotland, even though the latter tends to have higher elevations, and therefore higher average slopes and higher annual rainfalls. The difference between the regions is the higher grazing intensity in the English and Welsh uplands compared to upland areas in Scotland. Using the equations calculated by Worrall et al. (2012a), it is possible to predict a map of total fluvial carbon export for the UK (Figure 8). Again this highlights the importance of the grazing on organic soils in the uplands and has exports up to 25 tonnes C/km²/yr. Although this upper value is smaller than that reported by, for example, Evans et al., (2006), the larger reported values were for small areas of highly degraded peatlands, rather than areas typical of the English uplands. Similarly, the map of PON export was to that of fluvial export of dissolved N (Worrall et al., 2012b). PON export is much less than total fluvial N export (Figure 9): the majority of total fluvial N flux occurs from areas of organo-mineral soils under heavy grazing but does not mean that for individual N-species (e.g. nitrate) other land-uses and managements dominate. The results generated here could be used to update estimates of fluvial flux of carbon and nitrogen for the UK (Worrall et al., 2007, 2009, 2012a, b).

**Fluvial flux of carbon from the UK**

For POC, results suggests the mean POC flux since 1974 was 863 ktonnes C/yr a 41% increase compared to the previous estimate of 613 Ktonnes C/yr. Furthermore, Equations (ix) and (x) show that there is a loss term with increasing catchment area for both POC and PON and, thus, it is not only possible to estimate the flux of both from the UK but also to calculate the loss at source, i.e. at zero catchment area. The loss of the POC in transit through the
catchment can now also be estimated as 264 ktonnes C/yr, which gives an average POC flux at source of 1127 ktonnes C/yr.

Quinton et al. (2006) suggested organic carbon losses from soil erosion in England and Wales were between 200 and 760 ktonnes C/yr of which 120 and 460 ktonnes C/yr was delivered to streams. Rescaling the POC flux from the soil source predicted in this study to the area of England and Wales suggests that on average 720 ktonnes C/yr are delivered to first-order streams, i.e. greater than that predicted by Quinton et al. (2006) but within the range of their erosion predictions. In addition to other estimates of the other fluvial carbon components (DOC and excess diss. CO₂ – Table 3) shows that the total flux of carbon at source for the UK would be 5020 ktonnes C/yr, equivalent to 21.8 tonnes C/km²/yr, the flux at the tidal limit would be 1508 ktonnes C/ yr, equivalent to 6.5 tonnes C/km²/yr (note that due to re-assessment of rounding errors and using the most up-to-date data these values differ slightly from those reported in Worrall et al, 2013a – Table 4). The difference between the flux at the tidal limit and that at source is not necessarily a loss of carbon to the atmosphere from UK rivers as the loss may represent changes to in-stream biological production or loss to long-term storage in fluvial sediments (e.g. floodplain sedimentation).

If all the POC loss across the study catchments is assumed to be loss to carbon turnover and subsequent release to the atmosphere without loss to any stores, then the net loss of C to the atmosphere from the entire catchment area would be 3512 ktonnes C/yr, equivalent to 15.2 tonnes C/km²/yr. If all the loss to the atmosphere were as CO₂, then the greenhouse gas flux would be 12882 ktonnes CO₂eq/yr or 56 tonnes CO₂eq/km²/yr. The present UK greenhouse gas inventory suggests that UK GHG flux is 553 Mtonnes CO₂eq/yr in 2011 (Salisbury et al., 2013), i.e. the estimated greenhouse gas flux from UK rivers would represent an additional 2.3%.
The turnover of POM, or POC, within the streams of a catchment is not the whole impact that POC may have on the atmosphere. As POC leaves the fluvial network at the tidal limit, it will continue to be processed in estuaries and coastal waters, further contributing to releases to the atmosphere, before sedimenting out and being stored in marine sediments. Galy et al. (2007) report very high burial efficiencies (approx. 100%) of fluvially-derived carbon in the Ganges-Brahmaputra fan, which they ascribe to rapid burial, but these sediments also have remarkably small POC contents (0.6 x 10^{12} mol C/yr from 1 x 10^9 tonnes of suspended sediment, equivalent to less than 1% C content – Frances-Lenard and Derry, 1997) and therefore the Ganges-Brahmaputra has an export equivalent to 4.4 tonnes C/km^2/yr compared to the 3.5 tonnes C/km^2/yr that the UK exports at its tidal limit. Equally, the estimate of 100% burial, and therefore a large carbon sink due to the Ganges-Brahmaputra fan, has neglected to account for the in-stream losses of carbon from particulates before reaching the sea. For other rivers Burridge (2005) suggest a removal rate from source to ocean sediment of 70% based upon a measured burial efficiency in ocean sediment of 30%. Tappin et al. (2003) have reported a POC budget for the Humber estuary (17% of UK’s runoff drains through this estuary – residence time of 2-3 months) and found that for 3 years between 1994 and 1996 the flux of POC from the estuary was between 16 and 43% of the fluvial POC flux into the estuary and that burial rate was 4% of inputs with the remainder (between 36 and 54%) of the fluvial POC flux input to the estuary being mineralised. Extrapolating for the remaining UK runoff, then there is between 58 and 72% in-stream removal of POC discharge from UK estuaries to the shelf seas. If there is no further mineralisation in shelf seas, this suggests that a 30% burial efficiency is a conservative estimate for POC from the UK, i.e. 338 kt tonnes C/yr.

Implications for soil erosion as a carbon sink
At the soil source, POC flux studies such as Stallard (1998) have argued that the erosion of POC from soils constitutes a carbon sink since the eroded soil organic carbon lost to POC is replaced and the eroded POC itself is stored by burial. Although later studies (e.g. Van Oost et al., 2007) showed that between 53 and 95% of POC was retained and buried within a catchment, and only 26% of this replaced, this still suggests a net carbon sink from global soil erosion of 120 Mtonnes C/yr. However, as noted by Van Oost et al. (2007), no allowance was made for in-stream loss once out of the immediate catchment area, or for the burial efficiency in marine waters. Van Oost et al. (2007) report between 470 and 610 Mtonnes C/yr were lost due to soil erosion of which between 240 and 570 Mtonnes C/yr was retained in the immediate catchment, which means between 30 and 220 Mtonnes C/yr were exported to streams. On the basis of results presented here, we would argue that 70% would be removed before burial, i.e. between 20 and 150 Mtonnes C/yr would be lost to the atmosphere. Given that Van Oost et al. (2007) suggest that only 26% of the eroded C is replaced (60 to 270 Mtonnes C/yr), then the median soil erosion-driven sink of C is more like 80 Mtonnes C/yr (0.08 PgC/yr), but the range of values would be from a source of 90 Mtonnes C/yr to a sink of 250 Mtonnes C/yr and thus the possible range includes the possibility that soil erosion is a net source of C and not a net sink.

The same approach can be applied to the UK (Figure 10). Quinton et al. (2006) suggested that 60% of eroded soil organic carbon (SOC) was transferred into POC in catchments; based on the values of POC lost at the soil source to streams from this study (1127 ktonnes C/yr), this would mean 1878 ktonnes C/yr of SOC lost in soil erosion. Van Oost et al. (2007) found 26% of eroded soil organic carbon was replaced, which would mean that 488 ktonnes C/yr is replaced each year and stored in the soil. This would leave 751 ktonnes C/yr stored as part of internal redistribution that never gets to the stream network. This study would suggest that 264 ktonnes C/yr is lost in the fluvial network prior to export.
to estuaries. In calculating values in Table 3 this study assumed that all in-stream loss of POC was loss to the atmosphere and not losses to increased stream biota or losses to long-term sedimentary storage: this would mean that 264 ktonnes C/yr is lost to the atmosphere. Given the percentage losses estimated by Tappin et al. (2003) for the Humber estuary, then from an average input of 863 ktonnes C/yr as POC leaving UK rivers at the tidal limit and entering UK estuaries, the estuaries would store 34 ktonnes C/yr as permanent burial, 389 ktonnes C/yr would be mineralised, and 440 ktonnes C/yr would be exported to the shelf seas of the UK. Given Buridge’s (2005) value of 30% burial efficiency of sediment from source to burial in shelf seas, this would mean that 338 ktonnes C/yr are permanently buried and would leave a further 102 ktonnes C/yr to be mineralised. Using the convention that a negative value in a carbon budget represents a net sink to the soil, we conclude that the carbon balance due to soil erosion in the UK is between +3 and +267 ktonnes C/yr, i.e. most likely to be a source rather than a sink, even if all of the net in-stream loss of POC estimated in this study were losses to burial in fluvial sedimentation or changes in biological production.

The trade-off between replacement within catchment, transfer to the stream network and then loss in stream can be simply expressed as:

\[ replacement \ rate \geq delivery \ rate \times (1 - burial \ efficiency) \ (xi) \]

where: \( replacement \ rate \) = the proportion of the soil erosion of soil organic carbon that is replaced (e.g. 0.26 – Van Oost et al., 2007); \( delivery \ rate \) = the proportion of eroded soil organic carbon delivered to the stream network (e.g. 0.6 - Quinton et al., 2006); and \( burial \ efficiency \) = the proportion of POC flux that is buried in marine sediment (0.58 – 0.72 – this study).
Similarly, the results here can be used to improve previous estimates of nitrogen flux and add an estimate of in-stream PON loss (Table 4). The new estimate, based on fluxes and turnover rates predicted here and those produced from Worrall et al. (2012b), is that the UK is losing 814 ktonnes N/yr from the river network to estuaries (equivalent to 3.5 tonnes N/km²/yr), while at the soil source the flux was 2209 ktonnes N/yr (equivalent to 9.6 tonnes N/km²/yr). Previous estimates of the net loss of dissolved nitrogen (DON, nitrate, nitrite and ammonium) could not discount the fact that loss of dissolved N was due to immobilisation of N into particulates. Since net PON flux is now included, and since it was assumed that there was no net change in immobilisation, the net catchment loss of N would be to the atmosphere. Average net loss to the atmosphere across UK catchments is estimated to be 1395 ktonnes N/yr (equivalent to 5.7 tonnes N/km²/yr). The overwhelming majority of this loss will be as N₂ but Baulch et al. (2011) found a consistent N₂O yield of 0.75% across 72 watersheds in the US which would mean for the UK an N₂O flux from the river network of 10.5 ktonnes N/yr, equivalent to 33 ktonnes N₂O/yr. The present estimate of N₂O flux from UK rivers is 24 ktonnes N₂O/yr, based on IPCC guidelines that the N₂O yield would be 2.5% of leached N, where leached N is calculated as 30% of applied fertiliser and manure N when runoff is greater than 50% of pan evaporation (IPCC, 2007) It was not possible to use the same runoff criterion for this study as pan evaporation are not known, but total dissolved N at source was 1996 ktonnes N/yr (the present value used is 616 ktonnes N/yr) of which 2.5% would be 49.5 ktonnes N/yr, equivalent to 154 ktonnes (N₂O)/yr. The greenhouse gas warming potential of this would be 45892 ktonnes CO₂eq/yr over a 100-year window – an 8% addition to the current UK greenhouse gas inventory. 

*Alternative POM loss mechanisms*
This study assumes that the difference in POM flux with catchment size is due to loss of organic matter and in Figure 10 a question mark has been left against the amount of POM that is retained within the fluvial network, i.e. as permanent burial within fluvial sediments. Other than due to turnover to the atmosphere, the change in POM flux across a catchment could be due to fractionation during the in-catchment sedimentation processes which could preferentially remove the highly organic sediment compared to more mineral-rich sediment. Alternatively, the sediment sources could change through a catchment with mineral-rich sources being more prevalent with increasing catchment size. Slopes lessen with increasing catchment size and land use changes, but the approach here has explicitly accounted for changes in suspended sediment sources with both soil and land use.

In the UK, mineral soils and arable land are more common near the tidal limits, and UK uplands are more typically dominated by organic and organo-mineral soils on grazed land but, by including all of these in the analysis, such variations have been accounted for. Also, the maximum altitude of each catchment was considered, so changes in source are accounted for, although it is possible sources may vary with changing slope and the absence of a slope factor may explain the relatively low $R^2$ of equation (iv). Alternatively, the POM could enter permanent burial within the fluvial network. Walling et al. (2002) noted that in-channel storage was between 2 and 5% of the catchment outlet flux and, further, Walling et al. (1999) estimated the rate of contemporary overbank sedimentation was between 39 and 40% of catchment outlet flux. However, overbank sedimentation does not necessarily represent a permanent burial of carbon and POM stored in floodplain sediment might still be lost to the atmosphere. Erkens (2009) gives long-term, Holocene accumulation rates of total sediment in the Rhine floodplain as 27% of the upstream input, but this was not a measure of the organic carbon storage. Hoffman et al. (2009) suggest that the long-term storage of carbon on the Rhine floodplain is equivalent to the downstream flux of POC at the catchment.
outlet. In contrast, Gomez et al. (2003) have found only 4% POC storage in a New Zealand floodplain. Given the nature of the monitoring used in this study, the likelihood that times of overbank sedimentation have been captured is very small and as such the loss POM from the fluvial network estimated here is unlikely to include overbank sedimentation and more likely to represent the in-channel sedimentation and turnover to the atmosphere. Therefore, this study has left the value of in-stream mineralisation versus long-term fluvial basin storage as unknown and has taken the precautionary and conservative approach of leaving the value of POC loss to mineralisation as that estimated in this study, i.e. 264 ktonnes C/yr.

The decline in suspended sediment export (often referred to as sediment yield in the literature) through a catchment has often been expressed as a sediment delivery ratio (e.g. Walling, 1983). Most contemporary sediment budgets do not include a component of carbon turnover; for example, of the 11 sediment budgets given in Walling and Collins (2008), not one includes a component of loss to the atmosphere. Given the average sediment delivery ratio for the UK is 10%, and suspended sediment flux at the tidal limit as calculated by Worrall et al. (2013a), then the amount of suspended sediment that would have to be stored would be of the order of 90%, or 84 Mtonnes/yr. This decline in sediment yield has also been associated with storage of suspended sediment in channel and on to floodplains - Collins and Walling (2007) measured this for a UK stream as between 18 and 57% of the suspended flux at the catchment outlet for two lowland streams in the UK but noted that most of this storage was transient. Of course, each alternative mechanism for the reduction in POM flux with catchment requires that POM is preferentially removed, but low-density POM may be preferentially lost in low-slope catchments and it is known that organic particles may be preferentially eroded from soils (Quinton et al., 2006). Furthermore, if fractionation of POM into long-term fluvial sediments is invoked to provide an alternative to explain loss of POM across catchments as turnover to the atmosphere, then it must also be assumed that, once
stored in channel or overbank sediments, it is not turned over to the atmosphere there or conversely stimulates additional carbon storage from additional biomass in those stores. A number of laboratory studies have considered the turnover of POC in streams and Moody et al. (2013) found between 38 and 87% removal of peat-derived POC over a 10-day period, i.e. a measured removal rate larger than estimated from this study.

5. Conclusions

This study has estimated that:

i) The median POC content of suspended sediment at the tidal limit between 1974 and 2010 was 15.8%, giving a median concentration of 2.2 mg C/l;

ii) The median POC flux at the tidal limit (between 1974 to 2010) was 3.3 tonnes C/km²/yr. The estimated average POC flux from the UK at the tidal limit was between 312 and 2178 ktonnes C/yr, with the proportion of POC to suspended sediment flux ranging from 2.4 to 22.8%;

iii) Between 1974 and 2010 there was no significant trend in the POC flux but the proportion of the suspended sediment flux that is POC has significantly increased by 0.15% per year;

iv) Despite a lack of significant long-term trend in concentration or flux of POM, there was a significant decline in concentration and flux of POM after implementation of the Urban Wastewater Directive in 1992;

v) The study has shown net watershed losses equivalent to loss of 1.1 tonnes C/km²/yr for POC and equivalent to 0.22 tonnes N/km²/yr for PON;

vi) This study estimates that for total nitrogen species UK rivers are gaining 2209 ktonnes N/yr (9.6 tonnes N/km²/yr) from the terrestrial biosphere but are losing 63% of this nitrogen by the tidal limit.
vii) The total flux of carbon to UK rivers from the terrestrial biosphere is estimated to be 5020 Ktonnes C/yr (21.8 tonnes C/km$^2$/yr) and the net catchment loss is 70%.

viii) The inclusion of the net catchment loss of POM means that it is unlikely that soil erosion leads to a net carbon accumulation; soil is likely to be a net source rather than a net sink of carbon therefore.

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References


Cambridge, United Kingdom and New York, NY, USA.


Figure 1. Location of monitoring points for which: a) suspended sediment export could be calculated for the period 1974-2010; and b) Location of monitoring points for which a PMM and POM export could be calculated for the period 2001-2010. Both maps are separated by the regions used for area-weighted averaging of fluxes.

Figure 2. The annual least mean square PMM and POM concentrations from 1974 to 2010 with and without consideration of the covariates.

Figure 3. The annual least mean square PMM proportions from 1974 to 2010 with and without consideration of the covariates.

Figure 4. The distribution of the average POM concentration for the country over the period 1974 - 2010.

Figure 5. The distribution of the proportion of POM flux within the suspended sediment flux across the country for the years 2001 to 2010.

Figure 6. The time series of the national flux of POM in comparison to the national flux of suspended sediment.

Figure 7. The time series of the national flux of POC and PON in comparison to the national flux of POM.

Figure 8. The projected map of: a) POC export at source; and b) total fluvial export of C at source.
Figure 9. The projected map of: a) PON export at source; and b) total fluvial export of N at source.

Figure 10. Schematic carbon budget for POM from the UK.
Table 1. The distribution and spatial coverage of catchments where POM flux could be calculated. Regions refers to those illustrated in Figure 1.

<table>
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<th>Area of study catchments (km$^2$)</th>
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<td>Thames Basin</td>
<td>1</td>
<td>12900</td>
<td>150</td>
<td>1.2</td>
</tr>
<tr>
<td>SE England</td>
<td>6</td>
<td>10979</td>
<td>1825</td>
<td>16.6</td>
</tr>
<tr>
<td>Hampshire Basin</td>
<td>6</td>
<td>6422</td>
<td>3268</td>
<td>50.9</td>
</tr>
<tr>
<td>SW England</td>
<td>6</td>
<td>14298</td>
<td>1496</td>
<td>10.5</td>
</tr>
<tr>
<td>Wales</td>
<td>9</td>
<td>20779</td>
<td>2238</td>
<td>10.8</td>
</tr>
<tr>
<td>Scotland$^3$</td>
<td>0</td>
<td>74087</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>N Ireland</td>
<td>0</td>
<td>13843</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>111</strong></td>
<td><strong>243564</strong></td>
<td><strong>63346</strong></td>
<td><strong>26.0</strong></td>
</tr>
</tbody>
</table>

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

$^3$ 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 proportion of the variance explained by factors, interactions and covariates for the ANOVA of PMM content and % PMM content.

<table>
<thead>
<tr>
<th>Factor (covariate)</th>
<th>PMM content</th>
<th>%PMM content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without covariates</td>
<td>With covariates</td>
</tr>
<tr>
<td>ln(flow)</td>
<td>0.2</td>
<td>1.3</td>
</tr>
<tr>
<td>ln(sedt)</td>
<td>95.3</td>
<td>3.5</td>
</tr>
<tr>
<td>Year</td>
<td>11.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Month</td>
<td>1.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Site</td>
<td>63.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Year*Month</td>
<td>13.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Error</td>
<td>9.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 3. The summary of the fluvial carbon fluxes for the UK.

<table>
<thead>
<tr>
<th>Carbon pathway</th>
<th>Flux (ktonnes C/yr)</th>
<th>Export (tonnes C/km²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Worrall et al. (2007)</td>
<td>Worrall et al. (2012)</td>
</tr>
<tr>
<td>POC</td>
<td>614</td>
<td>614</td>
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<tr>
<td>POC loss</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DOC</td>
<td>856</td>
<td>909</td>
</tr>
<tr>
<td>DOC loss</td>
<td>403</td>
<td>2650</td>
</tr>
<tr>
<td>Excess CO₂</td>
<td>598</td>
<td>598</td>
</tr>
<tr>
<td>Total loss at source</td>
<td>2472</td>
<td>4770</td>
</tr>
<tr>
<td>Total loss to atmosphere</td>
<td>1002</td>
<td>3248</td>
</tr>
</tbody>
</table>
Table 4. The summary of the fluvial nitrogen fluxes for the UK.

<table>
<thead>
<tr>
<th>Carbon pathway</th>
<th>Flux (kttones C/yr)</th>
<th>Export (tonnes N/km2/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Worrall et al. (2009)</td>
<td>Worrall et al. (2012)</td>
</tr>
<tr>
<td>PON</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>PON loss</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DON</td>
<td>160</td>
<td>105</td>
</tr>
<tr>
<td>DON loss</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>Nitrate</td>
<td>517</td>
<td>402</td>
</tr>
<tr>
<td>Nitrate loss</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>27</td>
<td>120</td>
</tr>
<tr>
<td>Ammonia loss</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Nitrite loss</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total loss at source</td>
<td>2165</td>
<td>2209</td>
</tr>
<tr>
<td>Total loss to atmosphere</td>
<td>1421</td>
<td>1395</td>
</tr>
</tbody>
</table>