Biogeochemistry (2007) 86:63–75
DOI 10.1007/s10533-007-9145-8

ORIGINAL PAPER

The flux of carbon from rivers: the case for flux from England and Wales

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Received: 22 June 2006 / Accepted: 30 June 2007 / Published online: 9 August 2007

Abstract This study uses the extensive monitoring datasets of the Environment Agency of England and Wales to calculate the flux of dissolved organic carbon (DOC); particulate organic carbon (POC); and excess dissolved CO_2 through English and Welsh rivers. The innovation of this study's approach is to account for the losses of carbon within the fluvial system as well as fluxes at the catchment outlet. In order to make this assessment this study considers: the biochemical oxygen demand (BOD) as a measure of the degradation of DOC; and the dissolved CO_2 concentration of groundwater as calculated and apportioned into surface waters on the basis of Ca concentrations. The study shows that the best estimate of carbon export, via rivers, from England and Wales is 10.34 Mg C/km^2/year, with 4.19 Mg C/km^2/year of this going to the atmosphere. The mapping of the carbon export shows that there are regional hotspots of carbon export and in a small number of cases rivers could be net sinks of carbon due to their low dissolved CO_2 content relative to the atmosphere. The flux calculated by this approach is probably still an underestimate of the carbon flux through fluvial systems but the scale of the export is greater than that previously reported and there is evidence that the fluvial flux of carbon is increasing on a decadal scale.

Keywords Carbon · Rivers · DOC · POC · Dissolved CO_2

Introduction

Several attempts to understand the role of rivers in the global carbon cycle have been limited by incomplete inclusion of within river processes. Most of these studies have considered particulate organic carbon, dissolved organic carbon and dissolved inorganic carbon flux from land to sea (e.g. Schlesinger and Melack 1981; Meybeck 1982, 1993). Meybeck (1993) estimated that the flux of dissolved organic carbon (DOC) and DIC from the World's rivers to the oceans was of the order of 542 Tg C/year of atmospheric carbon with the proportions 37:18:45 split between DOC:POC:DIC. A further 217 Tg C/year are transported resulting from weathering. These studies all calculate dissolved inorganic carbon at the river outlet and are concerned with flux to the oceans they cannot be applied to understanding loss of carbon from the terrestrial reserves of carbon. Such

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an approach ignores the fact that any water on the surface of the earth is in contact with a CO_2 containing atmosphere. Most rivers will be at or near equilibrium with the atmosphere and would contain the equilibrium amount of CO_2 whether inorganic carbon was coming from the terrestrial biosphere or not, i.e. the calculation of the dissolved inorganic carbon flux would be an overestimate. Therefore, the calculation should be of the excess dissolved CO_2, i.e. of the concentration of dissolved CO_2 present above that which would be present due to equilibrium with the atmosphere. Secondly, the outlet of the river and the river itself are not the source of the majority of the carbon, the river is largely the conduit of the carbon. The river represents a finite travel time and the flux is being measured at the end of that time and not at its beginning at the source of the majority of the carbon. By calculating the flux at the river output the calculation ignores what has happened in getting to that point. Cole et al. (1994) have shown, in a survey of 1,835 lakes across the globe, that on average lakes were supersaturated with respect to the atmosphere by a factor of three and that assuming this value then degassing of CO_2 from lakes would represent an additional 140 Tg C to the atmosphere per year, i.e. carbon flux estimates appear to underestimate the importance of dissolved CO_2. In soils and rocks groundwaters are out of contact with the atmosphere and acquire additional CO_2 from the biosphere, upon release to the surface these water are carrying excess dissolved CO_2 which will degas to the atmosphere upon emergence. The timescale for water obtaining equilibrium with the atmosphere is of the order of 100 h, i.e. close to the water residence time in many rivers (Morel and Hering 1993). Therefore, by measuring the dissolved CO_2 at the river outlet to the sea the carbon lost to the atmosphere during the flow of the river is not accounted for and that carbon from the terrestrial biosphere is therefore underestimated. An example of this is seen in Worrall and Lancaster (2005) where for the Thames basin (9,948 km^2) the export of excess dissolved CO_2 as assessed at the catchment outlet is 0.18 Mg C/km^2/year, however, when assessed in terms of that released from the soils and groundwater of the catchment the export becomes 2.14 Mg C/km^2/year.

Thirdly, not only is dissolved CO_2 lost in transit within the river system. DOC is mineralised within the river system from its source to the river outlet, and therefore measuring DOC flux solely at the river outlet is again an underestimate. DOC is also produced within the river system and assessing the DOC flux at the river outlet will therefore be able to make an allowance for this component after respiration. However, a range of studies have shown that in-stream production of DOC is not as great as the amount of DOC coming from the source. Worrall and Burt (2004) working on the River Tees (818 km^2) have shown an average net loss of 40% of DOC from source to outlet.

Cannell et al. (1999) have produced an inventory of UK terrestrial carbon stocks for 1990 based upon the IPCC guidelines (Houghton et al. 1996). Included in the inventory of Cannell et al. (1999) are some sources and sinks not included in the IPCC guidelines (Houghton et al. 1996). The sources and sinks include the flux of DOC and POC from rivers. Cannell et al. (1999) report the UK terrestrial carbon as a net source of 4.0 Tg C/year and as part of this they report UK rivers as being a net source of 1.4 Tg C/year to the oceans (0.53 Tg C/year for England and Wales—3.5 Mg C/km^2/year) based largely upon the study of Hope et al. (1997).

So, this study sets out to calculate carbon flux from the rivers of England and Wales to the oceans and to the atmosphere accounting for losses within the river system.

Methodology

The study considers the following carbon species: DOC; particulate organic carbon (POC); dissolved CO_2—expressed as excess CO_2 (Dawson et al. 2002). The defined flux as the total mass of material whereas export refers to the flux per unit area.

The data from the harmonised monitoring network for England and Wales is collected at 214 river sites in England and Wales. The monitoring site at Norham on the River Tweed is included in the study even though it comes within Scottish jurisdiction as its catchment represents the boundary of England and Scotland. Rivers for monitoring are selected as the tidal limit of rivers with an average annual discharge over 2 m^3/s; in addition, any tributaries that have a discharge above that level are included as well. In the case of this study this means that catchment sizes considered varied from 87–9,948 km^2. The monitoring process is the responsibility of the regional office of the Environment Agency in England and Wales and in the case of the River Tweed, the Scottish Environment Protection Agency. All methodologies are the standard methods, for particular discussion of methodologies established as part of the harmonised monitoring scheme see Blake (1983) and Simpson (1980). These regional offices are not obliged to monitor any of these three parameters at each of the harmonised monitoring sites and so not all sites have records for these parameters.

Dissolved organic carbon is not measured at every location and so when it is not directly available a range of other water quality parameters are used to estimate the DOC concentration, the ones pertinent to this study are: water colour (hazen units), chemical oxygen demand (COD—mg O_2/l), and biochemical oxygen demand (BOD—mg O_2/l). The particulate organic carbon is not measured in the Harmonised Monitoring Scheme and so this study uses suspended sediment (mg/l) measured within the scheme and then estimates of the organic carbon content of the suspended sediment are utilised to estimate POC content. The excess CO_2 is calculated using the method of Neal et al. (1998a) that utilises available pH, Ca and alkalinity measurement. Instantaneous flow and average daily flow are available from the Harmonised Monitoring Scheme. However, data sets for sites are not necessarily complete. The study considers the year 2002, and although at a small number of localities sampling was as frequent as weekly, sites with less than one sample per month in the year 2002 were not considered. The location of the sites that could be used are shown in Fig. 1.

DOC

Dissolved organic carbon data was not always available for all sites but in a number of cases data was available for the allied parameters: water colour, and COD. In order to assess DOC flux for sites where these parameters rather than DOC were available calibration curves between DOC and water colour, and between DOC and COD, were constructed for sites where both parameters were available. Curves so developed were then applied to sites were DOC was not available. For sites where the suite of measurements varied over the period of sampling then calibration curves developed for that site were used to fill in breaks in the record. The flux from England and Wales was then calculated using an area weighted average of DOC export rates based upon the harmonised monitoring regions rather than the countries as a whole. These are the same regions as used by Hope et al. (1997). This approach better represents regional hot spots without biasing the national value due to uneven spatial distribution of available records. Because DOC is an analysis not required within the Harmonised Monitoring Scheme not all regions include it in their suite of analyses, and thus a method representing regional differences is more appropriate. This study has made several improvements over that of Hope et al. (1997) in that it: had proportionately more sampling sites (79 catchments in total); the sites represented a better regional spread; and all site information was used in the calculation of the export rather than analysis based upon 17 representative catchments.

In order to make an allowance for in-stream processes and the turnover of DOC, the flux of BOD is considered. The BOD flux could be assessed on the basis of 62 catchments. The biochemical oxygen demand represents the amount of dissolved oxygen that a water will consume and given the general stoichiometry of organic matter turnover the consumption of dissolved oxygen represents the production of CO_2, and hence the BOD can be used as a measure of the river water capacity to mineralise DOC. The BOD flux is being measured at the catchment outlet and so is a measure of the potential mineralisation at that point and not at the source of the DOC. As many studies have suggested, DOC is most labile at its point of production rather than after transit through the river system (Kalbitz et al. 2003). However, no other measure of mineralization potential is available on this scale. The BOD is measured over a 5 day period and so it does represent that loss of DOC over a period similar to the residence time in many river systems, though it should be considered as an underestimate.

Particulate organic carbon

For the purpose of comparison with estimated DOC fluxes values of the annual POC flux are estimated from the suspended sediment flux. Unlike DOC, suspended sediment concentrations are monitored

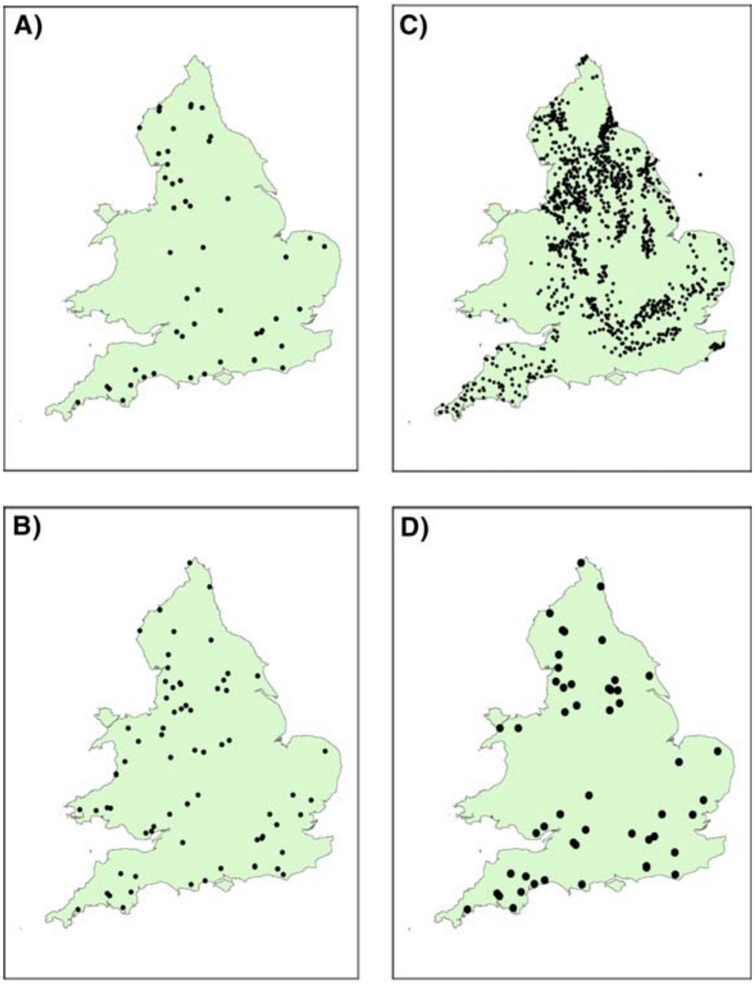

Fig. 1 Location of sites used in this study where harmonised monitoring data was available for: (**A**) DOC; (**B**) POC; (**C**) Boreholes where dissolved CO_2 could be calculated; and (**D**) BOD

within the Harmonised Monitoring Scheme as a national obligation under the Oslo and Paris Treaties (OSPAR Commission 2004). Therefore suspended sediment fluxes have been reported for the UK from 1990 onwards although only 70 catchments had sufficient data to calculate a flux. The suspended sediment concentration can vary in its organic carbon content and for British rivers, Hope et al. (1997) give a preferred value of 14%, while Hillier (2001) measuring the carbon content of suspended sediment from throughout the River Don in Scotland (catchment area = 1,320 km^2) showed values that varied between 6.9 and 14.1%. Neal (2003) studied sediment from rivers with catchment areas from 373 km^2 to 8231 km^2 and organic carbon contents to vary from 5% to 17%. As the latter study is the most comprehensive in terms of area and river type this study will calculate POC flux considering a range of organic carbon content of suspended sediment of 5–17% with the median value of 11% being taken as the preferred value.

Dissolved CO_2

In order to calculate the export of dissolved CO_2 for the region it is necessary to know the amount of dissolved CO_2 at source and not at the catchment outlet. The flux of carbon dioxide via this route can be calculated if the excess CO_2 of the source groundwater is known and the proportion of the source at the catchment outlet.

The method calculates the excess dissolved CO_2. The excess CO_2 ($EpCO_2$) is defined as the amount of dissolved CO_2 in the water in comparison to that expected in equilibrium with the atmosphere. Neal et al. (1998a) have suggested a series of methods for calculating $EpCO_2$ from stream monitoring data with a more sophisticated method being possible depending upon the level of monitoring data available. Where Ca concentrations are available a complete speciation can be performed using the method of Neal et al. (1998a) and Worrall et al. (2005a). However, both these manuscripts have typographic errors in their methods and this study has corrected Worrall et al. (2005a) in the following ways:

$$-\log_{10} K_2 = 0.022379(273+T) + \left(\frac{2902.39}{(273+T)}\right) - 6.498$$

$$-\log_{10} K_6 = 0.01705(273+T) + \left(\frac{4471.33}{(273+T)}\right) - 6.0846$$

$$K_{\mathrm{H}} = 0.034e^{\left(\frac{-4.772}{0.001987}\left(\frac{1}{298}-\frac{1}{(273+T)}\right)\right)}$$

where T = water temperature in °C.

When there is no Ca concentration data available, Worrall and Burt (2005a) have shown that a strong linear correlation exists between $\mathrm{EpCO_2}$ as calculated based upon pH, alkalinity and stream temperature alone and that calculated using Ca concentration data. This strong linear correlation has been observed in three different catchments (Worrall et al. 2005a) and was observed to hold true for a range of $\mathrm{EpCO_2}$ values and across the water year but only for pH > 5.5. Thus $\mathrm{EpCO_2}$ can be calculated as:

$$\mathrm{EpCO_2} = \frac{0.719(0.95\mathrm{Alk_{Gran}} + 10^{(6-\mathrm{pH})} + 10^{(6+\mathrm{pH}+\mathrm{pK_6})})10^{(6-\mathrm{pH})}}{(6.46-0.0636T)(1+2.3810^{(\mathrm{pH}-\mathrm{pK_2})})} \tag{1}$$

where $\mathrm{Alk_{Gran}}$ = the Gran Alkalinity in μEq/l. Thus $\mathrm{EpCO_2}$ can be calculated with only a knowledge of streamwater alkalinity, pH and temperature. The $\mathrm{EpCO_2}$ is converted to a concentration by knowledge of the Henry's constant for the situation. The alkalinity, Ca and pH data from the Environment Agency of England and Wales' groundwater monitoring network was utilised (Fig. 1). This dataset covers 1,514 monitoring sites, mainly boreholes but including some springs. These monitoring points include all major and minor aquifers across the two countries. For each borehole the average excess dissolved $\mathrm{CO_2}$ concentration for 2002 is calculated.

Jones and Mulholland (1998) have suggested that stream temperature is indicative of the groundwater temperature. The temperature range of the Thames has been reported by Neal et al. (1998b) who observe values between 10°C and 23°C, while Webb and Zhang (1999) for chalk streams in southern England showed a range of between 5.5°C and 12.1°C in winter and between 11.5°C and 20°C in summer. For the purpose of this study the temperature used in the calculation of $\mathrm{EpCO_2}$ is varied within this range in order to assess sensitivity to this variable.

In order to estimate the flux of dissolved $\mathrm{CO_2}$ from groundwater it is necessary to understand how much of each groundwater sampled contributes to river flux. In order to do this the average Ca concentration of each groundwater monitoring point in the study for the year 2002, is also calculated along with the average excess dissolved $\mathrm{CO_2}$ concentration. The average Ca concentrations in the monitored groundwater are mapped across England and Wales, as is the average Ca concentration at all the harmonised monitoring network surface water sites. These two maps are compared to map the proportion of groundwater in the surface waters of England and Wales. This approach is that of Jones and Mulholland (1998) and assumes that surface waters can be explained by a two end-member mixing model, where one end-member is Ca-rich groundwater.

River flux error analysis

The calculation of flux has several sources of error. Firstly, a wide range of methods have been proposed for calculating river fluxes from concentration and flow data (e.g. De Vries and Klavers 1994; Littlewood 1995). These methods differ between interpolation methods (e.g. Webb et al. 1997) and extrapolation methods (e.g. Duan 1983). Webb et al. (2000) generated synthetic concentration time series and tested a number of flux estimation methods and suggested that interpolation methods were generally more reliable and less prone to errors than the more complex extrapolation methods. Littlewood et al. (1998) recommend the use of method 5 where data is relatively sparse as for the harmonised monitoring scheme, but showed that the best estimation method could vary between determinands and between catchments—they did not review data for DOC, dissolved CO_2 or POC. Furthermore, extrapolation methods work best where a good rating curve between concentration and flow can be found, but this is not true with determinands where there is a strong seasonal component. The DOC and dissolved CO_2 have a strong seasonal component (Naden and McDonald 1989), and the sparcity of POC data relative to the hydrological cycle means that extrapolation methods are not appropriate. This study uses "method 5" (Littlewood et al. 1998):

$$\text{Flux} = K \frac{\sum_{i=1}^{n} [C_i Q_i]}{\sum_{i=1}^{n} Q_i} Q_T$$

where: K = conversion factor allowing for period of sampling; C_i = concentration of determinand in sample i; Q_i = instantaneous discharge at sampling time i; Q_T = mean river discharge over the period; and n = no. of samples.

A second source of error is the sampling frequency. The detail of the monitoring at these sites maintained by water companies makes it possible to assess the error in making flux estimations from sparsely sampled data. The daily measurements of water colour at the Broken Scar water treatment works for the year 2002 were examined to assess the likely error incurred by estimating flux from 12 monthly spot samples. From the daily measurements 200 sets of 12 random data points, one from each month, are selected and the flux calculated. The distribution of these fluxes based on monthly spot calculations is compared to flux calculated on the basis of all 366 data points.

An additional source of error is the scaling up of the flux from the individual catchments to the region. As data are only available for a limited number of catchments within each region there is an inherent sampling error. In order to estimate the scale of this uncertainty, for the year 2002, the lower and upper quartile of export for each Harmonised Monitoring Scheme region is considered as the best estimate for the whole region and then these estimates are scaled to the England and Wales as a whole.

For the calculation of the DOC flux there is the separate source of error due to calibration between DOC and colour or COD when direct DOC data is not available. In these cases the error in the fit of the calibration is considered relative to error in calculating flux and scaling up export estimates as outlined above. For the POC flux the variation in the organic carbon content of the POC is also considered with the range stated above (5–17% organic carbon content) being used.

Results

Calibration and error analysis

The calibration between water colour (Hazen) and DOC was possible on the basis of information from 44 sites. The best-fit regression is:

$$\text{DOC} = 0.379\text{Colour}^{0.83} \quad r^2 = 0.72, n = 477 \tag{2}$$

where: DOC = dissolved organic carbon (mg C/l); and Colour = water colour (Hazen). Watts et al. (2001) studied the relationship between Hazen and the absorbance at 400 nm for a range of UK reservoirs and showed that relationships were site-specific with some evidence of seasonal variation. However, Eq. 2 is a significant relationship across a wide range of years, seasons and flows, furthermore, this equation is only required for two sites out of the 79 available for the calculation of the DOC flux and so it is not considered important to assess the error in the DOC flux calculation relative to the use of this equation at only two sites.

The best-fit calibration between COD and DOC is:

$$\text{DOC} = 10.09\log_e(\text{COD}) - 7.19 \quad r^2 = 0.47, n = 489 \tag{3}$$

This equation had to be used for 42 out of the 79 sites used in the calculation of DOC flux. Although this equation, as with Eq. 2, was derived across a range of years, seasons, flow conditions and catchments its widespread use means that the error due to this calibration needs to be considered. In order to asses the error due to this calibration the standard error in the estimation of DOC is assessed across the range of COD observed (0–130 mg/l). The standard error in the estimation of DOC from this approach varies from ±1.5% to 7.2%, the largest error being at the bottom of the concentration range. The bottom of the concentration range is less important in flux calculation as these low concentrations contribute less to the overall flux.

The error in the calculation between flux calculated from monthly sampling compared to daily sampling is assessed as the difference between each of the 200 calculations taken from random data and the value of the flux calculated from the daily data. The flux based on daily data is 1.4 Gg C, the distribution of these differences is approximately normal with a mean of 0.2 Gg C, and a percentage standard error of 15%, i.e. the error on a flux calculated based on monthly data compared to daily data is taken as ±15%. This should be considered a sampling error and not as a systematic bias in the method. This is a larger source of error than that due to the calibration, firstly, because it is larger source of error; secondly, because it applies to all sites and not just a proportion; and thirdly, because such an area is true for the DOC, POC, DOC and BOD components of the flux and not just the DOC.

Webb et al. (1997) studied the application of different methods to the calculation of flux. For DOC they showed that between seven methods, including both interpolation and extrapolation methods, the percentage difference between the minimum and maximum estimates was 28% expressed as a percentage of the minimum estimate, slightly smaller than the uncertainty calculated above. The comparison of methods shows that the flow-weighted methods give generally higher values than those which are time-weighted—thus study uses a time-weighted method.

POC

Over the period 1990–2002 the flux of suspended solids varied from 1.2 Tg/year to 3.2 Tg/year (OSPAR Commission 2004). Given the assumption of carbon content of between 5% and 17% as stated above the POC export in 2002 was between 1.63 Mg C/km^2/year and 4.73 Mg C/km^2/year (Table 1), with a preferred value of 2.27 Mg C/km^2/year based upon a 11% carbon content (Hope et al. 1997). The range based upon the uncertainty in the organic carbon content of the suspended sediment is larger than that which would be predicted by a 15% error due to infrequent sampling. If the minimum and maximum flux values are examined, given an organic carbon content of 11%, the range is from 0.84 Mg C/km^2/year to 25.1 Mg C/km^2/year. Such a large range suggests that the range of POC export between individual catchments is broad and has a highly skewed distribution with some catchments having sizeable fluxes. Very few studies are reported for large areas of England and Wales, but Arnett (1978) reports POC fluxes for English catchments up to 300 km^2 with export of up to 0.5 Mg C/km^2/year. This study suggests higher values with hotspots (Fig. 2). As a consequence of the contouring process and the fact that the HMS sites are generally located at the tidal limit the hotspots can appear to be at the coast when in fact it represents the whole of the catchment stretching back inland. However, there does appear to be a hotspot in the northwestern England and this probably related to highly eroded peat soils in the headwaters of these catchments that lie along the Pennine chain of hills that runs north–south in central England. There does appear to be an increasing trend in the flux of the POC (Fig. 3) over the period of reporting with a minimum in the year 1996. The multi-annual decline and recovery in POC flux occurs over the period of the driest years in the record which reached its minimum in the summer of 1995 which for some areas of the UK was a 1 in 100 year drought (Hulme 1998).

DOC

The export measured for DOC varies between 0.29 Mg C/km^2/year and 32.46 Mg C/km^2/year, with by far the highest values being found in the north west of England for rivers Ribble and Lune (Fig. 4). As for POC, apparent costal hotspots are a consequence of the site distribution and contouring, but the catchments that are highlighted as hotspots again drain the western edge of the Pennines where poor land management and atmospheric pollution has

Table 1 The summary of the export rates and estimated ranges for England and Wales

Carbon pathway	Flux (Tg C/year)	Preferred export rate (Mg C/km^2/year)	Percentage of total flux	15% error (Mg C/km^2/year)	Alternative error range
POC	0.38	2.27	25	1.93–2.62	1.62–4.73
DOC	0.53	3.97	35	3.37–4.56	1.91–9.73
BOD	0.25	1.66	16	1.63–1.91	0.62–2.62
Excess CO_2	0.37	2.44	24	2.07–2.88	–
Total	1.53	10.34		9.00–11.97	6.22–19.96

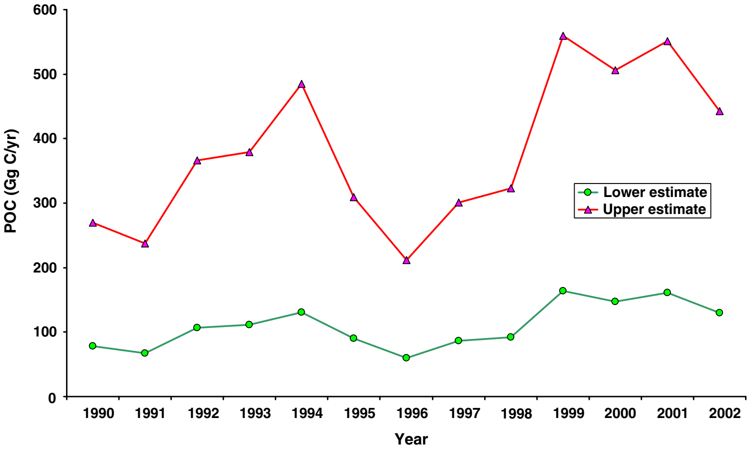

Fig. 2 The export of Particulate organic carbon (POC–Mg C/km^2/year)

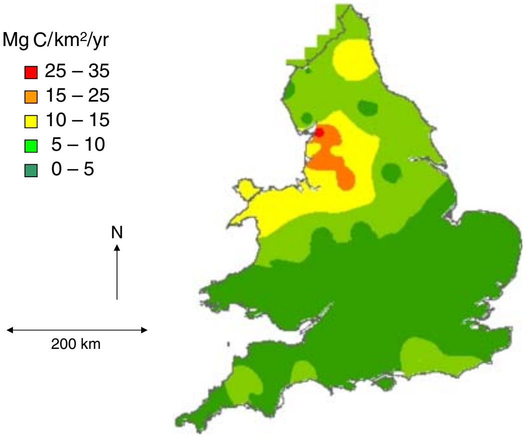

Fig. 3 The trend in particulate organic carbon flux since 1992 based upon the upper and lowest estimates of organic carbon content of the measured suspended sediment

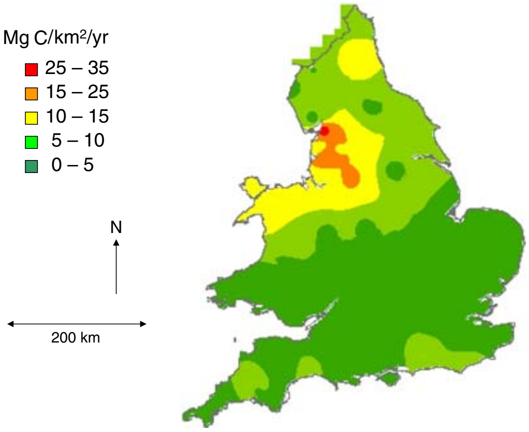

Fig. 4 The export of dissolved organic carbon (DOC–Mg C/km^2/year)

resulted in highly eroded peat soils that are both a good source of sediment and DOC (Evans et al. 2006). Using the areal weighted average approach the flux of DOC is 0.53 Tg C/year or 3.97 Mg C/km^2/year (Table 1). Taking a 15% error in the flux estimates the export of DOC would then vary from 3.37 Mg C/km^2/year to 4.56 Mg C/km^2/year. Mantoura and Woodward (1983) suggested values of

2.8 Mg C/km^2/year for the River Severn catchment (9,790 km^2). Using the maximum and minimum export for the rivers within each region gives an error estimate of 1.91–9.73 Mg C/km^2/year. Using the figures of Hope et al. (1997) they would estimate a flux of 0.42 Tg C/year. The difference between these two figures is unsurprising given the well documented increase in DOC concentrations in UK rivers through the 1990s (e.g. Freeman et al. 2001). Worrall et al. (2004) have used trend analysis based on the figure of Hope et al. (1997) to suggest that the flux would be 0.53 Tg C/year in the year 2002. Furthermore, Worrall and Burt (2005b), using a physical model for DOC flux, suggest that by 2002 the flux of DOC from the UK would be between 0.51 Tg C/year and 0.53 Tg C/year. These two independent estimates suggest that the figure of Hope et al. (1997) for 1993 is reasonable.

BOD

Biochemical oxygen demand records were only available from a limited range of sites (Fig. 1), with export varying from 0.05 Mg C/km^2/year to 5.11 Mg C/km^2/year, an export of 1.66 Mg C/km^2/year and an annual flux of 0.26 Tg C/year. Given the 15% estimated error this would suggest a range 0.25–0.29 Tg C/year, or 1.63–1.91 Mg C/km^2/year. Taking the maximum and minimum regional estimates gives a range 0.12–0.38 Tg C/year, or 0.62–2.65 Mg C/km^2/year. The export map suggests that BOD is greatest in the North–West region (Fig. 5). This is a heavily urbanised and industrial region suggesting that BOD flux as measured in this approach is dominated by anthropogenic sources rather than the turnover of natural DOC. However, the turnover of BOD still represents a loss of carbon during in-stream processing, but it does suggest that this is an underestimate and that the turnover of DOC will be higher.

Excess dissolved CO_2

The concentration of excess dissolved CO_2 as calculated varies from -12.94 Mg C/l to 246.43 Mg C/l with an average of 8.98 Mg C/l (Fig. 6). The negative concentrations suggest waters that are undersaturated with respect to atmospheric CO_2 and thus would absorb CO_2 on exposure to the atmosphere. The proportion of groundwater measured in the surface waters of the country varies from 0 to 1 with groundwater dominating in the south and east where the UK's largest aquifers are. Conversely, the proportion is lowest in the north and west where impermeable strata predominate. Given the concentrations in groundwater and proportion of groundwater across England and Wales the average concentration of excess dissolved CO_2 in surface water is 5.22 Mg C/l with a standard deviation of 5.8 (Fig. 7). The distribution of excess dissolved CO_2 does show very high values in south west England. These are the only catchments in the study draining granite catchments and so although how this increases the dissolved CO_2 is unknown to the

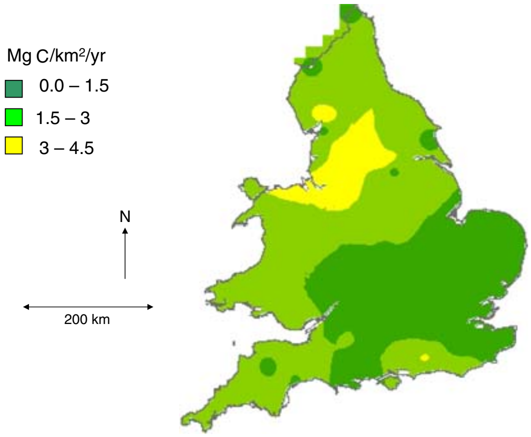

Fig. 5 The export of biochemical oxygen demand (BOD–Mg C/km^2/year)

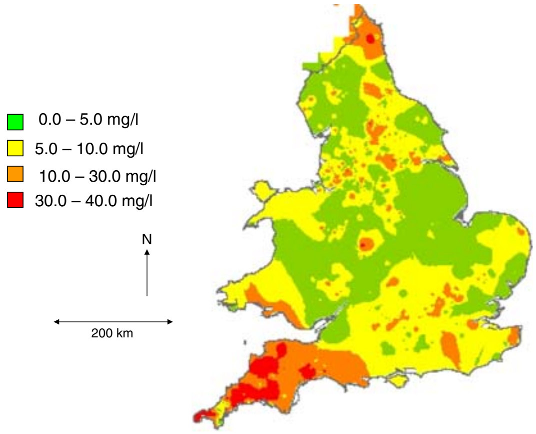

Fig. 6 The concentration of excess dissolved CO_2 in groundwater

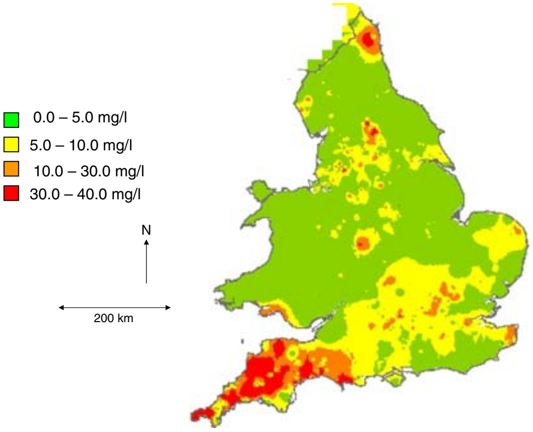

Fig. 7 The average excess dissolved CO_2 in surface waters contributed from groundwaters

authors. The range of values still suggests that there are small areas where the river water will absorb CO_2 from the atmosphere. The harmonised monitoring scheme also reports an annual discharge from England and Wales, which for 2002 was 193,954 Ml/day. At this flow rate the annual flux is 0.37 Tg C/year, or an annual export of 2.44 Mg C/km^2/year. If the 15% error in export is accepted then the range is 2.07–2.81 Mg C/km^2/year. Because of the approach it is not possible to calculate the error on the basis of minimum and maximum export. Worrall and Lancaster (2005) have calculated the excess dissolved CO_2 for the Thames basin based upon this method and found the export to be 1.59 Mg C/km^2/year. Distributing the flow across the catchment rather than based upon average content gave an export of 2.14 Mg C/km^2/year, i.e. the method used in this study could be an underestimate of the excess dissolved CO_2 flux.

Total fluvial flux

The fluvial fluxes are summarised in Table 1 where the total fluvial flux comes to 1.53 Tg C/year, or an export of 10.34 Mg C/km^2/year over a combined catchment area of 151,242 km^2. Alternatively, it is possible to think of the loss from rivers directly to the atmosphere. The export of POC and DOC is a loss from the terrestrial biosphere but not a direct loss to the atmosphere. The BOD and the excess dissolved CO_2 are measures of direct loss to the atmosphere, in which case the direct loss would be 0.62 Tg C/year, or an export to the atmosphere of 4.1 Mg C/km^2/year.

Discussion

Is this a good method for estimating the contribution of rivers to the carbon cycle? The methods used by this study for calculating POC and DOC export are well established. However, this study does not account for the loss of POC on high flows. Suspended sediment transport, and therefore POC transport, is highly dependent on flow with the majority of flux occurring on the higher flows. For most sites in this study where suspended sediment flux data are available only monthly data are available, in such sparse data it is appropriate to use an interpolation method of calculating flux, however, it is also likely that the concentrations on the higher flows would not be sampled. Thus, it is likely that this method underestimates the flux of POC. Furthermore, this study has considered unnecessary to account for any POC loss within the streams. Sedimentation and burial of POC in lakes, rivers, overbank sediments etc is not considered a loss of carbon from the terrestrial biosphere as this carbon is neither passes beyond the tidal limit to the oceans nor is it transferred to the atmosphere. However, this study has only one measure of in-stream mineralization of carbon and that is the BOD which is unlikely to fully account for any mineralization of POC.

It is the inclusion of excess dissolved CO_2 and BOD as a measure of the potential loss of DOC within the system that is innovative. The method for calculating the excess dissolved CO_2 does make a range of assumptions. Firstly, that all the Ca in the stream water comes from groundwater, this cannot be the case. Some Ca in the riverwater will come from rainwater and a portion of the Ca in the riverwater samples will come from soil water. The problem is that the model used here to assess the source of the riverwater is a two end-member mixing model—Ca-rich groundwater and Ca-poor rainwater. However, Worrall and Lancaster (2005) have demonstrated that Ca-rich soil water is also the CO_2-rich, at least as CO_2-rich as groundwater. So the assumption of the two end-member system would appear to be a good one, not because the system is hydrologically a two end-member system but rather because the additional end-members are as CO_2-rich. However, future approaches to this problem may have to consider more multiple end-member mixing models (e.g. Christophersen and Hooper 1992) if sufficient tracer information is available.

Secondly, this approach to calculating the fraction of groundwater at each of the river sites assumes that Ca concentration has been measured across the complete range of flow conditions for that river. If the Ca concentrations measured at any river site were all measured at below average flow then it would be reasonable to say that the fraction of groundwater would be overestimated.

How do these figures compare with other values reported for other river basins? There are a large number of studies of DIC, but far fewer have converted this value to an amount of excess dissolved CO_2 (e.g. Sempere et al. 2001). Abril et al. (2000) estimate excess dissolved CO_2 flux into the Scheldt estuary from its incoming rivers. The values they report vary from 1.4 Gg C/year to 6.3 Gg C/year or an export of 0.60–1.39 Mg C/km^2/year. It is important to note that this study was measuring excess CO_2 flux at the river outlets and so a large proportion of the excess CO_2 would have been lost to the atmosphere. It is interesting to note that the smallest catchment considered by Abril et al. (2000) had the largest export, i.e. where the residence time was lower the apparent excess CO_2 flux was higher. Kempe (1982) measured export of between 0.23 Mg C/km^2/year and 1.2 Mg C/km^2/year for several major European rivers but again flux estimates were measured for the catchment outlets and not sources. Studies of small catchments show higher concentrations of excess dissolved CO_2. Hope et al. (2001), for a headwater peat catchment, measured values of excess dissolved CO_2 production at 14.5 Mg C/km^2/year. Hope et al. (2001) do review the amount of CO_2 coming from first order streams but they review evasion rates and not the total flux of excess dissolved carbon. Similarly, for a different peat headwater catchment, Worrall et al. (2005b) have estimated export from the peat profile of between 9.6 Mg C/km^2/year and 25.6 Mg C/km^2/year. Worrall et al. (2005a) found that for two forested catchments the annual flux of excess dissolved CO_2 flux at source varied between 1.68 Mg C/km^2/year and 14.17 Mg C/km^2/year.

Once in the river the excess dissolved CO_2 can be consumed by photosynthesis. However, examining the record at the outflow of the Thames, which is the largest catchment in the study and where the residence time in the fluvial system could be considered to be the largest, shows that the average $EpCO_2 > 1$. The fact that $EpCO_2 > 1$ suggest that the rate of photosynthesis is secondary to other processes.

The estimation of DOC degradation from the BOD is a better measure of loss from the system than analysing the change in DOC concentration. This is because DOC can be lost from rivers by a number of processes, some of which do not result in conversion to CO_2 and loss to the atmosphere. For example, DOC can be immobilised as biota convert DOC into POC (Lock 1981) or, chemically, DOC can be removed by adsorption and/or precipitation (Thurman 1985). By using BOD this study is directly measuring mineralization rather than just loss.

However, using BOD would not account for losses due to photo-oxidation of DOC. Reported rates of photodecomposition DOC are slow relative to those for biodegradation, e.g. 32% reduction in DOC concentration over a period of 12 days (Hongve 1994). Photo-oxidation is known to be accompanied by measurable spectral changes in the character of the DOC (Corin et al. 1996) and so this could be used in a diagnostic of this process, but such data are not available to this study. Furthermore, laboratory experiments show that the easily degradable component of the DOC is removed first leaving a more resistant component (Kalbitz et al. 2003). This suggests that by taking BOD measurements at catchment outlets the study will underestimate losses as it is the mineralization of relatively old and resistant DOC that is being measured. Conversely, BOD is more likely to be a good estimate of the turnover of anthropogenic DOC, e.g. from sewage effluents, and so this may contribute to overestimation of carbon losses from the terrestrial biosphere, but still represents a loss of carbon to the atmosphere.

Conclusions

This study has proposed that fluxes of fluvial carbon have been underestimated because they do not account for in-stream losses of carbon. This study, using data for England and Wales, showed that fluvial export was 10.34 Mg C/km^2/year, with an uncertainty of between 6.2 Mg C/km^2/year and 20 Mg C/km^2/year. The total flux of carbon from English and Welsh rivers in 2002 was calculated as 1.53 Tg C, with the largest proportion of this flux being made up of DOC (42%) and of which 0.91 Tg C/year is being exported to the oceans, the rest is lost to the atmosphere from fluvial system (0.62 Tg C/year, or 4.19 Mg C/km^2/year). There is evidence that there is an upward trend on several of the components of the flux. The study has greatly improved the estimate of fluvial flux but probably still likely to represent an underestimate as the flux of POC on high flows could not be accounted for and estimation of in-stream DOC mineralization was made upon the more refractory fraction of DOC.

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