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A model of potential carbon dioxide efflux from surface water across England and Wales using headwater stream survey data and landscape predictors

B. G. Rawlins[1], B. Palumbo-Roe[1], D. C. Gooddy[2], F. Worrall[3], and H. Smith[1]

[1]British Geological Survey, Keyworth, Nottingham, UK
[2]British Geological Survey, Wallingford, UK
[3]Department of Earth Sciences, Durham University, Durham, UK

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Correspondence to: B. G. Rawlins (bgr@bgs.ac.uk) and D. Gooddy (dcg@bgs.ac.uk)

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Abstract

Measurements of CO_2 partial pressures (pCO_2) in small headwater streams are useful for predicting potential CO_2 efflux because they provide a single concentration representing a mixture from different hydrological pathways and sources in the catchment. We developed a model to predict pCO_2 in headwater streams from measurements undertaken on snapshot samples collected from more than 3000 channels across the landscape of England and Wales. We used a subset of streams with upstream catchment areas (CA) of less than 8 km^2 because below this scale threshold pCO_2 was independent of CA. A series of catchment characteristics were found to be statistically significant predictors of pCO_2 including three geomorphic variables (mean altitude, mean catchment slope and relief) and four groups of dominant catchment land cover classes (arable, improved grassland, suburban and all other classes). We accounted for year-round, temporal variation in our model of headwater pCO_2 by including weekly or monthly analyses of samples from three headwater catchments with different land use and geomorphic features. Our model accounted for 24 % of the spatial and temporal variation in pCO_2.

We calculated monthly long-term (1961–1990) average flow volumes (litres) on a 1 km grid across England and Wales to compute potential C fluxes to the atmosphere. Our model predicts an annual average potential C flux of 60.8 kt C across England and Wales (based on free C concentrations), with lower and upper 95 % confidence values of 52.3 and 71.4 kt C, respectively.

1 Introduction

There is increasing interest in approaches to compute fluxes in the global carbon cycle, including the role of freshwater channels (Benstead and Leigh, 2012) which are active conduits for the transfer of greenhouse gases to the atmosphere from the terrestrial biosphere (Battin et al., 2009). Evasion of carbon dioxide (CO_2) from surface waters

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may account for up to 10 % of net ecosystem exchange (Sun et al., 2011). In a recent study, Butman and Raymond (2011) used stream water pCO_2 values from samples collected at flow gauging stations (channels ranging from 1st to 10th order) in combination with estimates of stream surface area and gas transfer velocities to compute CO_2 efflux across the USA. For many continents, such large-scale geochemical datasets are unavailable, but it may be possible to develop alternative approaches to compute stream water pCO_2 values (and fluxes) from more readily available, landscape data.

Measurements of CO_2 partial pressures (pCO_2) in small headwater streams may be particularly useful for predicting CO_2 efflux because: (i) it has been suggested that the provenance of 77 % of the CO_2 evasion from channels in large river basins such as the Amazon is from soil respiration (Johnson et al., 2008), and headwater streams are closely connected to the soil, (ii) they provide a single concentration representing a mixture from different hydrological pathways and sources within the catchment including soil-water, both shallow and deeper groundwater contributions (Jones and Mulholland, 1998) and in-stream (e.g. through the mineralisation of organic carbon in stream water and bed sediments) sources of CO_2, and (iii) pCO_2 values typically decline with increasing stream order/catchment size (Butman and Raymond, 2011; Li et al., 2013) and accounting for lengthy upstream evasive losses (based on measurements from larger channels) may be prone to substantial error because the gas transfer coefficient (K_{CO_2}) exhibits a considerable degree of spatial and temporal variation (Wallin et al., 2011).

In our experience, measurements of headwater stream pCO_2 from large, landscape-scale surveys are rare. In this study we investigated those catchment characteristics which account for variations in pCO_2 using data from a headwater stream survey across England and Wales. We hypothesised that a range of upstream catchment characteristics – defined by the delineated watershed of a particular sampling location – could account for variations in headwater pCO_2. A similar approach was applied to channel water chemistry data from the channels of 814 substantially larger catchments (catchment area (CA) from < 1000 to > 10 000 km^2) across North America and

Canada. In this study, multiple analyses were available at each site from which a mean pCO_2 was computed (Lauerwald et al., 2013). In their study, Lauerwald et al. (2013) found that mean air temperature, mean catchment slope gradient and mean annual precipitation explained 43 % of the variation in the negative logarithm of mean pCO_2 in rivers from which these catchment characteristics were calculated; the proportion of agricultural land was not found to be a statistically significant predictor of mean mean pCO_2. Other studies have also shown that catchment characteristics including CA, dominant land cover class (including urban/suburban) (Butman and Raymond, 2011; Prasad et al., 2013; Li et al., 2013) and geomorphic features such as slope and elevation (Jones et al., 1998) account for variations in channel pCO_2. However, no previous studies have used landscape-scale data on *headwater* pCO_2 values from which evasive loss of CO_2 would be substantially smaller than for larger channels with larger (Strahler) stream orders (e.g. > 3). Lauerwald et al. (2013) reported there was no observable effect of including a temporal component into their multiple regression approach based on inclusion of average sampling year.

We consider that stream CA would likely account for more of the variation in headwater pCO_2 than stream order. Catchments in different geomorphic settings may exhibit a wide range of stream lengths for the same stream order; stream order being a significant control on CO_2 evasion (Butman and Raymond, 2011). By contrast, total upstream CA is a *continuous* quantitative measure which is more closely correlated with channel geometry (Booker and Dunbar, 2008). The advantage of establishing predictors of stream pCO_2 based on geomorphic features and land cover is that they can be derived for entire landscapes from widely available digital terrain and remotely sensed data, respectively. It may be possible to develop a statistical model to predict pCO_2 for those parts of similar landscapes where stream chemistry data are unavailable.

The vast majority of the sampling sites in our snapshot (one visit per site) survey dataset were headwater streams (CA 1–10 km^2). We wished to investigate whether it is possible – by undertaking a statistical analysis for catchments across a range of scales and considering other predictors – to determine a threshold scale below which

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stream pCO_2 are independent of CA. By restricting our analysis to those data below this threshold we will have confidence that our model does not underestimate pCO_2 due to downstream net loss. In other words, we estimate pCO_2 in the uppermost part of the stream network where rates of CO_2 evasion to the atmosphere are not substantially greater than inputs from groundwater or in-stream sources such as the turnover of fluvial carbon.

Where model predictions are available for headwater pCO_2 across a landscape it may be possible to use a simplifying approach to compute potential CO_2 evasion fluxes. The approximate timescale for dissolved pCO_2 to reach equilibrium with the atmosphere is around 100 h in a large river system (Morel and Hering, 1993), similar to the water residence time of many large waterbodies of England and Wales. In this study we compute CO_2 evasion fluxes assuming that channel residence times are sufficient for all free CO_2 to evade and also that there are limited downstream changes in water chemistry. This is different approach to efforts to model downstream losses based on gas transfer velocities and stream hydraulics (Raymond et al., 2012).

Headwater pCO_2 exhibit seasonal variations (Jones et al., 1998), so to compute potential CO_2 annual evasion fluxes it is necessary to account for this. In this paper, the large-scale survey dataset of headwater stream samples was undertaken between June and September. To encompass year-round variation we included in our predictive model datasets for a series of small ($< 10\,km^2$) headwater catchments which were monitored for a full calendar year or more (Dinsmore et al., 2010).

In this paper we develop a statistical model to predict monthly headwater stream pCO_2 using large-scale survey data from around 3000 locations across England and Wales, and a series of associated catchment characteristics. We determine an optimum set of land cover class groupings to include in our model by undertaking a series of significance tests. We also investigate the incorporation of the temporal variation of headwater pCO_2 into our predictive model. We apply the resulting model using landscape characteristics to predict pCO_2 values in flow from cells on a 1 km grid across England and Wales. After converting pCO_2 to free C concentrations in water we com-

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pute potential monthly C fluxes using flow volumes for a 1 km grid across England and Wales based on monthly estimates of hydrologically effective rainfall. We also calculate the 95 % confidence intervals for potential C fluxes based on the model predictions.

2 Methods

2.1 Headwater stream pCO_2

2.1.1 Large-scale headwater survey

The methods used in the large-scale headwater survey are described in detail in Johnson et al. (2005). Headwater stream samples were collected during the summer months (June–September) of the years between 1998 and 2002 (inclusive). Sampling was undertaken between 09:00 UTC and 17:00 each day but the precise time was not recorded. In our study we wished to avoid potential bias introduced by including stream water sampling and analyses undertaken during large channel flows (greater than mean flow), so we selected only those samples from sites where there had been no substantial rainfall for more than 7 days. We used information from local flow gauging stations to determine whether local flow conditions were below mean flow (Sect. 2.3). Details of each sampling location were recorded on a field card and collated in a database with a unique sample identifier. The sampling locations are shown in Fig. 1.

A total of four separate water samples were collected from each site so that a range of measurements could be made. These include (analyses in parenthesis):

1. a 250 mL Nalgene polyethylene bottle (alkalinity titration)
2. a 30 mL polyethylene bottle (conductivity and pH)
3. a 60 mL Nalgene bottle which is filtered (0.45 µm) and subsequently acidified (see below; prior to analysis by ICP-AES)

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4. a 60 mL Nalgene bottle which is filtered (0.45 µm) not acidified (ion chromatography/TOC analyser).

All samples were collected from the middle of the stream. In the case of samples 1 and 2 (above) the sample containers were thoroughly rinsed three times. The containers were then submerged in stream and sealed underwater to ensure that all the air had been expelled. On return to the field base all samples were refrigerated at around 4 °C prior to further analysis.

Conductivity and pH were measured on the evening of sample collection. Conductivity was measured using a Hannah HI9033 portable conductivity meter calibrated with a conductivity standard and thermometer. pH was determined using a radiometer PHM80 m with combination electrode using buffer solutions (pH 4, 7 and 9). Alkalinity measurements were made the day after sample collection based on a simple laboratory titration method using a bromocresol green indicator. Samples 3 and 4 were used to determine the concentrations of a range of cations (including Ca^{2+}, Mg^{2+}, Na^+, K^+; ICP-AES Fisons Instruments ARL 3580) and anions (NO_3^-, SO_4^{2-}, Cl^-). For a subset of samples dissolved organic carbon was determined using Shimadzu TOC 5000 analyser, purging all inorganic carbon with hydrochloric acid. Quality control was undertaken on these data using blank waters and duplicates collected in the field.

For each sample we calculated the theoretical partial pressure of CO_2 that would be in equilibrium with the dissolved inorganic carbon, using the aqueous speciation model PHREEQC (Parkhurst and Appelo, 1999) with the phreeqc.dat database. Temperature measurements were not available for the water samples and we assumed a stream water temperature of 12 °C in all these speciation calculations. We associated a unique site identifier with the estimated $p\mathrm{CO}_2$ value at each headwater survey site.

2.1.2 Seasonal variations in stream water $p\mathrm{CO}_2$

To account for seasonal variations in stream water $p\mathrm{CO}_2$ values we included data from three headwater catchments (with differing dominant land use types and mean eleva-

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tions) where monitoring was undertaken on either a weekly or monthly basis through complete calendar years. The features of these three catchments and the associated data are summarised in Table 1. In the case of the Pow and Wensum catchments, we used measurements of pH, alkalinity and dissolved cations and anions to predict pCO_2 values using the same approach as the headwater survey (based on the speciation model PHREEQC Parkhurst and Appelo, 1999). For these catchments stream water temperature data at the time of sampling were also available for the speciation calculations. We converted the sampling date to a numeric value representing day between 1 and 365 (1 January has a value of 1).

2.2 Catchment characteristics

2.2.1 Catchment area

We used the ArcHydro extension and a 5 m resolution Digital Surface Model (NEXTMap Britain elevation data from Intermap Technologies, Intermap, 2009) to create drainage catchments upstream of all the stream sampling sites ($n = 3274$). We created a series of catchment polygons with a unique sample identifier so we could estimate catchment properties from other landscape data. We calculated the total area of each catchment polygon and associated it with the unique identifier from each headwater survey site.

2.2.2 Geomorphic variables

Previous studies (Butman and Raymond, 2011) have shown that over prolonged periods total rainfall is negatively correlated with CO_2 evasion. In temperate climates there is typically a strong correlation between altitude and total rainfall, so the former may be a useful proxy for the latter where accurate rainfall data is unavailable at fine scales (e.g $< 10\,km^2$). Other geomorphic features such as catchment slope may also account for variations in stream water pCO_2 because it influences contact time between soil and

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percolating water. We used the Digital Surface Model to compute mean elevation (m), mean slope (°), and relief (difference between minimum and maximum elevation (m)) for each of the headwater catchments in our study based on the catchment polygons. We also calculated the same measures for a 1 km grid across all of England and Wales.

2.2.3 Land cover class

The dominant land cover class in each catchment was determined by intersecting the catchment polygons with a 25 m pixel Land Cover map of Great Britain 2000 (Fuller et al., 1994) and identifying for each catchment the class with the largest number of pixels. We also calculated the dominant land cover class for the 1 km grid across England and Wales.

2.2.4 Soil and geology

We also wished to establish whether spatial data on soils and hydrogeology could account for variations in headwater $p\mathrm{CO_2}$. We used a simplified classification to determine the dominant parent material (PM) group for each catchment polygon and associated the PM code with each catchment (Lawley and Smith, 2008). We also determined the mean BFIHOST value for each catchment. The 1 km grid BFIHOST data for England and Wales was derived from a combination of information on catchment baseflow index (Gustard et al., 1992) and associated maps classified by the hydrology of their soil types and substrates (HOST) (Boorman et al., 1995).

2.3 Removal of survey sites with the largest flows

We considered that bias might be introduced into our predictive model if we included stream sites which had large flows when they were sampled (Dinsmore et al., 2010). Time-series of headwater stream flow exhibit strong positive skewness; we chose to exclude sites where data from local gauging stations showed that flow on the stream sampling date was larger than mean daily flow. We used the *ann* function in the R

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package yaImpute (Crookston and Finley, 2007) to determine the nearest neighbouring National River Flow Archive (http://www.ceh.ac.uk/data/nrfa/index.html) flow gauging station (based on their coordinates). We identified a total of 93 local gauging stations (Fig. 1) which were nearest neighbouring stations to the selected sampling sites and which also had flow data spanning the full period of sampling. We then extracted the mean daily flow data for each of these gauging stations for the full-year period spanning the dates over each full year for which the samples were collected (1 January 1988 to 31 December 2003). We computed the mean of the mean daily flow values for this period for each of the 93 gauging stations and compared these to mean daily flow on the sampling date recorded for each nearest neighbouring, large-scale survey site. By doing so, we identified 85 sites (from a total of 3274 sites) where mean flow was exceeded. We removed the data for these sites from our survey dataset prior to further statistical analysis (Fig. 2).

2.4 Model of stream water pCO_2

We undertook preliminary exploratory statistical analyses using the headwater survey data. The steps we undertook in developing and applying a model to predict stream water pCO_2 across England and Wales using the available data are summarised in Fig. 2. These include selecting subsets of the data, applying a transformation to the pCO_2 values, predicting pCO_2 on the transformed values, including the calculation of confidence intervals for these predictions, and computing potential C fluxes based on flow from a 1 km grid across England and Wales. We describe below the rationale for developing the model and its implementation.

The calculated pCO_2 values at the stream survey sites were strongly positively skewed (skewness coefficient = 2.66). We found that a logarithmic transformation of the pCO_2 applied after the addition of a small positive value (linear shift) of 3×10^{-5} produced a variate with an normal approximately normal distribution (skewness coefficient = −0.06). We undertook all subsequent statistical analyses using this transformed data, and backtransformed the values to original units for the calculation of C fluxes (Fig. 2).

2.4.1 Catchment area threshold

The stream sites which were sampled as part of the large-scale headwater survey exhibited a range of catchment areas from 0.01 to 254 km^2 with a mean of 5.49 km^2. We needed to ensure that estimates of pCO_2 from all these sites were representative of headwaters; there is strong evidence (Butman and Raymond, 2011) that as CA (or stream order) increases from the smallest catchments, pCO_2 decreases because evasion exceeds inputs of CO_2 from a combination of groundwater and in-stream sources. In their study, Lauerwald et al. (2013) did not observe any correlation between CA and negative log pCO_2 because their analyses were based on substantially larger catchments (generally greater than 1000 km^2; two orders of magnitude larger than in our study) from which a substantial proportion of CO_2 will have evaded to the atmosphere. To investigate this further, we formed a scatterplot of pCO_2 vs. CA (Fig. 3). This suggested that those sample sites with the larger CA had – on average – lower pCO_2 values. To determine if there was a threshold CA below which this effect was not statistically significant, we fit ordinary least squares models (using the *lm* function in the R computing environment, R Development Core Team, 2012). In each case the predictors were CA values for subsets of headwater sites truncated at thresholds of < 2, < 4, ..., < 20, < 50, < 100 and $< 250\,km^2$ and the predictand was the series transformed pCO_2 values. We investigated: (i) whether CA is a statistically significant predictor of pCO_2 ($P < 0.05$) for this range of CA values, and (ii) if there is a threshold at which CA was no longer a statistically significant.

2.4.2 Land cover: orthogonal contrasts

In their study, Butman and Raymond (2011) showed that land use was strongly related to area normalised C fluxes from surface water for a range of drainage basin regions

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across the USA. Preliminary exploratory analyses (Fig. 4) suggested that catchment dominant land cover class would likely be a statistically significant predictor of headwater stream pCO_2 in our survey data from England and Wales. There are reasons why we might expect the magnitude of ecosystem soil respiration (a major factor in controlling streamwater pCO_2) to reflect land cover type. For example, the addition of nutrients (fertilisers) to maximise agricultural production enhances both net primary production and also soil heterotrophic respiration, leading to larger soil gas pCO_2 values (Smith, 2005). Therefore we might expect mean pCO_2 values in streams draining agricultural catchments (arable or improved grassland) to be greater than those draining less managed or semi-natural habitats. Catchments dominated by urban land use may also have larger pCO_2 values because of nutrient inputs to managed gardens and increased heterotrophic respiration associated with nutrient loads in urban waste water. We wished to determine the most appropriate set of land cover classes for inclusion in our statistical model. The ten dominant land cover classes (from the Land Cover Map) were: Arable, Bog, Broadleaf, Coniferous (Forest), Fen, Heather, Heather Grass, Improved Grassland, Rough Grassland and Suburban. We formed an hierarchical classification (Fig. 5) of these groups and undertook a statistical analysis using five orthogonal contrasts based on it:

1. managed land vs. less managed land + urban
2. urban vs. less managed
3. within less managed (forested vs. non forested)
4. within less managed: non forested (wetter vs. drier)
5. within managed (arable vs. improved grassland)

The orthogonal treatment contrasts were entered using the *contrasts* function in the R environment (R Development Core Team, 2012). Each of the contrasts was tested using the *aov* command to determine whether they were statistically significant ($P <$ 0.05).

2.4.3 Temporal variation

To account for seasonal variations in pCO_2 we converted sampling dates from all the headwater surveys into a year day value (numeric values between 1 and 365). We expressed the year day values on a radian scale (range from zero to $2 \times \pi$). To account for any seasonal trend we included terms for both sine and cosine of the radian-based units for year day in the ordinary least squares regression model.

2.4.4 Refining the model

Using a subset of the initial headwater survey data (based on an appropriate CA threshold) and including the temporal data from three headwater catchments (Fig. 2) we performed stepwise selection of the model predictors using the *stepAIC* function from the MASS library (Venables and Ripley, 2002). This tests the inclusion of predictors based on the Akaike information criterion; the k value (multiple of the degrees of freedom for penalty) was 2 and the mode of stepwise search was forwards and backwards. In our model specification we included an interaction term between elevation and the land cover classification (based on the findings from the orthogonal contrasts) as we considered this may be significant.

2.5 Monthly flow volumes

Our measurements of pCO_2 from headwater streams represent pathways combining shallow and deeper flow routes. Their relative magnitude depends on both geomorphology and the physical properties of local bedrock, any Quaternary deposits and the soils overlying them. We used data on long-term (1961–1990) average mean monthly rainfall (mm) and potential evapotranpsiration (mm) to determine the quantities of hydrologically effective rainfall on a 1 km grid for each calendar month across England and Wales. Data for the former was available on a 1 km grid whilst the latter was on a 40 km grid.

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2.6 Model of headwater stream temperature

The conversion of pCO_2 to free C concentration in freshwater relies on computation of Henry's constant which is temperature dependent. There is a substantial degree of variation in annual stream temperature in temperate regions such as the UK due to a combination of seasonal air temperature and variations in altitude. We used year-round data on stream water temperature from three catchments with widely differing mean elevations England and Wales (Upper Hafren (Neal et al., 2012); 550 m, Pow; 99 m, Wensum; 48 m) to establish a ordinary least squares model of stream temperature. The predictors of stream water tempertaure were altitude (alt) and a combination of sine and cosine coefficients of the transformed (zero to $2 \times \pi$) year day (yday) values for each observation. The sum of two sinusoidal terms is a phase shifted sine curve with a period of 365 days. The regression model took the form:

$$T_i = \alpha + \beta_1 \mathrm{alt}_i + \beta_2 \sin \mathrm{yday}_i + \beta_3 \cos \mathrm{yday}_i + \epsilon_i \tag{1}$$

where α and β are coefficients of the ordinary least squares model and ϵ is the random component of the linear relationship. We included interaction terms between the predictors and used the same stepwise selection procedure described above.

2.7 Potential monthly carbon fluxes and their uncertainty

We used the linear model (*lm* function in the R package) selected from the stepwise procedure (Sect. 2.4.4) to predict log pCO_2 in flowing water on 1 km grid across England and Wales. We made these predictions for each of 12 months based on: (i) the geomorphic and land cover predictors, and (ii) the year day value for the mid-point of each calendar month (Fig. 6). We used the model to predict the values for the 95 % confidence intervals (using the *interval* argument in the *predict* function) for each 1 km grid cell. We then backtransformed the predictions and the confidence interval values onto the original scale; the backtransformed values are the median values in the original units. We then used the model of stream water temperatures to convert pCO_2 (atm) to a dissolved gas concentration using Henry's Law and so estimated free C concentrations in water (mg L^{-1}). This concentration can be converted to a quantity of potential C evasion when it is multiplied by flow volume (Fig. 2).

3 Results

3.1 Predictive model

3.1.1 Catchment area threshold

The formation of linear models for the prediction of log pCO_2 based on subsets of a range of CA thresholds (< 2, < 4, ..., < 20, < 50, < 100 and < 250 km^2) showed that CA was a statistically significant predictor above 8 km^2, but not at smaller CA thresholds. This threshold is highlighted in Fig. 3. We infer that at positions on streams which drain catchments finer than this threshold area, the rate of CO_2 evasion is balanced by combined inputs from groundwater and in-stream sources. To ensure our final model of stream water pCO_2 was not biased by inclusion of observations from coarser catchments, we undertook all subsequent analysis on those catchments with areas less than 8 km^2.

3.1.2 Land cover: orthogonal contrasts

The results from significance tests for five orthogonal, land cover contrasts are shown in Table 2. It shows that the first (managed land vs. less managed land + urban), second (urban vs. less managed) and fifth (arable vs. improved grassland) orthogonal contrasts were all statistically significant ($P < 0.05$). By contrast, the third (forested vs. non forested) and fourth (non forested: wetter vs. drier) contrasts were not statistically significant. These findings suggest that the most effective reclassification of the land cover classes would be to group all the less managed, non-urban classes to form a single class, and retain three other separate classes: arable, improved grassland

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and urban. We undertook this reclassification before undertaking the stepwise model selection procedure, reported in the next section.

3.1.3 Final model data

Summary statistics for the final dataset used to form the model for prediction of headwater stream pCO_2 are summarised in Table 3. It is based on data from 2634 locations from the large headwater survey where pCO_2 measurements were restricted to 4 months (June to September), and three small headwater catchments where measurements were made through full calendar years.

The predictors (based on stepwise selection) which were included in the final linear model of log pCO_2 in streams across England and Wales are shown in Table 4. The sum of the model coefficients for sine and cosine functions multiplied by year day are presented in Fig. 6 highlighting the effect of temperature on ecosystem respiration and stream pCO_2 values throughout the year. The residuals were close to a normal distribution (histogram not shown: skewness coefficient = −0.31). This model accounted for 24 % of the variance (adjusted $R^2 = 0.24$) in pCO_2 values in the combined spatial and temporal dataset. Although there is a considerable amount of variation which the model cannot account for, we consider its performance is reasonable given that: (i) pCO_2 in stream water exhibits a substantial degree of spatial (Jones and Mulholland, 1998) and temporal (Dinsmore et al., 2010) heterogeneity, and (ii) the landscape predictors can be obtained for most terrestrial landscapes.

Those predictors which accounted for larger proportions of the variation in headwater pCO_2 were the temporal coefficients (sin and cosine of year day), plus mean slope and mean elevation, although in combination the land cover classes also accounted for a reasonable proportion of the variance. Mean catchment elevation has a strong positive correlation with rainfall. Greater rainfall leads to dilution of stream pCO_2 which likely explains why the variation of the latter is explained by difference in mean catchment elevation.

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It is noteworthy that neither PM class or BFIHOST values were statistically significant predictors of pCO_2. We infer that variations in headwater stream pCO_2 are more closely associated with those factors closely related to the generation of soil gas CO_2 (such as land cover type) and less related to the transport pathways determined by variations in soil parent material and hydrogeology. However, mean catchment slope is a significant predictor of headwater pCO_2. Steeper average slopes likely lead to shorter contact times between soil and water before it reaches a channel, and so smaller average pCO_2 values.

3.2 Model of headwater stream temperature

The range of headwater stream temperature values for the three sites was 0.89 to 18.1 °C, with a median of 12.25 °C. In combination, the use of sine and cosine functions based on year day and elevation (in metres) accounted for 78 % of the variance in headwater stream temperature. A summary of the model coefficients are presented in Table 5. We considered the model provided a reasonable basis for predicting stream temperatures on a 1 km grid across England and Wales for the mid point of each calendar month which we used to convert pCO_2 to its free CO_2-C concentration in water.

3.3 Model predictions: England and Wales

To highlight differences in free C concentrations in flow throughout the year across England and Wales, Fig. 7 presents model predictions for the months of May and November showing the differences in temperature controlling ecosystem respiration. Free C concentrations in flow are larger in May reflecting the greater concentrations of CO_2 derived from of soil and in-stream respiration, but also greater dilution in November associated with larger quantities of rainfall (Table 6). The maps also reflect the differences in land cover type; the south and east of England is dominated by arable agriculture over neutral soils with fertiliser inputs which enhances ecosystem respiration. By contrast, soil pH is more acidic in the north and west (of England and also in

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Wales) where and land cover types(Improved grassland or less managed habitats) are subject to smaller, or no, nutrient additions.

The predicted median free C concentrations in May and November across England and Wales were 1.78 and 1.11, respectively. The median free C concentrations for the lower and upper 95 % confidence intervals were 1.97 and 1.47 for May and 0.91 and 1.24 for November.

Based on the quantities of flow from each 1 km grid square (Fig. 2) we present the potential monthly evasion fluxes for May and November using data on mean monthly annual rainfall (Fig. 8). For years in which monthly rainfall is near the long-term average quantities, the largest potential C fluxes (> 70 kg C km^{-2} $month^{-1}$) occur generally in the winter months (November–February) in upland (> 300 m elevation) areas subject to the largest monthly rainfall (north-west England, Wales and south-west England). The lowest potential fluxes occur in lowland settings with the smallest monthly flow quantities. Potential C efflux is dominated by flow volumes rather than free C concentrations in surface water; Table 6 shows there is a 30-fold difference in maximum (December) and minimum (June) monthly flow volume, whilst there is less than a two-fold difference in mean free C concentrations (1.18 and 1.78 mg L^{-1}, also December and June). So despite larger free C concentrations in surface water during summer months (with average rainfall), potential C fluxes are substantially smaller than for average winter months.

Our model predicts a mean annual flux of 0.41 t C km^{-2} yr^{-1} (expressed on the basis of total land area, not stream surface area, as is often used in other studies). The total potential annual C efflux from flow across England and Wales (summing across 12 months) is 60.8 kt C (kilo tonnes carbon), with the lower and upper 95 % confidence intervals of 52.3 and 71.4 kt C, respectively. The confidence intervals we present only reflect the uncertainty associated with prediction of pCO_2 values and do not account for the uncertainties in the computation of flow or with stream temperature estimation (used to compute Henry's constant). For the year 2002, Worrall et al. (2007) estimated the total fluvial flux of C from the terrestrial biosphere to surface water across En-

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glish and Welsh rivers to be 1530 kt C yr^{-1} (mega tonnes carbon per year; equivalent to 10.3 t C km^2 yr^{-1}). They estimated around 32 % (620 kt C) of the total from (equivalent to 4.2 t C km^2 yr^{-1}) was lost to the atmosphere from surface water. The largest proportion of this flux was DOC (42 %), but their flux of excess dissolved CO_2 was 0.37 Mt C yr^{-1}. This estimate was based on measurements of $p$$CO_2$ in groundwater from those regions with major aquifers, having made assumptions concerning mixing with surface waters. This estimate by Worrall et al. (2007) for the year 2002 is around six times greater than our model prediction of potential CO_2 flux from surface water to the atmosphere (0.06 Mt C yr^{-1}) based on mean annual flow. In their study, Worrall et al. (2007) computed an average free C concentration in surface water of England and Wales of 5.2 mg C L^{-1} which is between 3 and 4 times larger than the overall mean concentration of 1.48 mg C L^{-1} predicted by our model. It may be helpful to compare the methodology applied by Worrall et al. (2007) and that used in this study to determine why the former has much larger free C concentrations, based on mixing of ground and surface water.

Our model could be applied using future land use change scenarios to estimate the magnitude of their impact on potential C evasion fluxes from surface water, an approach similar to that used to assess changes in greenhouse gas emissions from soil (Smith et al., 2010). The model could also be modified to assess differences in the magnitude of potential annual C efflux based on yearly variations in monthly rainfall or changes in mean monthly temperature.

We recognise that our model cannot currently account for all the processes influencing the magnitude of potential CO_2 evasion from surface water at the landscape scale. Our approach does not account for changes in headwater stream CO_2 flux due to variations in discharge; although dissolved CO_2 concentrations in headwater catchments are lower at larger discharges (Dinsmore et al., 2013) total fluxes increase during storm events. To ensure our model was not biased by the inclusion of $p$$CO_2$ measurements from streams at the largest flow conditions we excluded sites where daily flow was likely greater than long-term mean daily flow (based on local gauging stations). To account for variations in flow would require a much shorter time-step (e.g. daily)

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and parameters to predict concentration–discharge relationships. Our model does not account for in-stream sources of CO_2 in the reaches of larger channels downstream of their headwaters. Our model accounted for a smaller proportion (24 %) of the variation in channel $p$$CO_2$ by comparison to that presented by Lauerwald et al. (2013) (43 %). There are two main factors which could account for this difference: (i) Lauerwald et al. (2013) used mean $p$$CO_2$ values from a series of water samples compared to the more variable, single snapshot observations used in our study, (ii) the observations reported by Lauerwald et al. (2013) were for substantially larger catchments providing more opportunity for smoothing of the variation, in contrast to our smaller catchments which likely exhibit greater variation.

A further improvement on our current approach would be to compute actual rather than potential CO_2 evasion fluxes using functions which predict variations in downstream gas transfer velocities using parameters of stream hydraulics (Raymond et al., 2012) and channel surface area. A recent study showed that channel wetted widths across England and Wales are strongly influenced by catchment area and hydrological source of flow (Rawlins et al., 2013).

4 Conclusions

Using analyses of more than 3000 snapshot headwater samples across different landscape settings of England Wales we showed that below a CA threshold of around 8 km^2 there was no statistically significant difference in stream $p$$CO_2$ – evasion losses of CO_2 from stream channels below this scale are balanced by inputs from groundwater and in-stream sources. We used estimates of $p$$CO_2$ from catchments with areas less than 8 km^2 to assess other landscape predictors of stream $p$$CO_2$, including data from three catchments in which $p$$CO_2$ had been measured throughout a full calendar year. Based on a series of orthogonal contrasts we found that grouping dominant catchment land cover types into four classes provided the optimum classification for $p$$CO_2$. Mean catchment elevation (interacting with land cover class), mean catchment slope and catchment relief (maximum minus minimum altitude) were also statistically significant predictors of pCO_2. We formed a model from these factors and stream water temperature which accounted 24 % of the combined spatial and temporal variation in pCO_2 across England and Wales. We predicted free C concentrations in water for a 1 km grid across England and Wales using their catchment characteristics and a model of stream water temperature as predictors. We also used average monthly hydrologically effective rainfall to compute flow on a 1 km grid across England and Wales. By combining the predicted free C concentrations and flow for each 1 km grid cell, we computed monthly and total annual potential C fluxes (60.8 kt C) from surface water to the atmosphere, assuming that all CO_2 entering surface water evades to the atmosphere.

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Table 1. Features of three headwater catchments where weekly or monthly stream water measurements or speciation-based estimates of pCO_2 were included in the predictive model (cf: Fig. 2).

	Regional catchment (headwater catchment)		
	Esk (Black burn)	Eden (Pow)	Wensum (Blackwater)
Catchment Area (km^2)	3.4	10	8
Dominant land cover	Bog	Impr. grass	Arable
Mean elevation (m)	280	99	48
Mean slope (°)	1.4	1.4	0.73
Relief (m)	60	96	26
Monitoring frequency	weekly	monthly	weekly
pCO_2 measurements[a]	D	S	S
Reference	Dinsmore et al. (2010)	Owen et al. (2012)	Wensum Alliance (2013)

[a] D = direct, S = estimated by PHREEQC speciation using measurements of alkalinity, pH plus major anions and cation concentrations for the Wensum.

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Table 2. Results from orthogonal contrasts between groups of selected land cover classes based on the hierarchical classification (Fig. 5).

	Estimate	Std. Error	*t* value	*P* value
Contrast1	−0.021	0.003	−6.82	1.1×10^{-11}
Contrast2	−0.024	0.008	−3.13	0.002
Contrast3	−0.007	0.009	−0.74	0.47
Contrast4	0.012	0.01	1.23	0.22
Contrast5	0.088	0.006	15.4	$< 2 \times 10^{-16}$

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Table 3. Summary statistics for geomorphological and land cover predictors (for catchments derived from 2637 sample sites) used to form the model of stream pCO_2, and for a 1 km grid ($n = 147\,829$) across England and Wales.

	Model data[a]	1 km grid
Geomorphic data		
Minimum of mean elevation (m)	0	0
Mean of mean elevation (m)	215	124
Maximum of mean elevation (m)	722	945
Minimum of mean slope (°)	0.09	0
Mean of mean slope (°)	4.76	3.78
Maximum of mean slope (°)	34.8	33.2
Minimum relief (m)	0	0
Mean relief (m)	99.5	58
Maximum relief (m)	626	669
Land cover class[b] (%)		
Arable	34.7	41
Improved grassland	34.1	28.8
Suburban	0.007	0.09
Less managed	30.5	21.4

[a] Data from catchments of headwater streams with CA < 8 km^2.
[b] Dominant land cover class in catchment or grid cell.

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Table 4. Summary of the model from stepwise selection of predictors of log pCO_2 in stream water based on geomorphic variables, land cover classification and year day. The coefficient (estimate) for the three land cover classes shown are expressed as differences from the Arable land cover class (not shown).

	Estimate	Std. Error	t value	P value
Intercept	−5.53	0.04	−131	$< 2 \times 10^{-16}$
sin(yday)	0.11	0.03	3.903	9.70×10^{-5}
cos(yday)	−0.24	0.03	−7.904	3.76×10^{-15}
Mean Slope	−0.06	0.006	−10.5	$< 2 \times 10^{-16}$
Relief	−0.0009	0.0002	−3.802	0.0001
Mean Elev.	−0.003	0.0004	−7.61	3.75×10^{-14}
IG[a]	−0.39	0.07	−5.44	5.75×10^{-8}
Urban	−0.09	0.36	−0.260	0.79
LM[b]	−0.04	0.087	−0.47	0.64
Elev.[c]: IG[b]	0.002	0.0004	4.48	7.67×10^{-6}
Elev.[c]: Urban	0.001	0.002	0.47	0.63
Elev.[c]: LM[b]	0.0015	0.0004	3.72	0.0002

[a] Improved grassland, [b] Less managed (non urban), [c] mean Elevation.

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Table 5. Summary of the ordinary least squares model used for the prediction of daily headwater stream temperature for the 1 km grid across England and Wales. Year day (yday) is the transformed numeric value of day in the calendar year. A colon (:) denotes inclusion of an interaction (a product term) of predictors.

	Estimate	Std. Error	*t* value	*P* value
Intercept	10.2	0.024	434	$< 2 \times 10^{-16}$
sin(yday)	−2.37	0.05	−47.6	$< 2 \times 10^{-16}$
cos(yday)	−3.23	0.031	−103	$< 2 \times 10^{-16}$
Elev.	−0.004	0.0001	−38.1	$< 2 \times 10^{-16}$
sin(yday):cos(yday)	−2.64	0.088	−29.8	$< 2 \times 10^{-16}$
sin(yday):Elev.	0.001	0.0002	8.17	3.38×10^{-16}
cos(yday):Elev.	0.0003	0.0001	2.147	0.031
sin(yday):cos(yday):Elev	0.005	0.0003	17.0	$< 2 \times 10^{-16}$

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Table 6. Summary of monthly predictions across all of England and Wales for total flow volume (giga litres; GL) based on mean monthly annual rainfall minus evapotranspiration (1961–1990), mean concentration of free C ($mg\,L^{-1}$) and potential carbon efflux (kilo tonnes carbon; kt C).

	Flow (GL)	mean free C ($mg\,L^{-1}$)	C efflux[a] (kt C)
Jan	11 026	1.34	12 419
Feb	6740	1.52	8435
Mar	5409	1.69	7003
Apr	1304	1.77	1363
May	364	1.78	311
Jun	380	1.74	321
Jul	387	1.64	303
Aug	1415	1.47	1206
Sep	800	1.30	552
Oct	7540	1.16	6924
Nov	10 521	1.11	9973
Dec	11 952	1.18	11 959
Total	57 840	–	60 770

[a] Potential C efflux – assumes all free C evades to the atmosphere.

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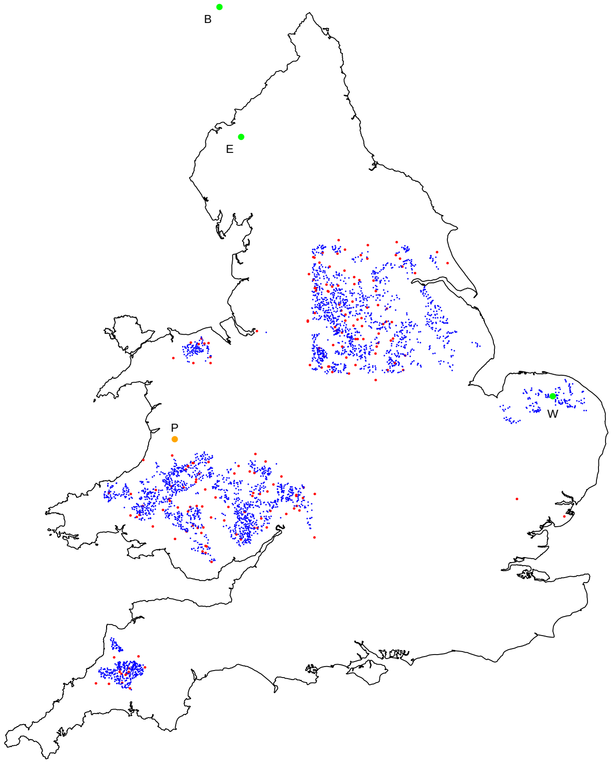

Fig. 1. Locations of sites referred to in this study across England and Wales (coastline shown). Blue symbols show the headwater stream survey sampling locations. Red discs show the nearest national river flow archive gauging stations to the survey sites. Green symbols are headwater sites from which temporal (weekly or monthly) data were available for pCO_2 and stream temperature: E = Eden (Pow), W = Wensum, B = Black burn in Scotland). Orange disc shows the location of the Upper Hafren at Plynlimon (P) from which stream water temperature data was used.

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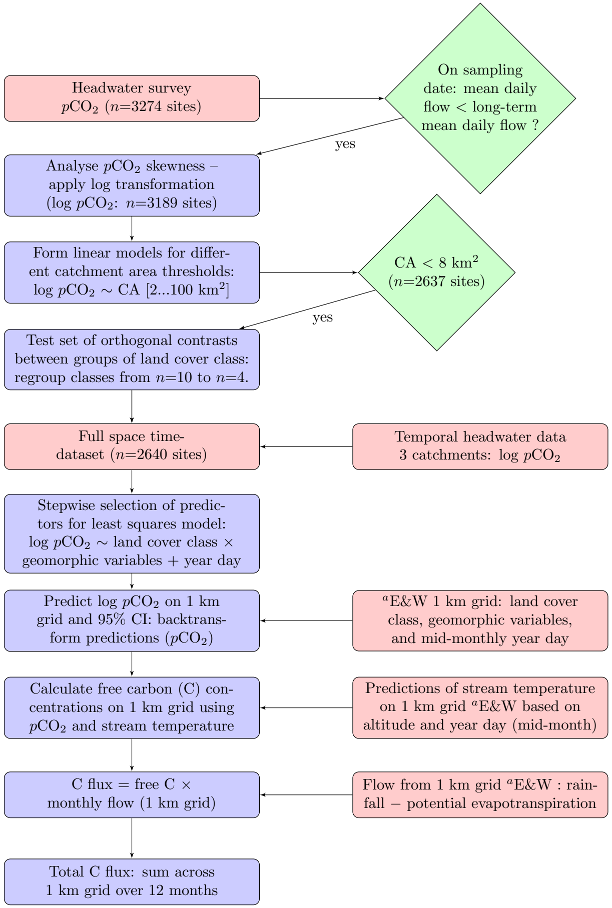

Fig. 2. Flow diagram showing stages in the development and application of a model to predict potential C (CO_2) fluxes from surface water across England and Wales. Red boxes=datasets, green boxes = data selection, blue boxes = computations. [a] England and Wales.

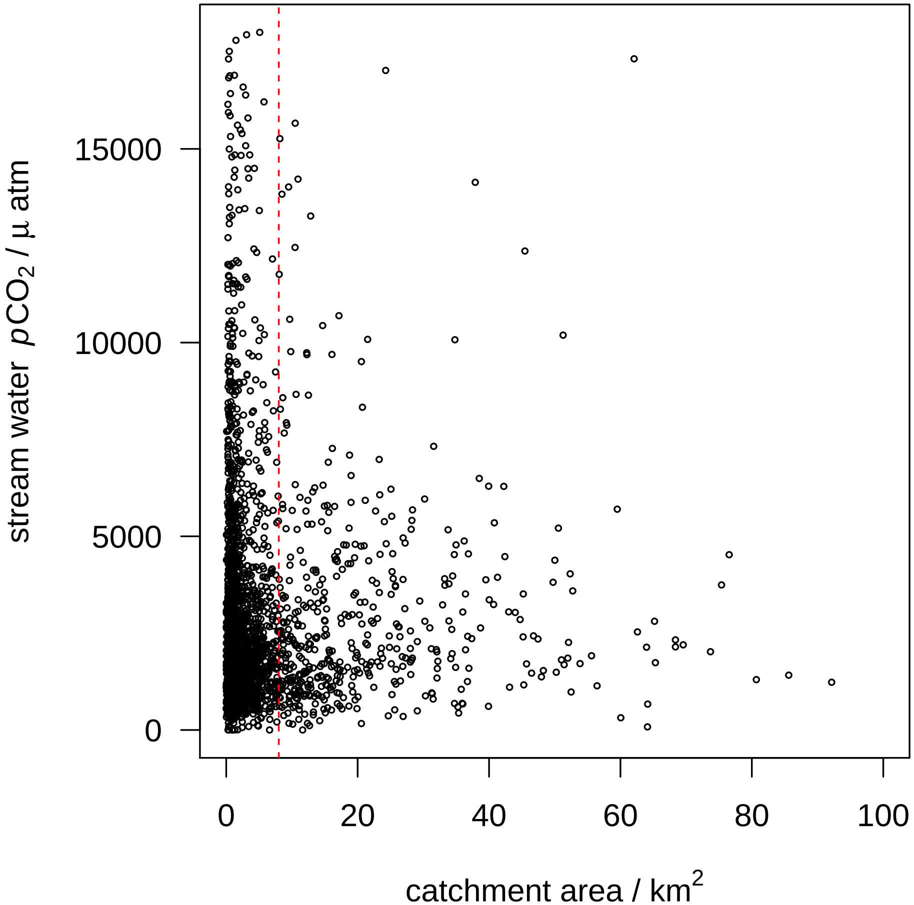

Fig. 3. Scatterplot of headwater catchment area (CA) vs. stream water pCO_2 (μatm). The threshold chosen to select a subset of the data corresponding to the smallest headwater catchments (< 8 km^2) is shown by the red dashed line.

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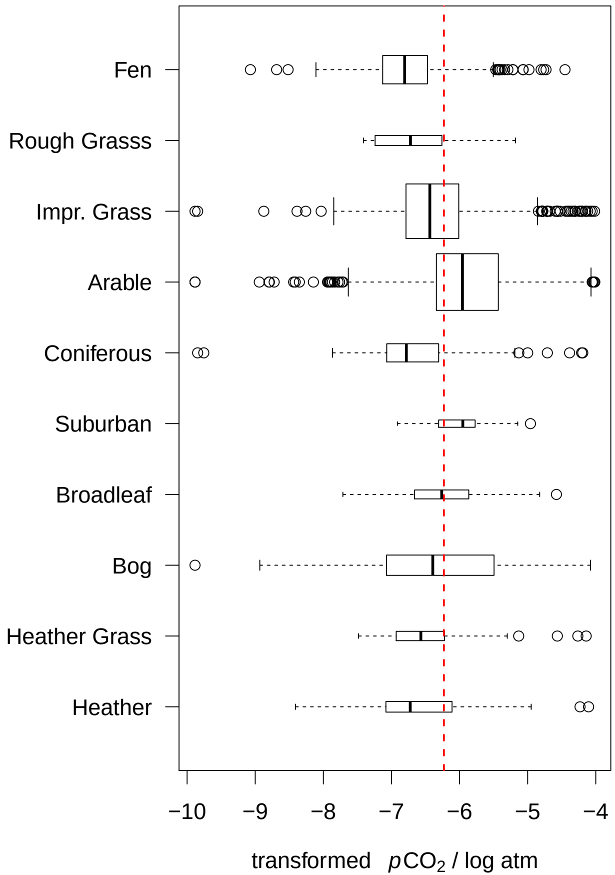

Fig. 4. Boxplot of headwater stream pCO_2 values by dominant land cover class for each catchment ($n = 2637$) based on broad habitat types. Box widths are proportional to number of samples in each class. The red dashed line is the overall median of the data.

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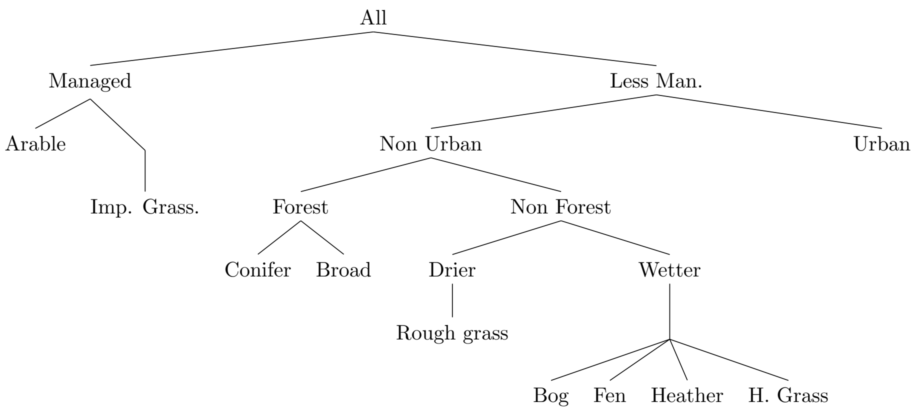

Fig. 5. Hierarchical classification of the ten land cover classes used to define groups for statistical analysis using orthogonal contrasts. Less Man. refers to less managed land cover types in contrast to more intensively managed (agricultural) land.

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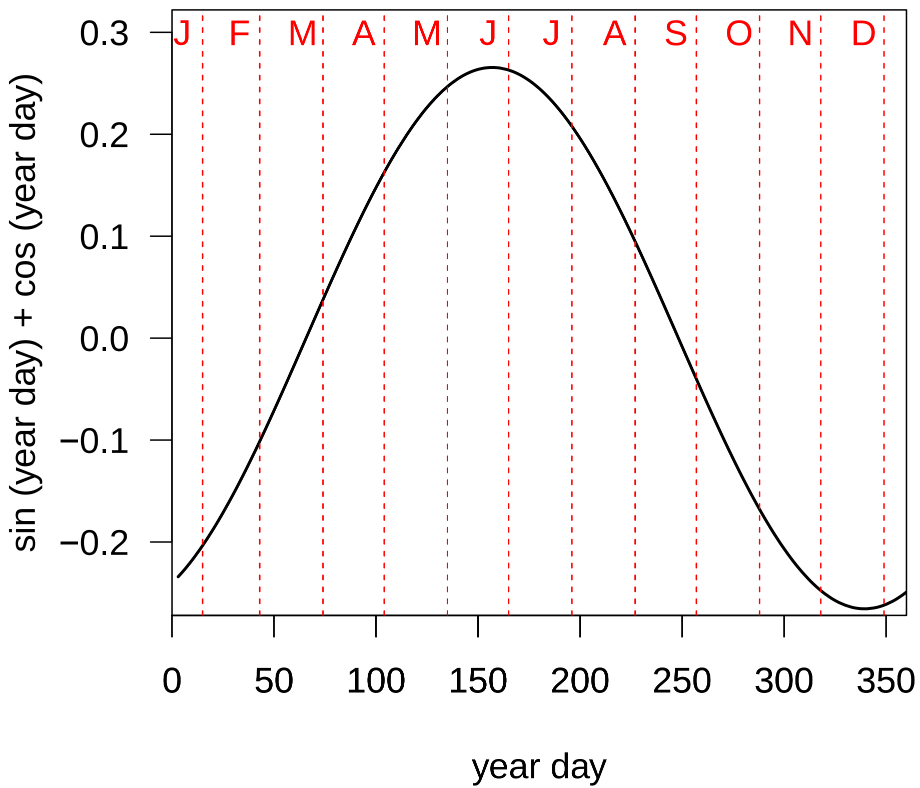

Fig. 6. The sum of sine and cosine model coefficients multiplied by year day highlighting the seasonal effect of temperature on headwater stream pCO_2. Differences in the magnitude of the coefficients used to apply the model at the mid point of each calendar month (J = January, F = February, etc.) are highlighted by the dashed red lines.

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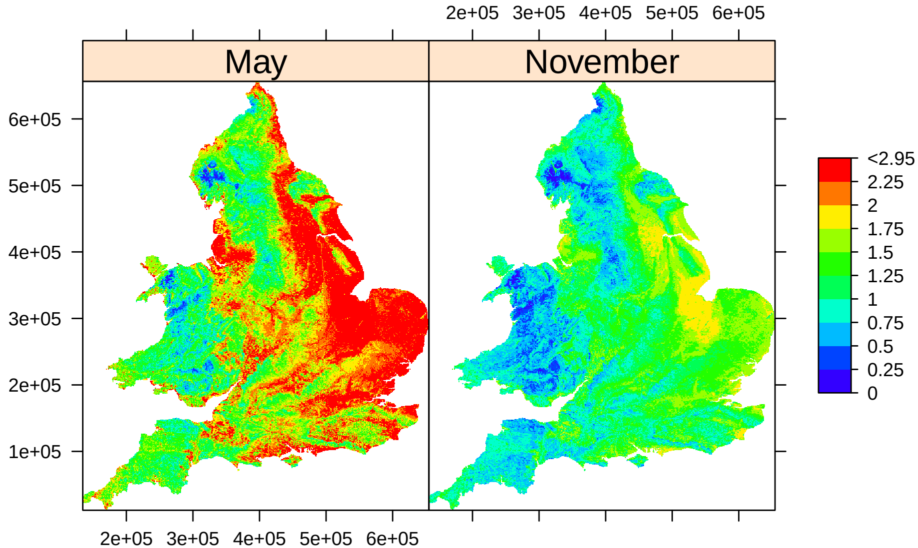

Fig. 7. Predicted free carbon concentration ($mg\,L^{-1}$) in flow for a 1 km grid across England and Wales: May and November. Coordinates are metres on the British National Grid. Note the maximum class limit is greater than the arithmetic scale used in the other classes.

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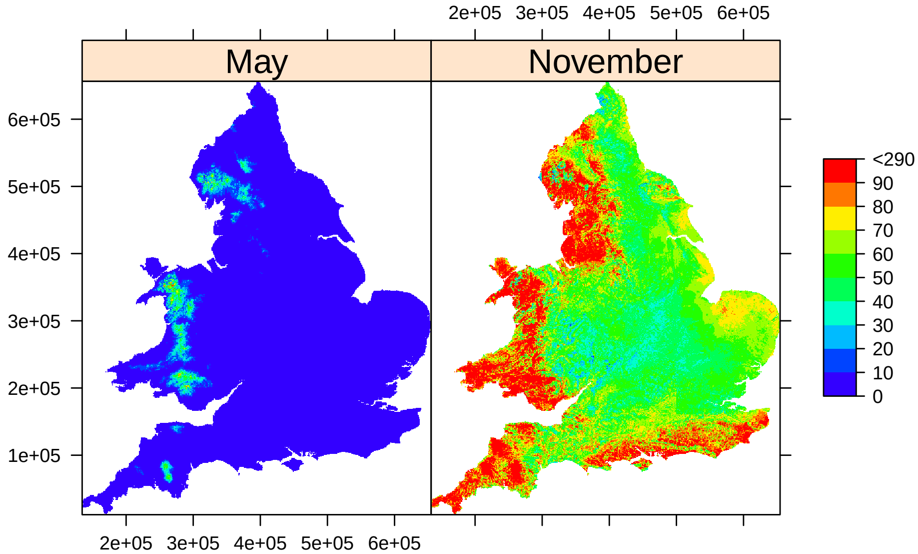

Fig. 8. Predicted potential monthly source of carbon (kg) efflux based on flow for a 1 km grid across England and Wales (May and November). Coordinates are metres on the British National Grid. Note the maximum class limit is greater than the arithmetic scale used in the other classes.

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