

The release of CO₂ from riverwaters – the contribution of excess CO₂ from groundwater

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Abstract. The dissolved CO₂ concentration of stream waters is an important component of the terrestrial carbon cycle and an important pathway for release of CO₂ to the atmosphere. This study uses data from the UK's largest groundwater monitoring network to estimate the importance of groundwater in contributing excess dissolved CO₂ to the atmosphere. The study shows that:

- (i) the arithmetic mean concentration of excess dissolved CO₂ in the groundwater was 4.99 mg C/l with a standard deviation of 2.53
- (ii) for the groundwater composition of excess dissolved CO₂ analysis shows no statistical difference between years but does show a significant intra-annual effect and a significant difference between aquifers
- (iii) A weighted average of the estimate the areal export of excess dissolved CO₂ from the groundwater of the catchment is between 1.4 and 2.9 t C/km²/year.
- (iv) the flux of excess dissolved CO₂ at the catchment outlet over the period between 1975 and 2002 averages 1.79 kt C/year.

If this were replicated across the UK then the flux of CO₂ from rivers would be 0.65 Mt C/year.

Introduction

Janssens et al. (2003) have suggested that Europe's terrestrial ecosystem takes up between 7% and 12% of the region's anthropogenic CO₂ emissions, but that 70 Tg of the carbon adsorbed from the atmosphere is not taken into carbon stocks with the terrestrial ecosystem, i.e. the amount of carbon exchange measured is greater than the amount that is stored – this difference equates to 7 t C/km²/year. Siemens (2003) has identified fluvial fluxes of carbon as the missing carbon flux from the figures presented by Janssens et al. This fluvial flux could consist of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), free dissolved CO₂ and particulate organic carbon (POC) (Dawson et al. 2002). Of these the least well understood and the most difficult to estimate is the flux of the dissolved CO₂ (Abril et al. 2000).

Dissolved CO₂ in streams and rivers is typically supersaturated with respect to the atmosphere, even up to 20 times atmospheric partial pressure and greater (Kling et al. 1991; Jarvie et al. 1997; Cole and Caraco 2001). This supersaturation means that this dissolved CO₂ is present in excess and will be

released directly to the atmosphere (Hope et al. 2001). Cole et al. (1994) have shown in a survey of 1835 lakes across the globe that on average lakes were supersaturated with respect to the atmosphere by a factor of 3 and that assuming this value then degassing of CO_2 from lakes would represent an additional 140 Mt C to the atmosphere per year – about half the value of export of DOC and DIC from world rivers as estimated by Meybeck (1993).

The concentration of CO_2 in a riverwater is controlled by a number of factors (Jones et al. 2003). The CO_2 in riverwater can be sourced from the water entering the stream as both ground and surface waters tend to be oversaturated with respect to CO_2 . Internally, CO_2 can be sourced from the turnover of organic matter within the river but consumed by photosynthesis (Barth and Veizer 1999), lost by evasion at the air-water interface (Ludwig et al. 1996) or even precipitated as carbonates (Hartley et al. 1996). This complexity means that it is difficult to assess the flux of CO_2 via rivers. Several studies have considered the flux of dissolved carbon dioxide at points within a catchment but these studies are likely to be underestimates because they do not account for the evasion and production prior to the monitoring point and if in general rivers are oversaturated with respect to CO_2 then if monitoring is not done at source then the estimate will underestimate the flux due to dissolved CO_2 evasion. In this sense dissolved CO_2 is special amongst flux studies in that to assess the amount of dissolved CO_2 coming via rivers it is necessary to study the sources and not the outlets. Jones and Mulholland (1998) developed a method for back-tracking dissolved CO_2 concentrations at monitoring point on a stream. Using this approach Worrall et al. (in press a) have shown that by making corrections for in-stream production and for stream evasion it was possible to show that the dissolved CO_2 flux from the catchment was at least 3 times higher than that estimated at the catchment outlet for an 11.4 km² up-land peat catchment. Furthermore, this correction allowed soil respiration to be reconstructed and that the dissolved CO_2 flux from a peat catchment was equivalent to 26% of the soil respiration from the catchment.

Therefore, the purpose of this study is to understand the occurrence of excess dissolved CO_2 in a large river basin and to assess the amount of CO_2 being contributed from groundwater to the atmosphere.

Approach and methodology

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 catchment used is the Thames of southern England where extensive carbonate aquifers contribute to the flow and where the UK most extensive network of groundwater and riverwater monitoring exists. For this catchment the excess dissolved CO_2 content of ground and surface water is

compared to the source of the water at the most downstream surface water monitoring site in the catchment.

Study site

The Thames is the second largest catchment in the UK covering an area of 9948 km² and is dominated by lowland agriculture overlying a series of carbonate and sandstone aquifers interspersed by clay aquicludes (Figure 1). The lowest monitoring point is the tidal limit at Teddington Wier (River site 1 – Figure 1). At this site the river flow has been recorded since 1883 and water quality monitored since April 1974. Between 1974 and 1984 the site was sampled for Ca, alkalinity, pH and stream temperature on an approximate weekly basis, from 1985 to 1988 sampling was fortnightly, and from 1990 to 2002 sampling was monthly. The year 2002 was the last year for which complete data was available and less than 12 samples were taken during 1989 and so that year has been excluded from the analysis. The data from Teddington was used to calculate the time series of excess dissolved CO₂ from the catchment. A further 7 surface water monitoring sites were included in the study where both river flow and Ca concentration data were available (River sites – Figure 1). Furthermore, the flow records from 93 gauging stations throughout the region were available to the study in order to assess the regional distribution of flow. For each of these sub-catchments the proportion of aquifer types is estimated from available maps.

As part of their groundwater monitoring programme, the Thames Region of the UK Environment Agency monitors groundwater quality at 359 sites across the region. The region covered by the monitoring points (Figure 1) includes data for several major UK aquifers (Chalk, Jurassic limestone, Greensands, Corallian limestone, Lias and river gravels – Figure 2). Many of the results reported in the database are from sites of multiple public supply boreholes. For these sites the records from each of the wells were examined and where boreholes from the same site were sampled on the same day only record for one borehole was taken. In total excess dissolved CO₂ could be calculated for 167 wells and springs from 1972 to 2003, however, substantial data is only available from 1992 through 2003 with the exception of 2001 when the outbreak of foot and mouth disease in the UK restricted the access to the monitoring sites.

Groundwater from the aquifers given above is not the only source of dissolved CO₂ to the catchment, but dissolved CO₂ could also be sourced from emerging soil water in surface water catchments. Surface water at source as it emerges from or runs off of soil is rarely sampled but yet it is water near to source that is required for this study in order to preserve the excess dissolved CO₂ concentration. Within the catchment the authors know of only one locality where a surface water dominated catchment has sufficient water quality monitoring for the calculation of excess dissolved CO₂. The small, clay catchment at Wytham (Figure 1) is monitored as part of the Environmental

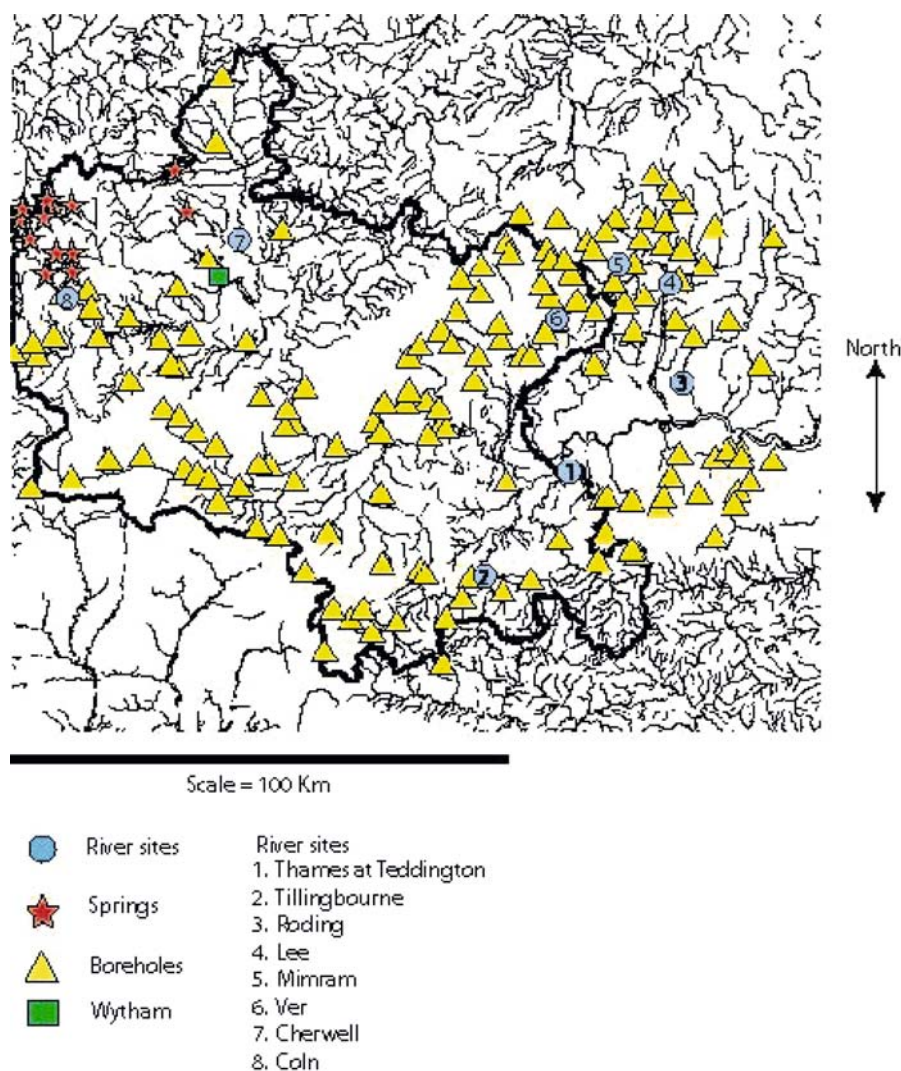


Figure 1. Location of the river monitoring; spring and borehole sites used in the study. The watershed of the Thames to Teddington is outlined.

Change Network (ECN). As part of the ECN monitoring the outlet of the catchment has been sampled for pH, alkalinity and Ca concentration on a weekly basis since June 1993. The flow and meteorological data are monitored on a sub-daily for the catchment and mean that flux of excess dissolved CO_2 can be calculated for the catchment.

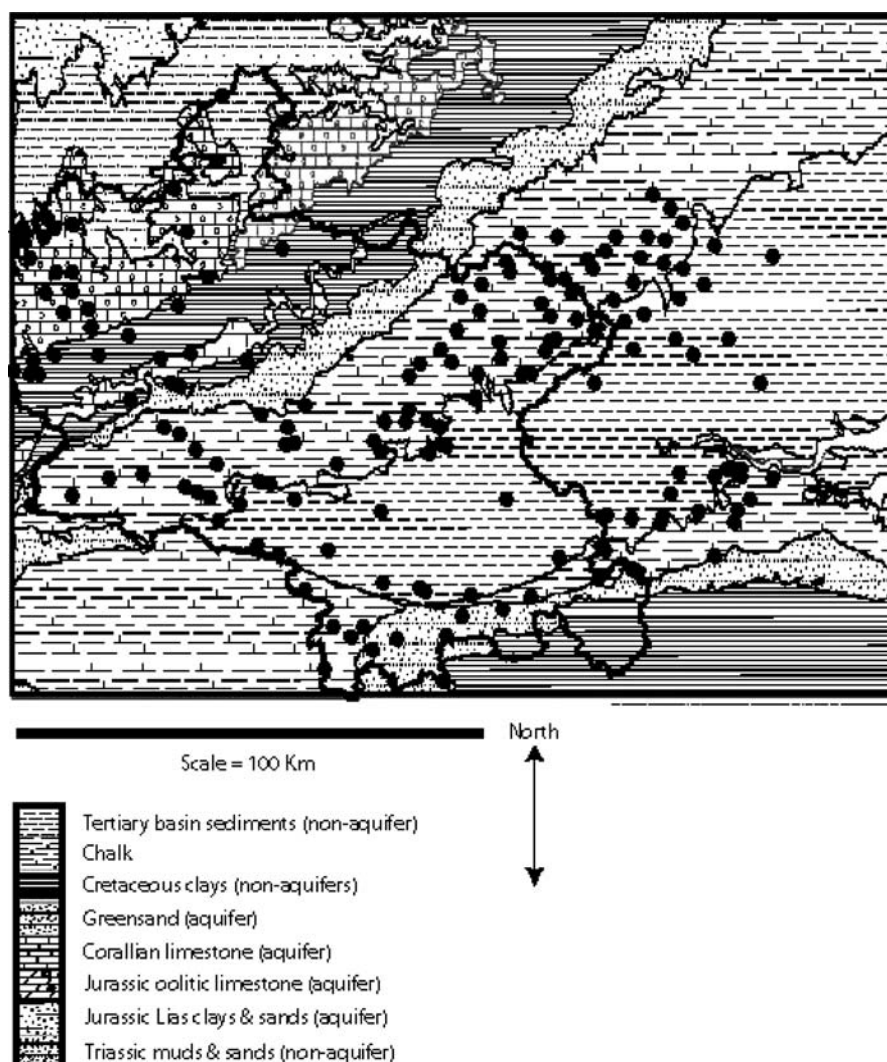


Figure 2. The geology of the study catchment.

Estimating excess dissolved CO₂

The excess CO₂ (EpCO₂) is defined as the amount of dissolved CO₂ in the water in comparison to that expected in equilibrium with the atmosphere:

$$\text{EpCO}_2 = \frac{[\text{CO}_2]_{\text{water}}}{[\text{CO}_2]_{\text{epm}}}$$

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. The simplest calculation can be achieved when pH and alkalinity data are available, with improvement being made when stream temperature can be included in the calculation and the best estimate made when Ca concentration data are also available.

Where Ca concentrations are available a complete speciation can be performed using the method of Neal et al. (1998a). Where there is no Ca concentration data available here, Worrall and Burt (in press) have shown that a strong linear correlation exists between 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. in press b) and was observed to hold true for a range of EpCO_2 values and across the water year but only for $\text{pH} > 5.5$. Thus EpCO_2 can be calculated as:

$$\text{EpCO}_2 = \frac{0.719(0.95\text{Alk}_{\text{Gran}} + 10^{(6-\text{pH})} + 10^{(6+\text{pH}+\text{pK}_6)})10^{(6-\text{pH})}}{(6.46 - 0.0636T)(1 + 2.3810^{(\text{pH}-\text{pK}_2)})} \quad (1)$$

where Alk_{Gran} = is the Gran Alkalinity in $\mu\text{Eq/l}$; and T = water temperature in $^\circ\text{C}$. Thus EpCO_2 can be calculated with only a knowledge of streamwater alkalinity, pH, and temperature.

Estimates of EpCO_2 are corrected for changes in pressure with altitude using method of Smithsonian Institute (1966):

$$\frac{P_a}{P_0} = \left(\frac{(288 - 0.0065a)}{288} \right)^{5.256}$$

$$\text{EpCO}_2 = \frac{P_a}{P_0} \text{EpCO}_{2(\text{calculated})}$$

where a = monitoring point altitude in (m); P_0 = atmospheric pressure at sea level; and P_a = atmospheric pressure at altitude a .

EpCO_2 is converted to dissolved concentration of CO_2 given the following equilibrium:

$$[\text{CO}_2]_{\text{eqm}} = K_H \text{pCO}_2$$

where K_H = Henry's constant; $[\text{CO}_2]$ = concentration of CO_2 ; and pCO_2 = partial pressure of CO_2 . Henry's constant is varied according to:

$$K_H = \log_{10} \left(0.034e^{\left(\frac{-4.772}{0.001987} \left(\frac{1}{298} - \frac{1}{(273+T)} \right) \right)} \right)$$

where T = temperature in degrees Celsius.

Dissolved CO₂ is converted to units of mg C/l. The dissolved CO₂ content of water equilibrium with the atmosphere is easily calculated by letting $\text{EpCO}_2 = 1$. The difference between the dissolved CO₂ content at equilibrium and the calculated CO₂ content represents the additional CO₂ carried by the river and also the amount of CO₂ that would be expected to exsolve from the streamwater and enter the atmosphere.

Temperature is not directly measured as part of the monitoring programme. 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 and 23 °C, while Webb and Zhang (1999) for chalk streams in southern England showed a range of between 5.5 and 12.1 °C in winter and between 11.5 and 20 °C in summer. For the purpose of this study the temperature range is varied within the range reported by Neal et al. (1998b) in order to assess the sensitivity of the calculation to this variable.

Budget estimation

Budget estimation was performed by two methods. Firstly, it was assumed that the excess dissolved CO₂ content of the catchment on any day can be the concentration of excess dissolved CO₂ in anyone of the samples from the surveyed springs and boreholes. This first approach assumes that each source of dissolved CO₂ is equivalent and that there is no spatial or temporal differentiation of excess dissolved CO₂ between areas within the catchment or at different times. Rather than calculate the flux for all the excess dissolved CO₂ concentrations estimated for all the groundwater samples a random selection is obtained. In order to make this calculation simpler, 100 sets of 365 estimates of excess dissolved CO₂ content and Ca concentration were chosen at random from all the sample estimates of excess dissolved CO₂. Each of these 100 sets of 365 estimates is taken to estimate a year of data on the excess dissolved CO₂ concentration in the basin's groundwater. The random selections of groundwater data need to be combined with flow data. In order to calculate flux a year of flow data is chosen at random from the flow record at the catchment outlet at Teddington Weir. By selecting a complete years of flow data at random, rather than selecting flow measurements on individual days within the record, the annual cycle in the river flow is preserved into the flux calculation. However, because of the lack of detailed and long time series of Ca concentration data from the catchment outlet it was not possible to preserve any annual cycle or flow related changes in the Ca concentrations. Therefore 100 sets of 365 Ca concentrations were chosen at random from the available data. The proportion of groundwater at the catchment outlet was then taken as:

$$F_{\text{gw}} = \frac{[\text{Ca}]_{\text{co}}}{[\text{Ca}]_{\text{gw}}} \quad (2)$$

where: F_{gw} = fraction of the flow at catchment outlet that is sourced from groundwater for day i ; $[Ca]_{co}$ = Ca concentration at the catchment outlet on day i ; and $[Ca]_{gw}$ = Ca concentration in the selected groundwater sample. The flux estimate is then calculated as:

$$\text{Flux} = k \sum_{i=1}^{365} F'_{gw} [CO_2]_i Q_i \quad (3)$$

where: $[CO_2]$ = the excess dissolved CO_2 concentration in the selected groundwater sample; Q_i = the flow on day i at the catchment outlet; F_{gw} = the fraction of groundwater contributing to the flow at the catchment outlet on day i as derived from equation (x); and k = a conversion factor to ensure flux in the correct units. Equation (xi) is a form of Method 2 for the calculation of flux (Littlewood 1992).

In the second approach the spatial and temporal distribution of the excess dissolved CO_2 is considered. In order to test what level of information is appropriate for the calculation of the excess dissolved CO_2 concentration the results from the boreholes and springs are tested by ANOVA. For boreholes where sufficient data is available the following factors were considered: the difference between aquifers, the difference between sites; and the difference between years. The difference between the month of sampling is not considered as a covariate within the analysis as there was not sufficient monthly coverage for each of the aquifers to include it as a factor. On the basis of the ANOVA it was then possible to assess the spatial distribution to consider and what temporal scale should be included.

In order to facilitate the examination of the spatial distribution of sources of excess dissolved CO_2 the additional river sampling sites within the catchment are considered, e.g. the Cherwell at Enslow Mill (Figure 1). Of the 8 river sites where Ca concentration and river flow data were available 7 were catchments where only one aquifer geology was present (Table 2). Of these 7, 4 of these river sites were not within the Thames catchment but as they represented catchments with a single aquifer type they were retained because a better estimate of the typical areal export rate of a certain aquifer type could then be made. The flux of excess dissolved CO_2 in these sub-regions of the catchment can then be considered at the temporal scale found to be significant. For each of the seven river sites where the catchment consisted of a single aquifer type the calcium concentration data was compared to the river flow on the day of sampling to judge if a significant relationship or mixing model could be discerned. In none of the seven catchments was a significant relationship found to hold at the 95% significance level. Therefore, daily Ca concentrations in the streamwater at each of the seven river sites could also be used without further processing. However, because sampling at the sites was uneven over differing periods for the different river sampling sites the daily Ca concentration in the streamwater was generated by randomly sampling from the available sample information and for each river site 100 sets of daily streamwater Ca concen-

trations were generated. The fraction of flow in each of the catchments that was contributed by groundwater was calculated by comparing the Ca concentration in the dominate aquifer type for that catchment with the Ca concentration recorded at the river monitoring site. Thus 100 sets of the fraction of the daily riverflow that was generated from groundwater could then be calculated.

In order to complete the calculation of flux at each site it was necessary to have measure of the daily riverflow which was available as each of the river sites was also a river gauging station. These flux calculations could then be scaled up it will be necessary to assess the relative contribution of each sub-region to the catchment as a whole. The contribution of sub-regions was estimated by the flow records from the riverflow gauging station network within the catchment relative to the flow records at the catchment outlet.

Results

In total 3622 samples are considered by the study and the excess dissolved CO₂ concentration showed an approximate log normal distribution with a geometric mean of 4.99 mg C/l and an interquartile range of 6.26. The spatial distribution of the averages for the groundwater sampling localities does show a potential difference between aquifers with the higher values in the chalk regions than observed in the oolitic limestone aquifer (Figure 3). The excess dissolved CO₂ concentration from the clay catchment at Wytham ranges from 0.02 to 8.9 mg C/l with peak concentrations in June (Figure 4).

At the catchment outlet at Teddington, the EpCO₂ varies from 0.05 to 9.0 with a geometric average of 1.07, i.e. the catchment outlet is on average very close to equilibrium with the atmosphere and that there are times when the Thames would be a sink of CO₂ and not a source. Over the sampling period 8.9% of samples have EpCO₂ < 1. Sink conditions generally occur in the summer months (June – August, Figure 5). In terms of excess dissolved CO₂ concentration at Teddington varies from –0.27 to 8.68 mg C/l with an average of 0.79 mg C/l and where the negative concentration represents the amount that sample could absorb from the atmosphere. The flux of excess dissolved CO₂ can then be calculated for the catchment from the perspective of the outlet assuming that times when the riverwater is undersaturated with respect CO₂ represent a negative concentration then the flux of excess dissolved CO₂ from the catchment ranges from 0.17 to 4.21 kt C/year with an average of 1.79 kt C/year, this equates to an export rate of 0.017–0.42 t C/km²/year with an average of 0.18 t C/km²/year (Figure 6). If it assumed that during times of undersaturation no CO₂ is absorbed then the flux of excess dissolved CO₂ for the whole catchment is between 0.17 and 4.21 kt C/year with an average of 0.18 kt C/year, i.e. because undersaturated conditions occur at times of low flow they make little difference to overall flux. The change of annual flux over the period shows no significant trend but does show that the lowest values of flux during periods of drought, especially 1976 and between 1995 and 1997.

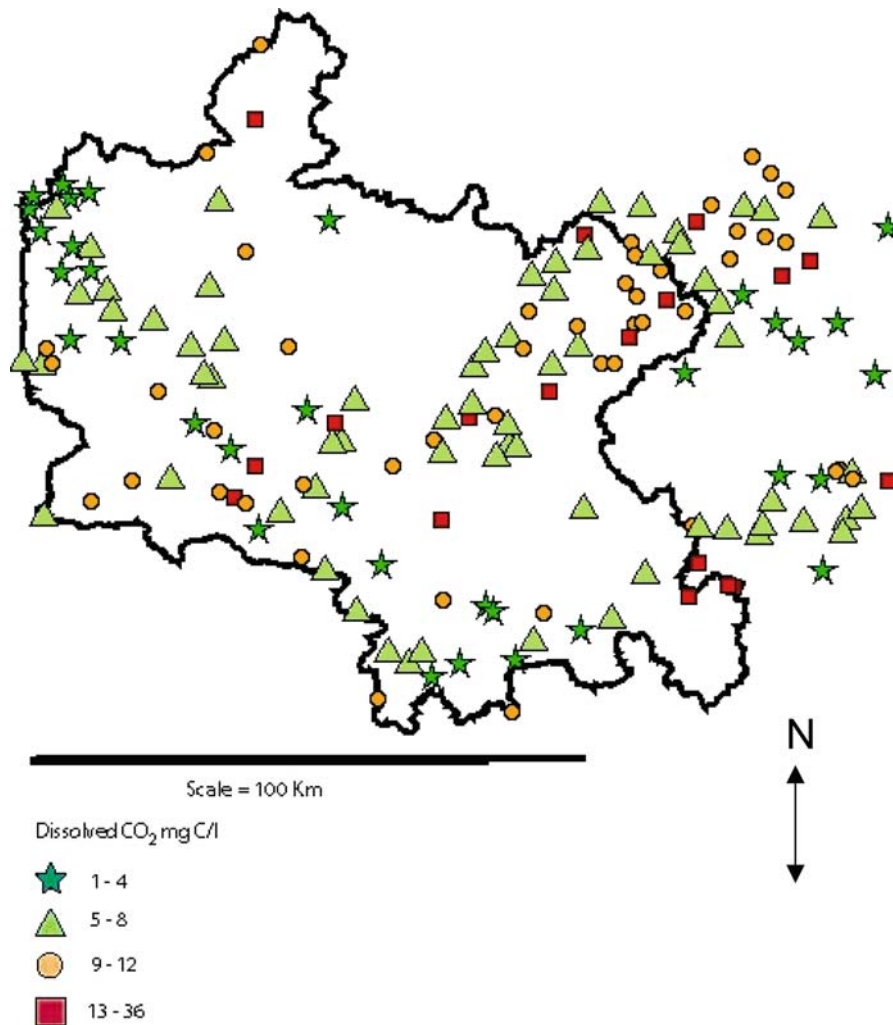


Figure 3. The average excess dissolved CO₂ concentration of the study boreholes over the complete sampling period.

The ANOVA was performed where there was sufficient data, firstly, boreholes and springs were included where there was at least one sample for each year from 1994 to 2003. Secondly, aquifers were considered where more than one borehole or spring was sampled and thus the difference between the Chalk, Greensand, oolite, Corallian and Lias aquifers could be considered. In total, data from 54 boreholes could be considered.

The results of the ANOVA (Table 1) show that there is no significant difference between years within the study. The largest proportion of the variance is explained by the difference between aquifers. The main effects plot for the

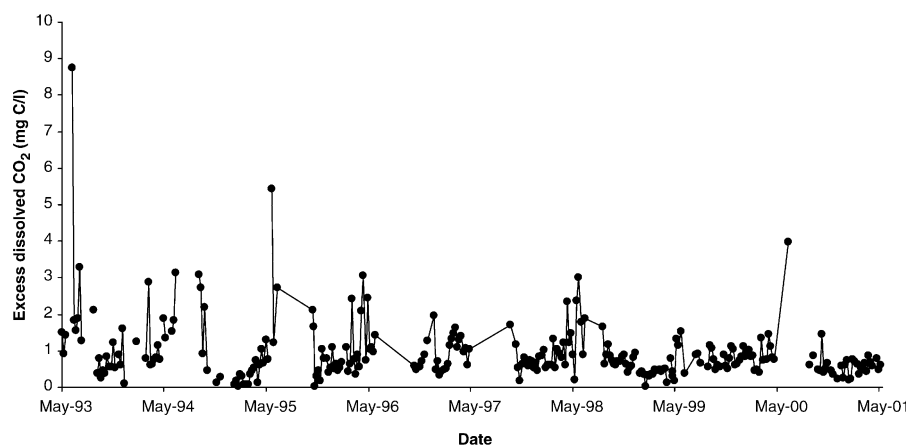


Figure 4. The time series of excess dissolved CO_2 concentration leaving the Wytham catchment.

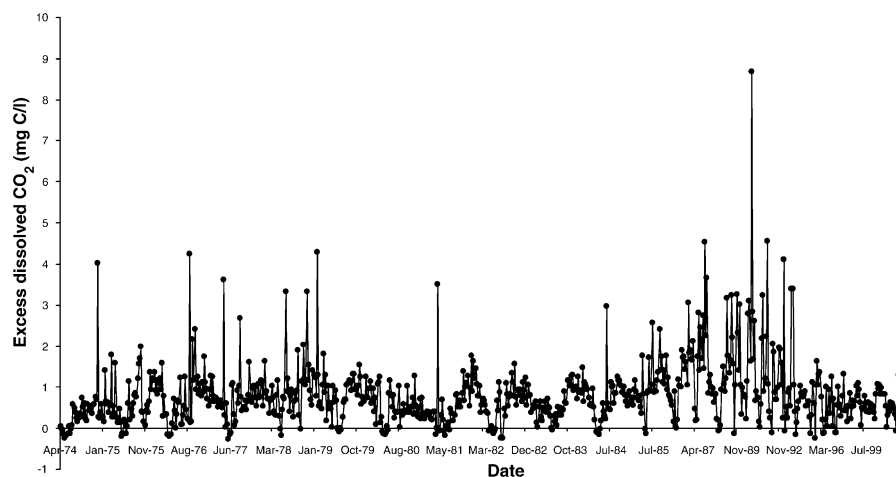


Figure 5. The time series of excess dissolved CO_2 concentration leaving the study catchment at Teddington.

difference between the tested aquifers shows that the highest average values are for the Lias followed by the Chalk with the lowest values for the oolitic limestone (Figure 7). The Tukey test is used to perform post-hoc comparisons between the values for each aquifer and shows that the aquifers fall in to two groups, firstly, the high CO_2 aquifers of the Chalk and Lias, and secondly, the lower values of the Corallian, Greensand and oolitic aquifers. Within these groupings there are no significant differences. No interactions between factors were found to be significant. The significant effect of including months in the above ANOVA suggests that an annual cycle in the dissolved CO_2 could be

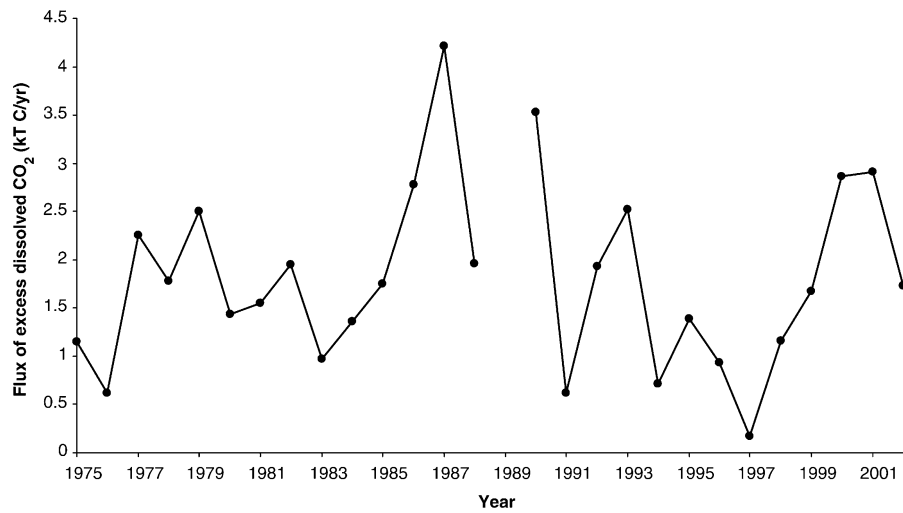


Figure 6. The flux of excess dissolved CO₂ from the study catchment.

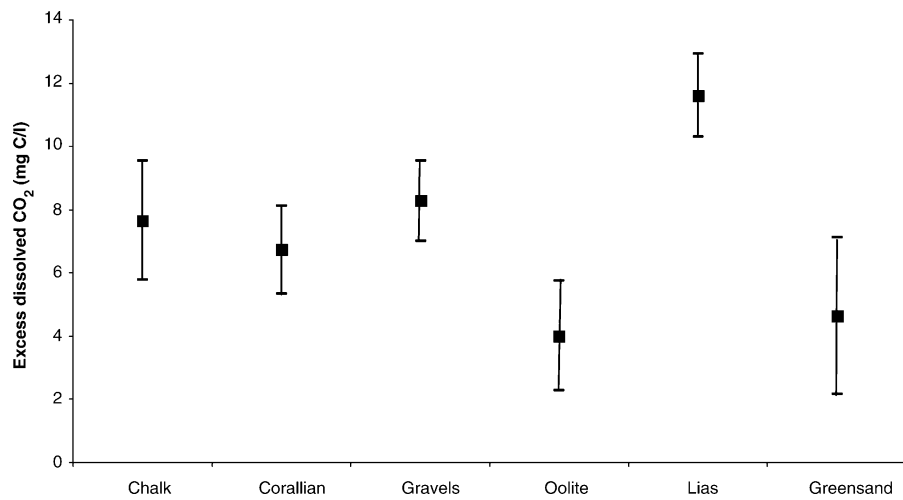


Figure 7. The main effects plot for the different aquifer units in the study.

established (Figure 8). The geometric average excess dissolved CO₂ for each month across all the sample localities shows an asymmetric annual cycle with a maximum in June remaining high through the autumn and a minimum in late winter. It can be hypothesized that this annual cycle represents the change in residence time of the groundwater over the year with changes in rate of recharge.

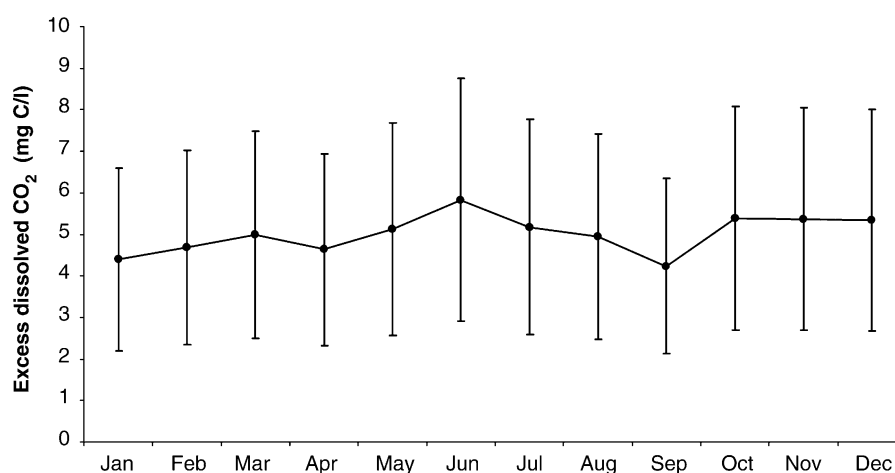


Figure 8. The estimated annual cycle of excess dissolved CO₂ concentration for all the study aquifers.

Table 1. Results of ANOVA for the difference between months of the year; between years and between aquifers within the study dataset. Significance is stated as the probability of the factor being different from zero.

Factor	Number of levels	Significance	Proportion of variance explained (%)
Month	12	0.99	6
Year	9	0.79	3
Aquifer	5	> 0.99	60
Error			31

Budget estimation

As the first method for the calculation is based upon 100 sets of calculations the average and results of the first method can be given as a distribution. The distribution is approximately normal and so the arithmetic mean flux is 15.7 ± 5.0 kt C/year where the error is given as the standard deviation and this equates to an export rate of 1.59 ± 0.5 Kt C/km²/year.

The second method uses the information from the ANOVA, i.e. that there is a significant difference between the months of the year and between the aquifers. Therefore the annual export should be calculated for each of the aquifers for each month. To do this each the average monthly dissolved CO₂ and Ca concentration were calculated for each aquifer geology type. Because there was no significant difference between years it was not necessary to preserve the precise riverflow time series for each of the river sites but because there is an annual cycle in the dissolved CO₂ concentration it is necessary to preserve the annual variation in the river flow at each site. In order to preserve

Table 2. The export of excess dissolved CO₂ from the catchments of the river sites where a single aquifer type dominates the catchment.

River	Site	Aquifer type	Export (t C/km ² /year)	Range
Mimram	Panshangar	Chalk	1.1	0.49–2.53
Roding	Redbridge	Clay		
Lee	Feildes Weir	Chalk	1.5	0.43–3.37
Ver	Hansteads	Chalk	0.9	0.21–2.77
Coln	Bibury	Oolitic limestone	1.4	0.43–1.88
Cherwell	Enslow Mill	Lias	1.5	0.53–2.20
Tillingbourne	Shalford	Greensand	1.4	0.97–1.89

the range of possible river flows considered, 100 sets of annual daily river flows were generated by sampling complete annual sets from the available river flow observations at each of the seven river sites. Where observations of flow at one of the river monitoring sites were shorter than 100 years the period was simply re-sampled from the start of monitoring period and this was repeated until 100 sets of data had generated. Thus it possible for each river sampling site where a single aquifer type dominated to generate 100 sets of annual fluxes.

Results from river monitoring sites, where the catchment was dominated by one aquifer type, show that although average export rates of dissolved CO₂ are very similar the distribution of the calculated values is larger for Chalk than for the other aquifer types (Table 2). The flux for the whole Thames catchment can then be calculated as a weighted average of the export rates for each aquifer type given the area of each aquifer type in the Thames catchment. In order to take account of the estimated distribution of data the 100 sets of dissolved CO₂ export rates calculated from each of the river monitoring sites were used and combined to provide 100 weighted estimates of the flux from the catchment. However, there were several estimates of the distribution of export rate for Chalk (from the Lee, Mimram and Ver) and each of these should be considered to assess the uncertainty in the estimate of the region's flux. Given these caveats, the best estimate flux from the catchment is 21313 t C/year with a range of 14285–28966 t C/year, this equates to an export rate of 2.14 t C/km²/year – range of 1.43–2.91.

Discussion

Is this a good method for estimating the contribution of CO₂ from groundwater? The method used here was tested against measurements of excess dissolved CO₂ for surface waters, including tributaries of the Thames, and the average percentage error was found to be 1.5% (Neal et al. 1998a). The method does assume that all the Ca in the stream water comes from groundwater, this cannot be the case. Firstly, some Ca in the riverwater will come from rainwater. Secondly, a portion of the Ca in the riverwater samples will

come from soil water. This can be observed for the Wytham where the average Ca concentration in a surface water dominated catchment is 151 mg/l. 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, as demonstrated at Wytham the Ca-rich end-member of soil water is also the CO₂-rich end-member and so the assumption of the two end-member system would appear to be a good one. 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.

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. In order to assess this assumption the range of riverflows on each of the days that each of the river sites were sampled for Ca concentration was examined in comparison to the range of river flows in the entire flow record for each of the gauging stations (Table 3). The general pattern is that the flows at the time of Ca measurements tend to occur at the upper end of the flow duration curve, and therefore the proportion of groundwater at each sampling site might be considered an underestimate. However, in flux terms it is the larger flows that dominate and these are the least likely to consist of groundwater. But again at no site was a significant relationship found between Ca concentration and flow even over the range of flows covered in the sampling.

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 CO₂ (e.g. Sempere et al. 2001). Abril et al. (2000) estimate excess dissolved CO₂ flux into the Scheldt estuary from its incoming rivers. The values they report vary from 1.4 to 6.3 kt C/year or an export rate of 0.60–1.39 t C/km²/year. It is important to note that this study was measuring excess CO₂ flux at the river outlets and so a large proportion of the excess CO₂ would have been lost to the atmosphere. It is interesting to note that the smallest catchment considered by Abril et al. had

Table 3. The maximum and minimum flow at the time of sampling for each river site in the study as a percentage of all the daily flows measured for each site.

River	Site	Maximum percentile flow	Minimum percentile flow
Thames	Teddington	99.3	12.8
Cherwell	Enslow Mill	99.4	6.7
Coln	Bibury	98	8.5
Lee	Feildes Weir	99.9	8.1
Mimram	Panshangar	99.7	3.6
Tillingbourne	Shalford	96.3	1.8
Ver	Hansteads	99.7	3.4

the largest export rate, i.e. where the residence time was lower the apparent excess CO_2 flux was higher. Kempe (1982) measured export rates of between 0.23 and 1.2 t C/km²/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 t C/km²/year. Hope et al. 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. (in press a) have estimated export from the peat profile of between 9.6 and 25.6 t C/km²/year. Worrall et al. (in press a) found that for two forested catchments the annual flux of excess dissolved CO_2 flux at source varied between 1.68 and 14.17 t C/km²/year.

This study has shown that in order to understand flux of excess dissolved CO_2 it is important to go to the source of the water. However, such an approach can only consider one of the factors that contribute to the potential loss of CO_2 from rivers. There are other sources that would have to be considered for a full understanding of the potential contribution of carbon from the study river to the atmosphere. As considered above soils in this catchment could be a major source within this catchment, but the other major source must be in-stream production by heterotrophic organisms. The DOC flux from the catchment in the year 2000 was 42 kt C, or 4.22 t C/km²/year (Worrall et al. 2004). At Wytham the areal DOC export between 1994 and 2000 averaged 10.20 t C/km²/year, varying between 2.30 and 15.92 t C/km²/year. The difference between these two export rates either represents the fact that the Wytham catchment has an unusually high areal export rate of DOC compared to other soils or catchment within the basin or represents within channel loss of DOC. It is likely that the Wytham catchment does have a relatively high areal export of DOC compared to the rest of the catchment as soils of the area are clay-rich, organic-rich compared to soils typical of the chalk regions of the basin. However, it does suggest that in-stream metabolism of DOC within the whole Thames basin could be equivalent to several t C/km²/year of CO_2 released, i.e. of at least the same order of magnitude as the release from dissolved CO_2 .

Once in the river the excess dissolved CO_2 can be consumed by photosynthesis but the fact that $\text{EpCO}_2 > 1$ even at the catchment outlet would suggest that the rate of photosynthesis is secondary to other processes or alternatively that photosynthesis is sufficient to consume the excess dissolved CO_2 coming from groundwater (Figure 5). However, there are other sources of dissolved CO_2 within the system that could supply photosynthetic processes. Firstly, as noted above, the mineralization of DOC could supply large amounts of dissolved CO_2 , and secondly, there is CO_2 in the water anyway by virtue of the water being in contact with the atmosphere. There are times at the catchment outlet when $\text{EpCO}_2 < 1$ but volumetrically they are close to insignificant because they occur at the time of very lowest flow. The time for dissolved CO_2

to equilibrate with the atmosphere in non-turbulent waters is typically 4 days (Stumm and Morgan 1996). If the residence time of waters in the channel network of the Thames basin is greater than 4 days then any excess dissolved CO_2 in the river at the catchment outlet is unlikely to be from the excess entering from the groundwater but more likely to be excess from the mineralization of organic matter. Therefore, one estimate of the amount of excess dissolved CO_2 due to in-stream processes is that amount of excess dissolved CO_2 leaving at the catchment outlet. This is probably a conservative estimate but it would mean that at least the amount of CO_2 being released from the rivers in the catchment is nearer the higher estimate given above of 2.9 t C/km²/year.

How representative is the Thames basin? The area of the Thames basin represents 7.5% of the land area of England, or 4.5% of the land area of Great Britain. The combination of aquifers and aquitards found in the basin are typical of much of Southern Britain and thus the Thames basin could be considered representative of south and eastern England. The North and West of Britain is dominated by surface water catchments rather than groundwater dominated catchments. However, the lack of significant regional aquifers in the North and West of the country does not mean that importance of excess dissolved CO_2 would decrease as both shallow groundwater and soil water have been shown in this study to contain large amounts of excess dissolved CO_2 . If the export rates observed for the Thames basin were a reasonable estimate for the rest of the country then the contribution of CO_2 to the atmosphere from groundwater would be 0.65 Mt C/year for Great Britain. Hope et al. (1997) have estimated that the DOC flux from UK rivers in 1993 was 0.7 Mt C, and Worrall et al. (2004) have estimated that by 2002 the flux of DOC would be 0.86 Mt C/year. Thus the flux of excess dissolved CO_2 is comparable to that of DOC but is of a greater impact on the atmosphere because the excess dissolved CO_2 would transfer to the atmosphere whereas the flux of DOC from UK rivers is a flux to the oceans.

Conclusions

The study investigated the importance of the contribution of groundwater to the flux of dissolved CO_2 from the river to the atmosphere. The study has shown that:

1. that there is no significant inter-annual variation in the dissolved CO_2 content of groundwater in the basin over the period of the study but there is a significant annual cycle and a significant difference between aquifers.
2. The average excess dissolved CO_2 concentration of the basins groundwater is 4.99 mg C/l which gives an annual export of upto 2.9 t C/km²/year. The study suggests that the flux of excess dissolved CO_2 from ground and soil water is of the order of 0.65 Mt C/year.

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