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Fluxes of dissolved carbon dioxide and inorganic carbon from an upland peat catchment: implications for soil respiration

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Abstract. This study uses long-term water chemistry records for a circum-neutral peat stream to reconstruct a 7-year record of dissolved CO_2 and DIC flux from the catchment. Combining catchment flux with a knowledge of in-stream metabolism and gas evasion from the stream surface enables an estimate of the dissolved CO_2 content of water emerging from the peat profile to be made; furthermore, these can be used to estimate soil CO_2 respiration. In this way multi-annual records of CO_2 production can be reconstructed, and therefore inter-annual controls on production examined. The results suggest that:

(i) Stream evasion of CO_2 within the catchment varied between 80 and 220 g C/m of stream/yr, while in-stream metabolism produces between 1.0 and 2.9 g C/m of stream/yr;
(ii) Export of dissolved CO_2 emerging from the soil profile, above that expected at equilibrium with the atmosphere, varies between 9.6 and 25.6 tonnes,C/km^2/yr; and
(iii) The export of dissolved CO_2 implies a soil respiration rate of between 64.2 and 94.9 tonnes C/km^2/yr.

The inter-annual variation in both dissolved CO_2 flux and soil CO_2 respiration suggests that severe drought has no long-term effect on CO_2 production and that temperature-based models of soil CO_2 respiration will be adequate in all but the severest of summer droughts. The inter-annual variation in CO_2 flux shows that CO_2 production is decoupled from dissolved organic carbon (DOC) production. The decoupling of DOC and dissolved CO_2 production shows that enzymatic-latch production of DOC is an anaerobic process and will not increase soil CO_2 respiration.

Introduction

Upland peat is the most significant wetland environment and the largest terrestrial carbon pool in the UK (Milne and Brown 1997; Cannell et al. 1999). Peatlands also form a significant carbon reserve in other countries of Western and Northern Europe as well as parts of Canada and Siberia. Though they form a significant reserve, studies have suggested that at the present day they can be both sinks and sources of carbon (Shurpali et al. 1993; Neumann et al. 1994; Whiting 1994; Waddington and Roulet 1996). Therefore, there is a greater need than ever to understand the behaviour of each of the release and uptake pathways of carbon from these upland reserves.

Studies based on UK data have tended only to include gaseous carbon emissions and have typically excluded the fluvial flux of carbon from peatlands. The fluvial flux of carbon from a peatland can occur via a number of forms of carbon – dissolved organic carbon (DOC), particulate organic carbon (POC), dissolved inorganic carbon (DIC), and dissolved CO_2.

Rising concentrations of DOC are a ubiquitous phenomenon in upland catchments of the UK. Freeman et al. (2001a) have shown increases of 65% for a series of UK stream and lake catchments over a period of 12 years. Worrall et al. (2003a) have shown significant increases in DOC concentrations over timescales of up to 39 years for catchments up to 820 km^2 in size. Increases in streamwater DOC concentrations in a catchment indicate a shift in the carbon budget with decreasing storage of carbon.

Why are such shifts in the carbon storage in peat occurring? Worrall and Burt (2004) have shown that increasing DOC cannot be readily explained by trends in streamflow, pH, alkalinity, turbidity or conductivity; that observed increases are independent of flowpath; and that increasing DOC concentration is associated with a significant increase in carbon flux from the catchments studied. In addition, they identified a step change in flux observed after a 1 in 100-year drought in 1976. Freeman et al. (2001a) correlated increasing DOC concentration with increasing temperature; however, Worrall et al. (2004) showed that increases in temperature alone could not explain the DOC concentration. Moreover, Worrall et al. (in press) showed that increasing trends in DOC concentration are found everywhere across the UK uplands and therefore any explanatory mechanism must be equally ubiquitous. They conclude that the only sufficient explanation is that enzymatic latches (Freeman et al. 2001b) are operating with land management, eutrophication, and temperature effects adding locally to the observed DOC increases.

Anaerobic degradation does not appear to occur in peats despite being present in other settings (Freeman et al. 2001b). In peat bogs, decomposition, and therefore DOC production, is restricted by repression of the major biodegrading hydrolase enzymes (Kang and Freeman 1999). Freeman et al. (2001b) have shown that this inhibition relates to the presence of phenolic compounds; these phenolic compounds can build up in peat because the activity of phenol oxidase is severely restricted in the absence of oxygen. Therefore, if the water table falls in a peat bog, the phenol oxidase activity increases destroying the phenolic compounds that repress the hydrolase activity. A loss of phenolic compounds means that decomposition can continue after the water table has risen again. This has been referred to as an “enzymic latch” mechanism (Freeman et al. 2001b), i.e. enzymes are switched on by water table drawdown but are not switched off immediately as the water table rises. This mechanism could lead to the increased peat decomposition, and therefore to increased DOC release following periods of drought or water-table drawdown. It is not known how long this effect might last following a drought or whether eventually hydrolase enzyme repression resumes.

The release of carbon as dissolved CO_2 has been studied far less than DOC release (Hope et al. 2001). Dissolved CO_2 in waters emerging into streams is typically present in excess of that in the atmosphere, which means that rivers generally act as a source of CO_2 (Dawson et al. 1995). Long-term records of dissolved CO_2 do not exist as they do for DOC, but can be estimated from long-term records stream chemistry (especially pH, alkalinity – Neal et al. 1998) and long-term records of stream chemistry do exist. Dissolved CO_2 present as water emerges into a stream is sourced from the CO_2 present in the soil profile and therefore dissolved CO_2 concentrations can be used to estimate soil CO_2 and hence soil CO_2 respiration (Jones and Mulholland 1998). If long-term records of dissolved CO_2 can be calculated, and thus soil CO_2 respiration estimated, it is then possible to examine such long-term records to understand controls upon CO_2 production. By reconstructing multi-annual records of soil CO_2 respiration it will be possible to better test present models of soil CO_2 respiration (e.g. Lloyd and Taylor 1994). Furthermore, it might be expected that if enzymic latches are causing shifts in the carbon balance of UK upland peats, then they may also be enhancing dissolved CO_2 flux and soil CO_2 respiration. If anaerobic degradation of peat is thus enabled in post-drought periods, it can be hypothesized that CO_2 fluxes would not increase, rather CH_4 fluxes would increase. That is to say that if DOC production would normally be associated with gas production in the form of CO_2 then anaerobic production of DOC might also be expected to be accompanied by gas production and that could be CH_4. This hypothesis could be tested by comparing dissolved CO_2 flux, soil CO_2 respiration and DOC flux.

The purpose of this study is, therefore, to construct a long record of dissolved CO_2 emerging from a peat profile, from which the history of soil CO_2 respiration over the study period can be estimated. The record will be used to assess the variability of dissolved CO_2 and soil CO_2 respiration at intra- and inter-annual scales to better understand the controls on CO_2 flux and to better estimate the carbon budgets for these important terrestrial stores of carbon. By understanding the controls on soil respiration this study will assess the adequacy of present models of soil CO_2 respiration, and test the hypothesis that soil CO_2 respiration should not respond to enzymatic latches.

Methodology

This study uses the long-term records of stream chemistry measured for an upland peat catchment to calculate fluxes of dissolved CO_2, DIC and to estimate soil CO_2 respiration. The study combines and adapts the method of calculating the inorganic carbon speciation of Neal et al. (1998) with the method of Jones and Mulholland (1998) for estimating the proportion of dissolved CO_2 coming from the soil–groundwater system.

Study site

Moor House National Nature Reserve (NNR) is situated in the North Pennine upland region, to the south of the summit of Cross Fell (National grid reference NY 756326, Figure 1). The Moor House NNR is part of the UK Environmental Change Network (ECN) and is classified as both a terrestrial and freshwater site. The ECN collects various hydrological data from the Trout Beck catchment that lies within the Moor House NNR; this catchment is one of the primary headwater tributaries of the River Tees. The Trout Beck catchment lies largely above 450 m above sea level with the highest point being the summit of Cross Fell at 893 m. The underlying geology is a succession of Carboniferous limestones, sands, and shales with intrusions of the doleritic whin sill (Johnson and Dunham 1963). This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat during the Holocene. Blanket peat covers 90% of Trout Beck catchment (Evans et al. 1999), some of which is either naturally eroded, or damaged by the practice of gripping (digging drainage channels). The vegetation of the reserve is dominated by *Eriophorum* sp. (cotton grass), *Calluna vulgaris* (heather), and *Sphagnum* sp. (moss). The mean annual temperature (1992–2000) is 5.8 °C; air frosts are recorded on over 100 days in a year. Mean annual precipitation (1953–2000) is 1953 mm (Burt et al. 1998) with snow being a significant proportion of precipitation – annual average snow cover at 500 m is 55 days (Archer and Stewart 1995). Any rainfall in the upper catchment produces a

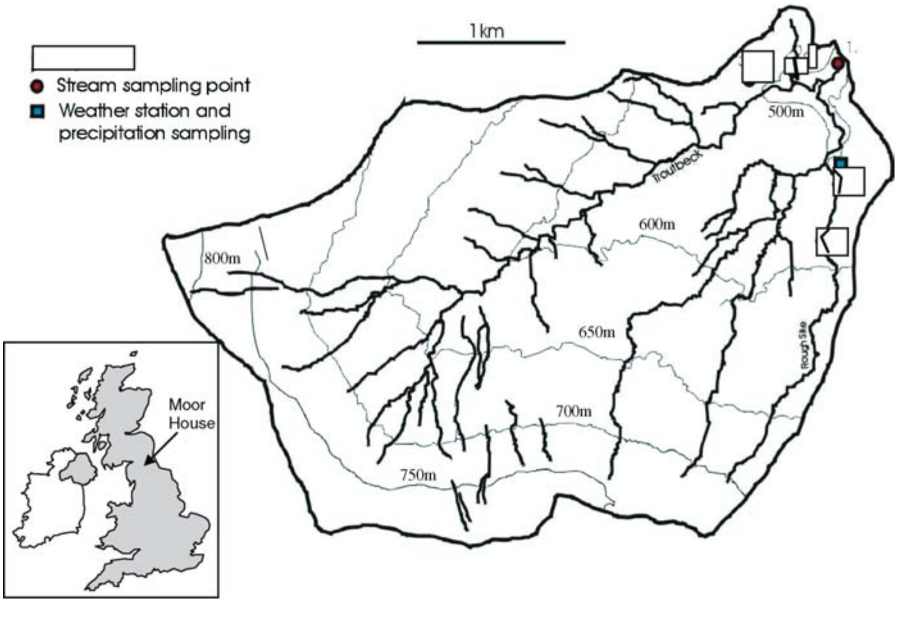

Figure 1. Location map of the Trout Beck catchment.

rapid runoff response: studies at Moor House have shown that the lag between peak rainfall intensity and peak flow can be as little as 30 min (Burt et al. 1998). The catchment area above the Trout Beck gauging site is 11.4 km^2.

ECN monitoring

Continuous monitoring within the catchment, includes rainfall, temperature, and streamflow at the catchment outlet. Water table elevation is measured at six piezometers within the catchment. Water samples are collected weekly for chemical analysis from the outlet of the Trout Beck catchment; rainwater samples are collected weekly for chemical analysis. Water samples are analysed for pH, alkalinity, calcium, magnesium, potassium, sodium, iron, aluminium, chloride, and sulphate. The methods of analysis are detailed in Sykes and Lane (1996).

Approach

Jones and Mulholland (1998) have proposed that dissolved CO_2 at the outlet of a catchment is the result of several processes. The dissolved CO_2 leaving a catchment originates in the soil–groundwater system, but upon entering into the stream dissolved CO_2 will degas in to the atmosphere but can also be added to by the turnover and mineralization of organic matter in the stream (Figure 2). Thus, the dissolved CO_2 content of the water leaving the catchment

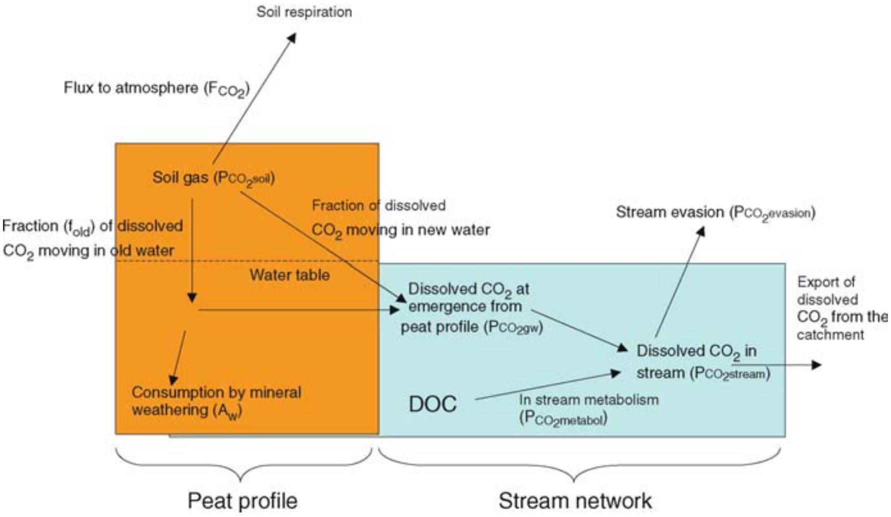

Figure 2. Conceptual model of dissolved CO_2 behaviour in the study catchment.

equates to:

$$\mathrm{pCO}_{2\mathrm{stream}} = \mathrm{pCO}_{2\mathrm{gw}} - \mathrm{pCO}_{2\mathrm{evasion}}\mathrm{pCO}_{2\mathrm{metabol}}$$

where $\mathrm{pCO}_{2\mathrm{stream}}$ is the dissolved CO_2 in stream at the catchment monitoring point; $\mathrm{pCO}_{2\mathrm{gw}}$, the dissolved CO_2 from the soil–groundwater of the catchment; $\mathrm{pCO}_{2\mathrm{evasion}}$, the dissolved CO_2 lost to the atmosphere between groundwater emergence and the catchment monitoring point; and $\mathrm{pCO}_{2\mathrm{metabol}}$, the dissolved CO_2 produced by in-stream metabolism between the discharge of groundwater into the channel and the catchment monitoring point. It follows that the dissolved CO_2 content of the water at emergence from the soil–groundwater system into the stream ($\mathrm{pCO}_{2\mathrm{gw}}$) can be calculated if $\mathrm{pCO}_{2\mathrm{stream}}$, $\mathrm{pCO}_{2\mathrm{evasion}}$ and $\mathrm{pCO}_{2\mathrm{metabol}}$ are known or can themselves be calculated.

Estimating stream dissolved CO_2

The method calculates the excess dissolved CO_2 (EpCO_2) which is defined as the amount of dissolved CO_2 in the water in comparison to that expected in equilibrium with the atmosphere:

$$\mathrm{EpCO}_2 = \frac{[\mathrm{CO}_2]_{\mathrm{water}}}{[\mathrm{CO}_2]_{\mathrm{eqm}}} \tag{1}$$

EpCO_2 can be calculated, iteratively, by comparing the estimate of alkalinity from the equilibria outlined in Appendix A with values measured for the outlet of the catchment. The method does require an initial estimate of EpCO_2 which can be calculated using the method of Neal et al. (1998):

$$\mathrm{EpCO}_2 = \frac{(0.95\mathrm{Alk}_{\mathrm{Gran}} + 10^{(6-\mathrm{pH})} + 10^{(6+\mathrm{pH}+\mathrm{p}K_6)})10^{(6-\mathrm{pH})}}{(6.46 - 0.0636T)(1 + 2.3810^{(\mathrm{pH}-\mathrm{p}K_2)})} \tag{2}$$

where $\mathrm{Alk}_{\mathrm{Gran}}$ is the Gran Alkalinity in μEq/l; K_6, K_2, equilibrium constants detailed in Appendix A, and T, water temperature in °C.

Thus EpCO_2 can be calculated with only a knowledge of streamwater alkalinity, pH, Ca, and temperature.

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

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

$$\mathrm{EpCO}_{2(\mathrm{altitude})} = \frac{P_0}{P_a}\mathrm{EpCO}_{2(\mathrm{calculated})}$$

where $\mathrm{EpCO}_{2(\mathrm{altitude})}$ is the EpCO_2 at the altitude of the study site; $\mathrm{EpCO}_{2(\mathrm{calculated})}$, the EpCO_2 calculated from Eq. (1); a, catchment 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 and the DIC contents can be calculated as:

$$\mathrm{DIC} = [\mathrm{HCO_3^-}] + [\mathrm{H_2CO_3}] + [\mathrm{CO_3^{2-}}] + [\mathrm{CaHCO_3^+}] + [\mathrm{CaCO_3}]$$

Both dissolved CO_2 and DIC are converted to units of mg C/l. In order to estimate the amount of dissolved CO_2 that would be transported at equilibrium, the inorganic carbonate speciation is calculated by setting the value of $EpCO_2 = 1$.

Stream temperature was not recorded as part of ECN monitoring and so, in order to estimate it, the model of the relationship between air and water temperature as presented by Crisp and Howson (1982) is used.

Evasion rate of stream CO_2

The evasion rate of CO_2 from the streamwater can be estimated from the stagnant two-film model (Liss and Slater 1974):

$$F = \frac{D_{\mathrm{CO_2}}}{z_{\mathrm{w}}}([\mathrm{CO_2}]_{\mathrm{water}} - [\mathrm{CO_2}]_{\mathrm{air}})$$

where F is the flux of CO_2 (mg C/cm^2/s); D_{CO_2}, diffusion coefficient of CO_2 in water (2×10^{-5} cm^2/s); z_w, water film thickness (4×10^{-4} cm); $[\mathrm{CO_2}]_{\mathrm{water/air}}$, CO_2 concentration in air/water (mg C/cm^3). The amount of CO_2 lost during the passage from groundwater discharge to the stream monitoring point can then calculated by knowledge of the residence time of the water in the stream. The residence time for the study catchment is estimated from the flow in the catchment and dimensions of the stream; it is assumed that on average groundwater enters the stream at the mid-point of the channel length.

Estimating stream production of CO_2

In-stream metabolism is estimated using estimates of the biochemical oxygen demand (BOD) measured for the Tees catchment (Wright 2003). Measurements of BOD are taken over 5 days and so in order to estimate stream metabolism, the BOD values are compared to stream residence time estimated for the Trout Beck stream. There is evidence that BOD is proportional to flow, but no allowance is made for this effect within this study.

Once the dissolved CO_2 content leaving the soil–groundwater system of catchment has been calculated, the flux of dissolved CO_2 and DIC is then calculated with reference to river discharge measurements using "method 5" (Walling and Webb 1985). The annual cycles of $pCO_{2\mathrm{gw}}$, $pCO_{2\mathrm{evasion}}$ and $pCO_{2\mathrm{metabol}}$ are calculated using the method of seasonal indices of Worrall and Burt (1999). The method of seasonal indices uses monthly medians, calculated for the whole dataset, normalized against the median for the whole dataset to provide a measure of difference between each month and the median.

Sources of inorganic carbon

The dissolved CO_2 and DIC emerging into the stream is the result of mineral weathering and soil respiration. Mineral weathering consumes dissolved CO_2 and generates DIC while soil respiration generates dissolved CO_2. The water entering the stream comes from a variety of flowpaths, the process of mineral weathering will predominate in the water emerging from deep in the soil profile and soil respiration in shallow flowpaths. The proportion of dissolved CO_2 and DIC in the separate flowpaths of the catchment can be calculated by reference to the proportion of "old" and "new" water in the stream discharge. The separation can be achieved assuming that old water comes via deep flowpaths, where it would interact with the local bedrock, and that new water has not interacted with the regolith either because it comes via shallower paths or has insufficient residence time to react. The proportion of old and new water in the stream discharge can be calculated with reference to any one of the chemical species measured in the stream water. For reasons associated with the dominant weathering processes of the catchment, Ca is used here. The log–log plot of Ca vs. stream discharge shows a straight line relationship implying two end-member mixing, the lower concentration can be readily identified as equal in concentration to average rainfall measured at the site. Given a two end-member mixing model, the proportion of old water in a sample of stream water is readily calculated.

The amount of dissolved CO_2 consumed by mineral weathering can be calculated if the rate and nature of the weathering reactions are known. The CO_2 concentration in soil water is (Figure 2):

$$\mathrm{pCO}_{2\mathrm{gw}} A_{\mathrm{w}} f_{\mathrm{old}} = \mathrm{pCO}_{2\mathrm{soil}}$$

where A_w is the amount of CO_2 consumed by mineral weathering; f_{old}, the fraction of the old water in the streamflow; and $\mathrm{pCO}_{2\mathrm{soil}}$, the dissolved CO_2 concentration in soil water.

Once the soil water CO_2 concentration has been estimated, it is then possible to make a further estimate of the soil respiration rate of CO_2 by applying the diffusion equation using the method of Kabwe et al. (2002):

$$F_{\mathrm{CO}_2} = D_{\mathrm{CO}_2} \frac{\mathrm{d}C}{\mathrm{d}z}$$

where F_{CO_2} is the flux of gaseous CO_2 from the soil (mg $CO_2/m^2/h$); D_{CO_2}, diffusion coefficient of CO_2 in soil (m^2/h); and $\mathrm{d}c/\mathrm{d}z$, the CO_2 concentration gradient (mg CO_2/m^3) where z is depth to the water table. The depth to the water table is taken here as the average of the six piezometers maintained as part of the ECN monitoring. The effective diffusion coefficient is calculated by combining the methods of Millington and Quirk (1961) and Bird et al. (1960):

$$D_{CO_2} = D_0 \frac{\theta_{\mathrm{air}}^{10/3}}{\eta^2} \left(\frac{T}{T_0}\right)^b$$

where D_0 is the free air CO_2 gas diffusion coefficient at temperature T_0 (m^2/h); θ, volumetric gas content of the peat; η, porosity; T, soil temperature (K); and b, empirical constant.

Soil water temperature is assumed to be equal to stream temperature. The porosity of peat in the acrotelm (upper layer of peat that is not permanently below the water table) is taken as 79% (Rowell 1994). The free air gas diffusion coefficient was determined to be 5.47×10^{-2} m^2/h at 293.15 K (Fuller et al. 1966) and the same study showed that a b value of 1.75 was appropriate.

Modelling soil respiration

In order to assess the inter-annual estimates of soil CO_2 respiration produced by the above approach the values are compared to estimates for soil CO_2 respiration calculated from other approaches. Lloyd and Taylor (1994) showed that for a range of environments a simple description of soil respiration was:

$$R = R_{10}\,\mathrm{e}^{308.56\left(\frac{1}{56.02} - \frac{1}{(T-227.13)}\right)}$$

where R is the soil respiration rate at temperature T; R_{10}, soil respiration rate at 10 °C; and T, air temperature (K).

This formulation of the Arrhenius equation for soil respiration is for all soil respiration and does not distinguish between CO_2 and CH_4. Christensen et al. (1996) used the approach of Lloyd and Taylor (1994) coupled with a measured percentage of gas efflux that was CH_4 (typically the percentage of the gas flux that is methane is of the order of 3%, Clymo and Reddaway 1971): the same proportion is assumed in this study. Monthly average temperature data from the study catchment is used to calculate a soil CO_2 respiration rate. No data are available to independently calibrate this model; however, the model can be calibrated against annual soil CO_2 respiration fluxes as calculated above from the dissolved CO_2 for 1994 and then used to calculate soil CO_2 respiration for each of the other years of the study. The results are used to demonstrate any differences in the inter-annual variation as predicted by the approaches of Lloyd and Taylor (1994) and that presented in this study.

Results

Alkalinity, pH and streamflow

The pH appears to be relatively stable across the period of study for this catchment (Figure 3). Values of pH are very low during the onset of the severe

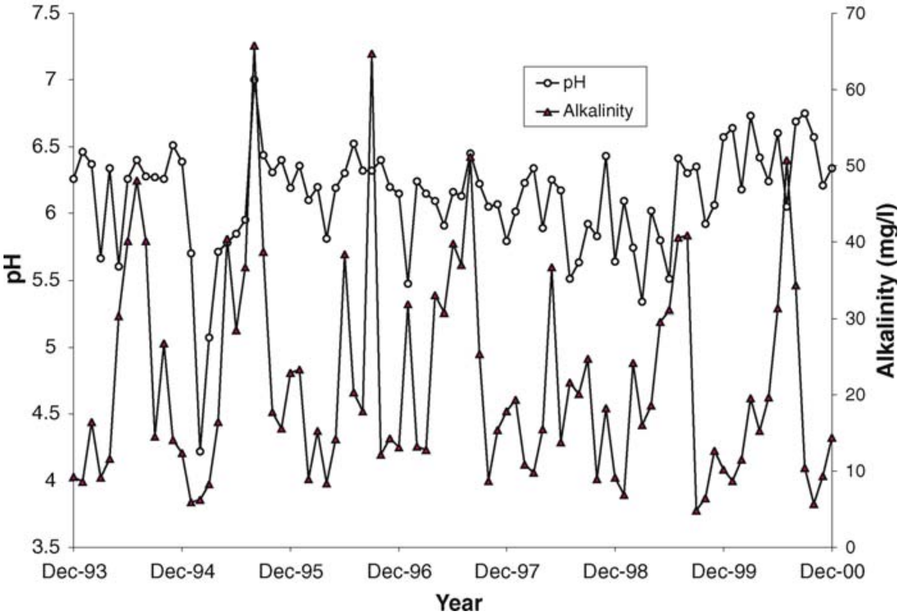

Figure 3. pH and alkalinity for the Trout Beck catchment over the period of the study.

drought of 1995 and values of pH may decrease for 3 years following the 1995–1996 drought but recover during the final 2 years of the study period. In direct contrast to pH, alkalinity values appear to peak during the period of the severe drought of 1995 and decline for the rest of the study period (Figure 3). The annual cycle of the pH has a relatively low amplitude in comparison to that for alkalinity (Figure 4). The seasonal cycles of alkalinity and pH appear to mimic each other save an apparent rise in alkalinity in August. This apparent increase in alkalinity would appear to be related to the time of maximum depth of the water table in peat; at this time deeper baseflow and groundwater from carbonate-rich flowpaths within the bedrock will dominate. Nevertheless, the results imply that the pH of streamwater is very well buffered. The streamflow showed no obvious trends across the period of study (not plotted). The annual cycle (Figure 4) shows the expected low values in summer compared to winter but with high values in September and March reflecting local rainfall and snow patterns.

Dissolved inorganic carbon

The concentration of DIC at the catchment outlet varies between 0 and 97.5 mg C/l (Figure 5). The flux of DIC varies between 9.7 and 28.9 tonnes C/km^2/yr (Figure 6). The trend in DIC flux shows a steady rise post the

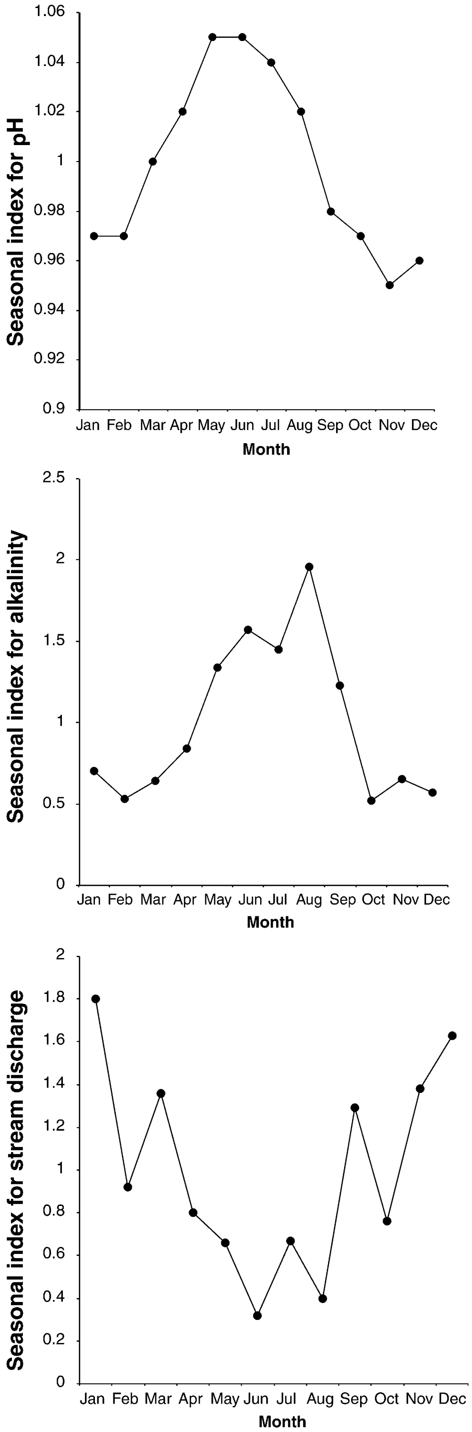

Figure 4. The annual cycle in pH, alkalinity and stream discharge for the Trout Beck stream.

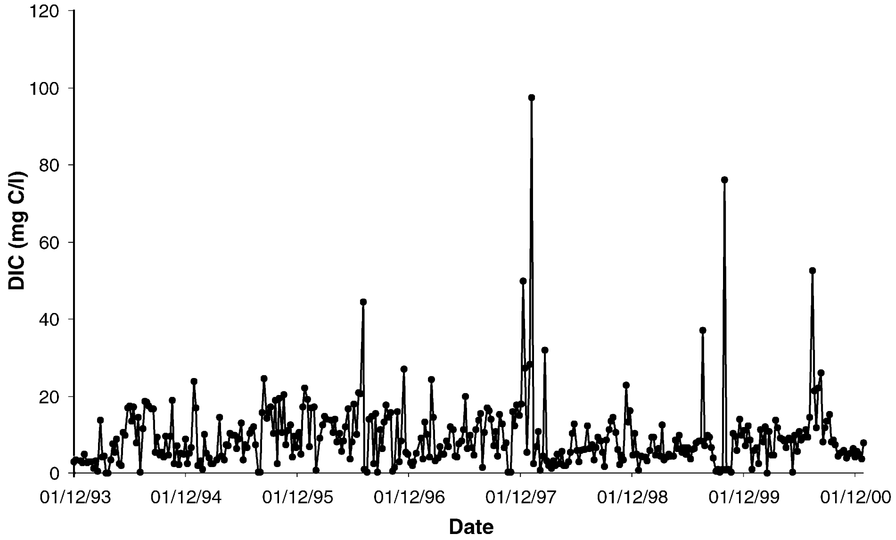

Figure 5. The calculated DIC for the Trout Beck catchment over the period of the study.

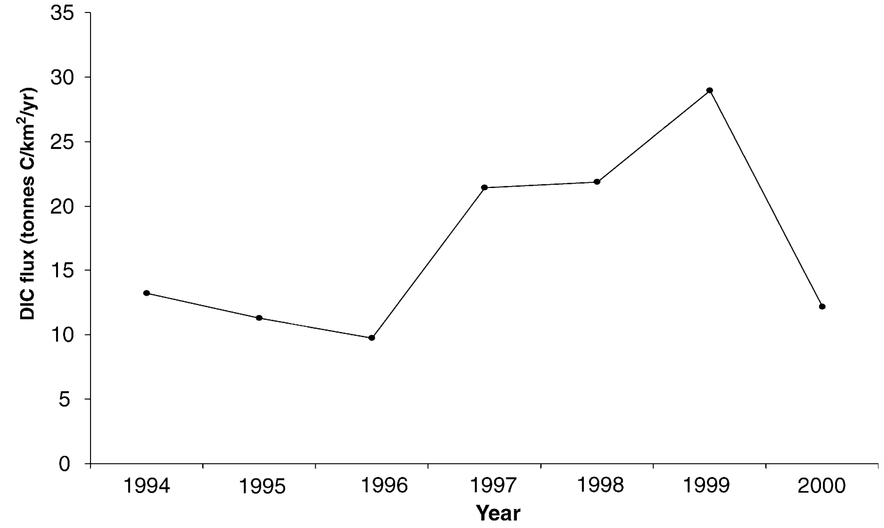

Figure 6. The annual DIC flux for the study catchment.

drought of 1995 but the increase really only starts in 1997 and lasts for only 3 years and appears to correspond to the changes in pH post-drought (Figure 3).

Stream production of CO_2

The amount of CO_2 produced within the streams of the catchment is small varying between 0.00 and 0.02 mg C/l; this equates to between 1.0 and 2.9 g C/m of stream/yr, which equates to 0.03–0.08 tonnes C/yr for the entire catchment. The annual cycle of the stream production shows a trend that is the inverse of streamflow even down to slight decreases in stream CO_2 production during March and September which were noted above as having unseasonally high flows (Figure 7). It is not surprising that, as streamflow increases, stream CO_2 production apparently decreases since it is calculated directly from the stream residence time.

Stream CO_2 evasion

The amount of CO_2 escaping from the stream varies from 0 to 1.6 mg C/l. The amount of CO_2 that is lost from the water of catchment varies between 2.2 and 6.6 tonnes C/yr, which equates to between 80 and 220 g C/m of stream/yr. The annual cycle of the stream evasion of CO_2 shows an annual cycle that is a trade-off between residence time of stream water within the catchment (Figure 7) and the factors that control the stream concentration of dissolved CO_2. The balance of these factors gives high evasion rates in summer months when dissolved CO_2 and stream residence times are high, but shows a sharp decline between September and October when high late summer alkalinity keeps dissolved CO_2 high even when residence times are becoming shorter with increasing flow into the autumn months.

Dissolved CO_2 and DOC

The excess dissolved CO_2 concentration, i.e. the concentration of dissolved CO_2 above that expected when in equilibrium with the atmosphere, at emergence from the peat profile into the stream varies between 0 mg C/l, i.e. water at equilibrium with the atmosphere, and 91.1 mg C/l (Figure 8). The time series of the dissolved CO_2 at emergence tends to show an annual cycle with a maximum in November (Figure 7). The annual cycle shows a minimum in May, which is consistent with the annual cycle observed for DOC in this catchment. The annual cycle of the DOC concentrations in streamwater is controlled by production of DOC above the water table, which reaches its maximum in the summer months; the DOC is flushed out during the late autumn/early winter when the water table is high and production, to replenish the supply, is low. The DOC seasonal cycle shows a minimum in late spring/early summer when reserves of DOC are diminished and stream discharge recedes as the summer period begins (Figure 7). The minimum in DOC concentration does not occur at the height of the summer because at that time DOC production is at its highest. Storm discharge from the peat can acquire

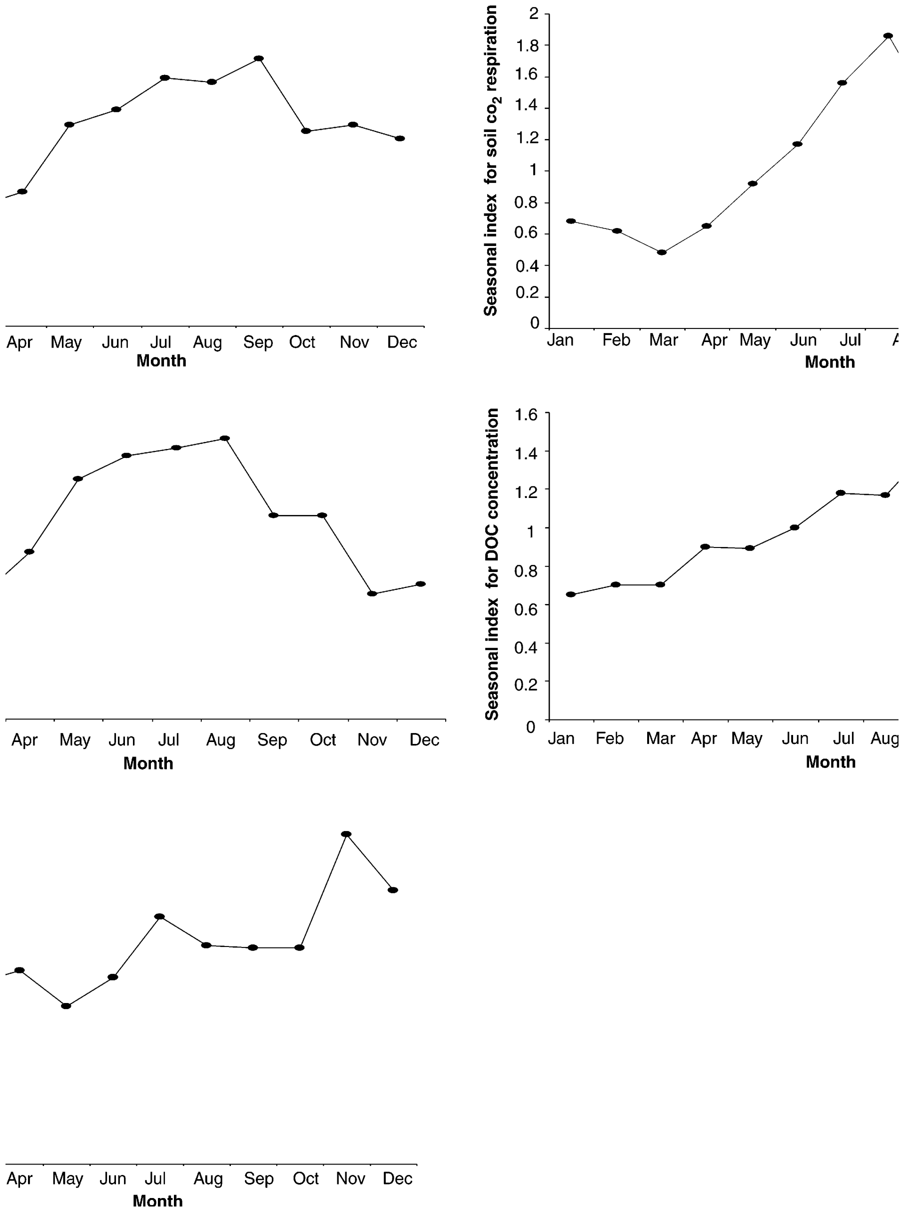

Figure 7. The annual cycle in the: stream production and stream evasion of CO_2; excess dissolved CO_2 at emergence; soil respiration of CO_2; and DOC concentration for the Trout Beck catchment.

very high concentrations of DOC so that peak values during the summer period can be similar to those found in the autumn months, this increases the average DOC concentrations during the summer months. A similar pattern is

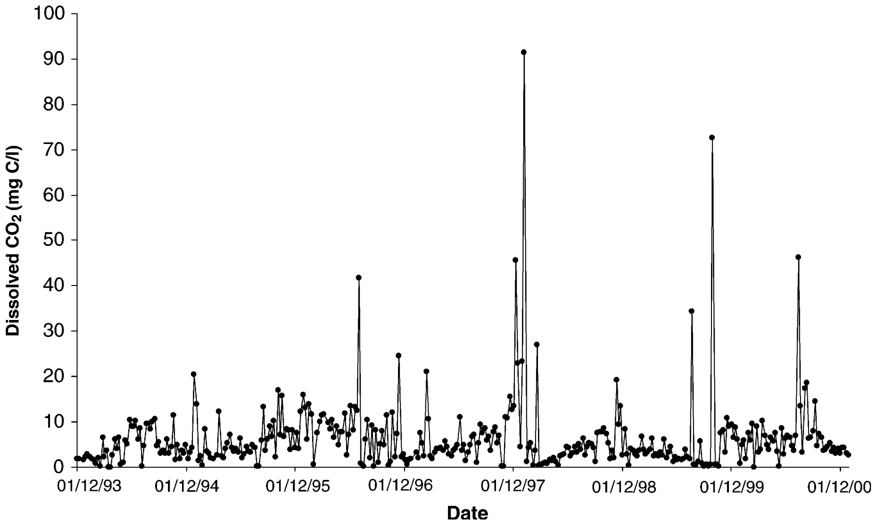

Figure 8. The calculated excess dissolved CO_2 at emergence from the peat profile over the period of the study.

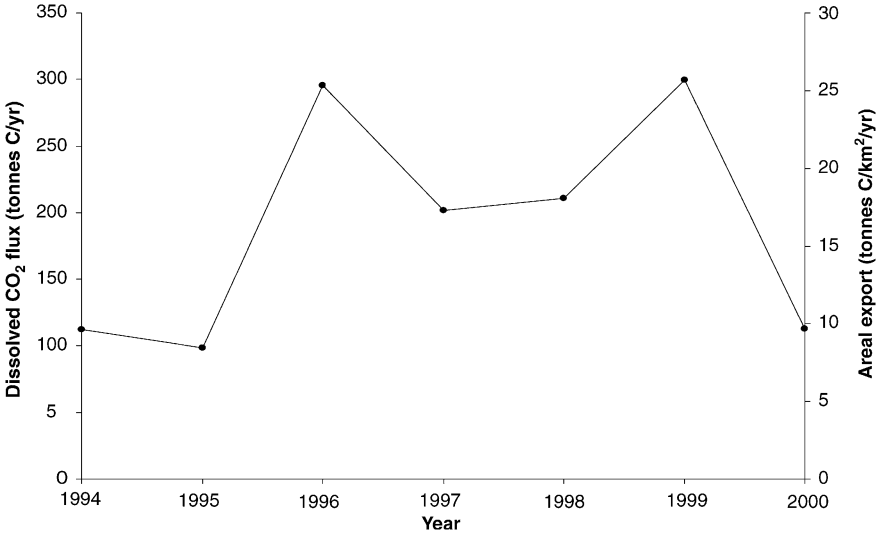

Figure 9. The annual flux of excess dissolved CO_2 at emergence from the peat profile.

observed for dissolved CO_2 concentrations and so the observed minimum in the annual cycle in May can have a similar explanation, i.e. lack of production of dissolved CO_2 until significant drawdown of the water table in the summer months. However, DOC concentrations peak in late September/October when water table rise into the autumn and DOC produced over the summer months

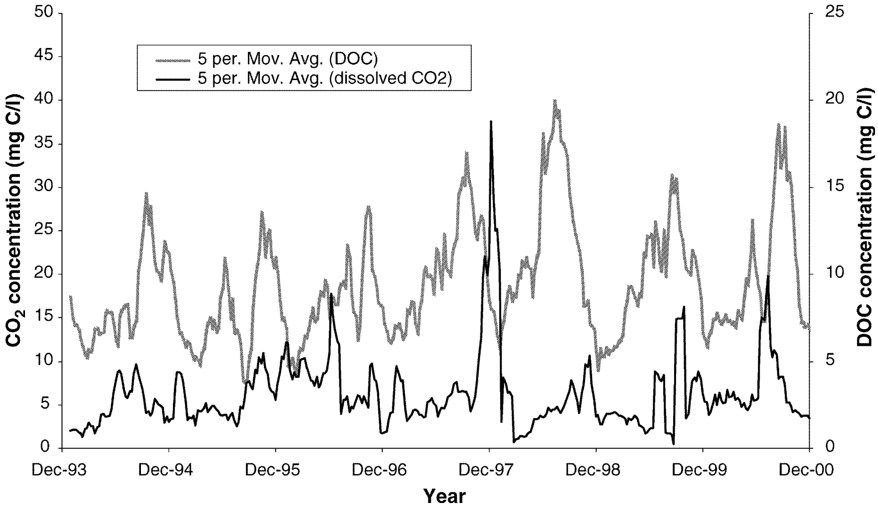

Figure 10. Comparison of the time series of excess dissolved CO_2 and DOC for the study catchment.

can be flushed out, while for dissolved CO_2 the peak comes later in the year – November/December.

The flux of excess dissolved CO_2 varies between 96 and 292 tonnes C/yr, which is an areal export of 9.6 and 25.6 tonnes C/km^2/yr (Figure 9). The flux of dissolved CO_2 peaks in 1996 and again in 1999; there is no evidence for any trend in the annual flux values across the study period, and no trend was observed in the concentration of dissolved CO_2 (Figure 8). Both the annual flux and the concentration time series suggest that the effect of the severe drought of 1995 is limited. The dissolved CO_2 time series indicates that the effect of the drought could last as long as 2 years with increased values of dissolved CO_2 present until approximately the end of 1997. However, there appears no sustained increase, decrease or trend in dissolved CO_2, this is in sharp contrast to the time series for DOC from this catchment for which concentrations continue to rise over the study period (Figure 10). The excess dissolved CO_2 is the amount of dissolved CO_2 that will eventual reach the atmosphere. In comparison to the stream evasion rates, a peat profile producing dissolved CO_2 at these rates would require approximately 120 km of stream/km^2 of peat in order to degas totally to the point at which the water is equilibrium if there was no further addition of CO_2 from in-stream processes.

Soil respiration of CO_2

Estimated values of soil CO_2 flux vary between 0.11 and 5.7 g C/m^2/day, which equates to an annual flux of between 64.2 and 94.9 tonnes C/km^2/yr (Figures 11 and 12). The annual cycle of soil CO_2 respiration peaks in August

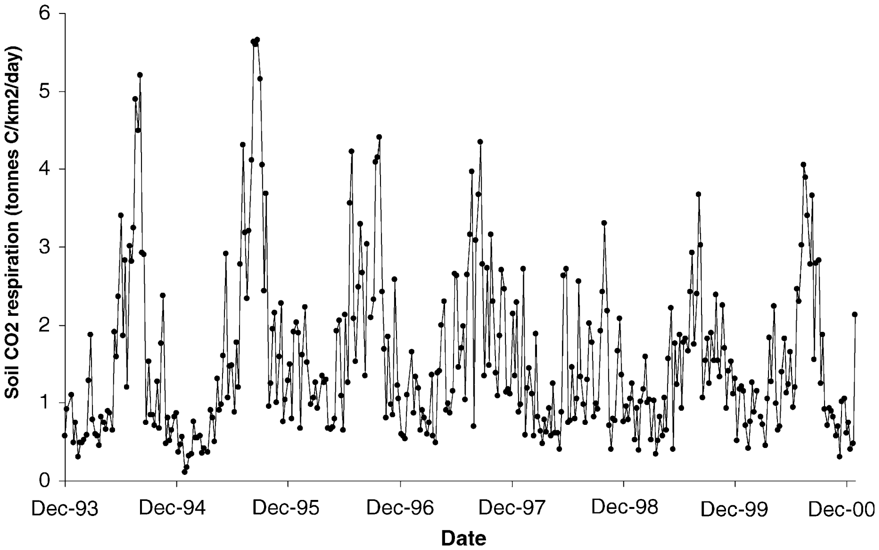

Figure 11. The calculated soil CO_2 respiration from the peat profile over the period of the study.

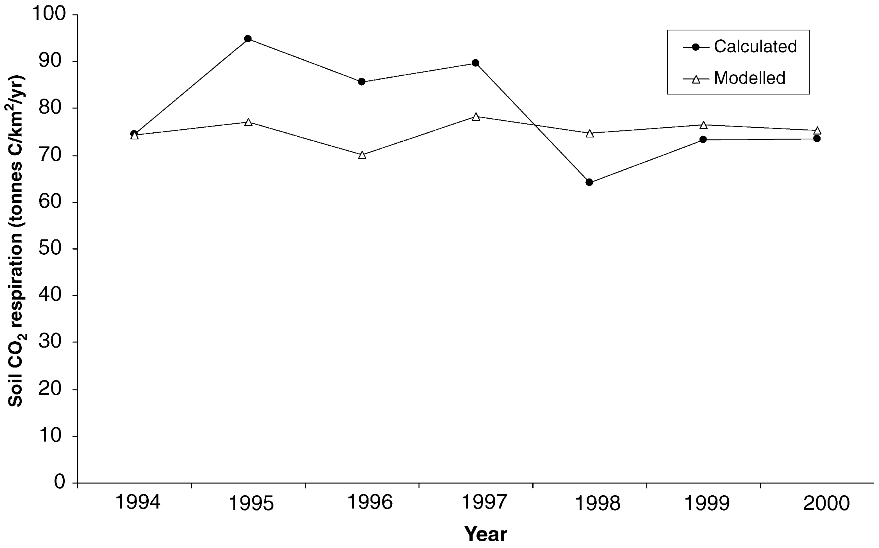

Figure 12. The annual flux of soil CO_2 from the peat surface.

when the water table is at its lowest and soil temperatures are at their highest (Figure 6): the minimum is in March.

Soil respiration of CO_2 peaks during the drought of 1995 and then declines for approximately 3 years after the drought with concentration values apparently steady for the final 2 years of the study (Figure 11). Therefore, as with dissolved CO_2, there is no increasing trend and no sustained trend of any kind after the drought. The flux of CO_2 from the peat surface shows a peak in 1995, but then rapidly returns to pre-drought values, i.e. there is no step change in soil respiration unlike that observed for DOC. This lack of a step change in soil CO_2 respiration after the 1995 drought agrees with the hypothesis that enzyme latch processes are anaerobic and that soil CO_2 and DOC production have become decoupled. There is good agreement as to the scale of inter-annual variation between the approach of this study and that of Lloyd and Taylor (1994) except during the drought years (especially 1995 – Figure 12).

Discussion

Is this a reasonable approach to understanding CO_2 production in a peat profile? Although an assessment of variability is considered in this study no assessment of uncertainty is considered. The approach uses field measurements the error on which will be small relative to the scale of effects. Therefore, the estimates of dissolved CO_2 will be subject to very little error as long as the speciation model is accurate. The speciation approach has been calibrated against real field measurements by Neal et al. (1998) who showed an average percentage error of 1.5%. Therefore, the time series of dissolved CO_2 estimated at the catchment outlet above can be considered sufficiently accurate to examine the processes that control it. Even for this time series (Figure 8), i.e. before stream evasion and production are accounted for, it is possible to see inter-annual variation and the consequences of the severe drought of 1995. The questions posed at the beginning of the study can be addressed purely on the basis of the time series of dissolved CO_2 leaving the catchment. Firstly, there is no step change in dissolved CO_2 flux after the severe drought of 1995, and therefore CO_2 production does appear to be decoupled from production of DOC. Secondly, the effect of the drought appears limited, suggesting that modelling on the basis of temperature variation alone is reasonable except in years of severe drought. Therefore, the conclusions of this study are reasonable because they are not dependent upon any assumption linking dissolved CO_2 flux from the catchment to soil CO_2 respiration.

The method for calculating firstly, dissolved CO_2 at emergence and then secondly, soil CO_2 respiration will be more uncertain because it is based upon processes and parameters that are not well known for this catchment. The primary production of CO_2 within the study stream has not been directly measured nor have the diffusion properties of the peat profile been measured specifically for this area. However, firstly, the results of the approach are consistent with observations of soil respiration for UK peat catchments. Secondly, if the logic of the approach is correct than the conclusions of the study can be derived from the dissolved CO_2 time series.

It is difficult to compare these results to others in the literature: the authors are not aware of any other study of $EpCO_2$ movement from a near-neutral

British peat catchment. The nearest comparisons is with that of Dawson et al. (1995) for a partially peat-covered catchment (64%) where the dissolved CO_2 flux was on the order of 0.4 tonnes C/km^2/yr and for two further catchments in Mid-Wales and NE Scotland fluxes were 0.26 and 0.88 tonnes C/km^2/yr, respectively (Dawson et al. 2002); these three catchments are significantly more acidic than Moor House. Hope et al. (2001) reported fluvial carbon fluxes for a peat-dominated catchment, although they did not report dissolved CO_2 at emergence; their results for the smallest catchment area, and therefore the least effected by evasion, indicated an average dissolved CO_2 concentration of 1.8 mg C/l and an areal export of 1.56 tonnes C/km^2/yr. In comparison, the values reported here are larger, but the results noted above are for far more acidic systems and are for the catchment outlet and not reported for water entering the stream. The study of Hope et al. (2001) reported CO_2 stream evasion rates which equates to between 60 and 3800 g C/m of stream/yr, is a broader range than reported in this study.

Several studies report CO_2 respiration rates from peat soils. Lloyd et al. (1998) showed CO_2 emissions from peat blocks to be dependent upon diurnal light variation, and allowing for this gave an average value of 50.5 tonnes C/km^2/yr. Over the period of year, Chapman and Thurlow (1996) measured CO_2 emission rates for an indigenous bog in Northern Scotland; by knowing the temperature range over which CO_2 emission was measured they were able to estimate the activation energy of CO_2 production. Using the temperature records at Moor House allows an estimate of CO_2 flux to be estimated – 35 tonnes C/km^2/yr. Clymo and Pearce (1995) measured between 13.1 and 32.5 tonnes C/km^2/yr depending upon the surface topography of the bog. The values reported by this study are larger, but close to the range of values reported elsewhere. At present the diffusion coefficient to be applied in soil is corrected for porosity, but this porosity value is not corrected for its water content. Allowing for water content in the unsaturated zone of the peat would decrease values of calculated soil CO_2 respiration.

Worrall et al. (2003b) have proposed a carbon budget for the catchment used in this study. The budget included both soil CO_2 respiration, dissolved CO_2 and DIC, but as stated earlier did not include did allow for stream CO_2 evasion and thus calculated the budget on the basis of dissolved CO_2 values leaving the catchment. Using the values for dissolved CO_2 at emergence and DIC derived above a revised carbon budget can be calculated that includes: net CO_2 exchange; CH_4 respiration, rainfall inputs of DOC and DIC; inputs of carbon from weathering; and fluvial export of DOC, DIC, dissolved CO_2 at emergence and POC (Figure 13). The values for dissolved CO_2 at emergence and DIC given in Figure 12 are the minimum export values given in this study in order to assess the maximum possible sink of carbon in the study peatland. Compared to the earlier estimate (Worrall et al. 2003b), the catchment, is now a small net sink of carbon (4.5 tonnes C/km^2/yr). Given the fact that this value for the magnitude of the carbon sink is considered using the minimum values of export rates for dissolved CO_2 at emergence and DIC, then there are

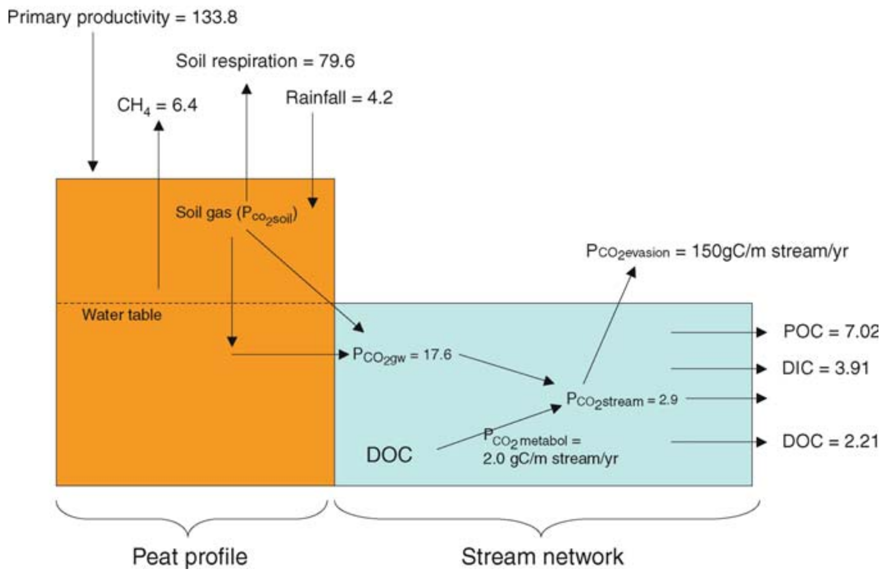

Figure 13. Carbon uptake and release pathways for upland peat as considered by Worrall et al. (2003b) with all values given as tonnes C/km^2/yr unless otherwise stated. Values of pathways not from this study are as given in Worrall et al. (2003b). All values are quoted as the median. POC = particulate organic carbon.

certainly years when the study peatland becomes a net source. However, it remains that no direct measures of either methane flux or net CO_2 exchange have been measured for the Moor House site. These values have been extrapolated as best estimates from other UK localities.

Present models of soil CO_2 respiration are based upon the Arrhenius equation, i.e. based solely upon temperature variation and not upon variation of the water table (e.g. Lloyd and Taylor 1994). Evidence from the inter-annual variation in soil CO_2 flux shows no step change subsequent to the drought of 1995, but does show an increase in CO_2 flux. This observation has two implications for the controls on the release of CO_2 from peat profile.

(A) The inter-annual variation is slight, except for the response to the 1995 drought, suggesting that in most years a description based upon temperature could be adequate, but that in extreme droughts soil respiration rises due to a combination of factors. Firstly, lower water tables lead to an increased zone of oxidation; indeed, models of CH_4 flux from soils often contain a description of depth to the water table (e.g. Bubier et al. 1993). Secondly, drought in the UK is usually accompanied by higher temperatures and not just by lack of water. Thirdly, drought conditions result in diminished runoff of CO_2 rich water and therefore increased residence time leading to diminished loss of CO_2 in water.

(B) There is no sustained rise of any of the components (pH, alkalinity and Ca) subsequent to the severe drought, unlike the sustained rise observed for DOC. This implies that enzymatic latches do not increase the flux of CO_2 by any pathway, and provides evidence for the hypothesis that, while enzymatic latches extend anaerobic degradation, they do not produce CO_2. However, if enzymatic latches produce increased DOC but do not increase CO_2 production, it might be possible that CH_4 flux would rise in response.

Conclusions

This study has reconstructed a multi-annual record of dissolved CO_2 from a headwater peat catchment and extended this to estimate soil CO_2 respiration from the peat profile. The results show that dissolved CO_2 flux at emergence from the peat profile is equivalent to between 20% and 36% of the soil respiration. The values of dissolved CO_2 and DIC suggest that this upland peat catchment is close to equilibrium with respect to its carbon budget and would be a net source during periods of drought. The record of dissolved CO_2 shows no sustained increase following a severe drought. Unlike DOC; this suggests that since enzyme latch mechanisms are an anaerobic process, the additional post-drought production of DOC is decoupled from CO_2 production.

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Appendix A

Dissolved CO_2 and DIC are calculated using the following equilibria:

$$[\mathrm{CO_2}]_{\mathrm{eqm}} = K_{\mathrm{H}}\mathrm{pCO_2}$$

$$(\mathrm{H_2CO_3}) = 0.00049k_0\mathrm{EpCO_2}$$

$$(\mathrm{HCO_3^-}) = K_1\frac{(\mathrm{H_2CO_3})}{(\mathrm{H^+})}$$

$$(\mathrm{CO_3^{2-}}) = K_2\frac{(\mathrm{HCO_3^-})}{(\mathrm{H^+})}$$

$$(\mathrm{CaHCO_3^+}) = K_3(\mathrm{Ca^{2+}})(\mathrm{HCO_3^-})$$

$$(\mathrm{CaCO_3}) = K_4(\mathrm{Ca^{2+}})(\mathrm{CO_3^{2-}})$$

$$(\mathrm{CaOH^+}) = K_5(\mathrm{OH^-})(\mathrm{Ca^{2+}})$$

$$(\mathrm{OH}^-) = \frac{K_6}{(\mathrm{H}^+)}$$
$$K_7 = (\mathrm{Ca}^{2+})(\mathrm{CO}_3^{2-})$$

where ( ) refers to the activity of that component; [ ] refers to concentration of the component. The equilibrium constants are allowed to vary with temperature according to the following equations:

$$\log_{10} K_0 = 0.01422(273 + T) + \left(\frac{2299.6}{(273 + T)}\right) - 13.417$$

$$\log_{10} K_1 = 14.8345 - 0.03279(273 + T) - \left(\frac{3404.71}{(273 + T)}\right)$$

$$\log_{10} K_2 = 0.022379(273 + T) + \left(\frac{2902.39}{(273 + T)}\right) - 6.498\sqrt{b^2 - 4ac}$$

$$\log_{10} K_3 = 2.95 - 0.0133(273 + T)$$

$$\log_{10} K_4 = 27.393 - 0.0561(273 + T) - \left(\frac{4114}{(273 + T)}\right)$$

$$\log_{10} K_5 = -1.4$$

$$\log_{10} K_6 = 0.017053(273 + T) + \left(\frac{4471.33}{(273 + T)}\right) - 6.0846$$

$$\log_{10} K_7 = 13.545 - 0.0401(273 + T) - \left(\frac{3000}{(273 + T)}\right)$$

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

where T is the stream temperature in °C and thermodynamic information comes from Harned and Davis (1943) (K_0 and K_1), Harned and Scholes (1941) (K_2), Jacobsen and Langmuir (1974) (K_3 and K_7), Reardon and Langmuir (1974) (K_4), Gimblett and Monk (1954) (K_5), Covington et al. (1977) (K_6), and Stumm and Morgan (1995) (K_H).

$$\frac{1}{(\mathrm{Ca}^{2+})} = \frac{40{,}000}{[\mathrm{Ca}^{2+}]}\left[\frac{1}{\gamma_2} + \frac{K_3(\mathrm{HCO}_3^-)}{\gamma_1} + \frac{K_4(\mathrm{CO}_3^{2-})}{\gamma_0} + \frac{K_5(\mathrm{OH}^-)}{\gamma_1}\right]$$

where $[\mathrm{Ca}^{2+}]$ refers to total measured Ca concentration rather than activity with adjustment made between the two being given by the Davis equation:

$$\sqrt{I} = 0.000564 + (\mathrm{OH})^{-} + (\mathrm{HCO}_3^{-}) + (\mathrm{H}^{+}) + \sqrt{2\left\{(\mathrm{CO}_3^{2-}) + \frac{[\mathrm{Ca}^{2+}]}{40{,}000}\right\}}$$

where

$$\log_{10}\gamma_1 = 0.3\sqrt{I} - 0.5\left[\frac{\sqrt{I}}{1+\sqrt{I}}\right]$$

$$\log_{10}\gamma_2 = 0.3\sqrt{I} - 2\left[\frac{\sqrt{I}}{1+\sqrt{I}}\right]$$

and

$$[\mathrm{Ca}^{2+}] = [\mathrm{Ca}^{2+}]_{\mathrm{free\,ion}} + [\mathrm{CaHCO}_3^{-}] + [\mathrm{CaCO}_3] + [\mathrm{CaOH}^{+}]$$

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