A 19-year long energy budget of an upland peat bog, northern England

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Abstract

This study has estimated the long term evaporation record for a peat covered catchment in northern England. In this study, 19 years of daily evaporation were estimated for rain-free periods using White's methods.Net radiation was measured over the study period; soil heat flux was calculated from temperature profiles; and sensible heat flux was calculated assuming the energy budget was closed. The calculated time series was compared to available environmental information on the same time step and over the same time period. Over a 19-year period it was possible to calculate 1662 daily evaporation rates (26% of the period). The study showed that the energy flux to net primary productivity was a small, long-term sink of energy but this sink was a virtue of high carbon accumulation in peat catchments: in catchments where there is no long-term dry matter accumulation, net primary productivity must be a small net source of energy. The study showed that evaporation increased over the study period whilst sensible heat flux significantly declined, reflecting an increased use of sensible heat energy to meet evaporative demand. The relatively small change in evaporative

flux compared to other energy fluxes suggests that this system is a “near-equilibrium” system and not a “far-from-equilibrium” system.

Keywords: evaporation; sensible heat flux; soil heat flux; net radiation; heat sink; evaporative cooling

Introduction

Peatlands have received considerable interest in recent decades because they represent a considerable store of carbon and an important sink of greenhouse gas at the global scale. Gorham (1991) has estimated that 20-30% of the global terrestrial carbon resides in peatlands, which represents only 3% of the global land area. The northern peatland carbon store is estimated to be approximately 455 Gtonnes C and over the Holocene northern peatlands have accumulated carbon at an average rate of 960 Mtonnes C/yr. Under a warming climate, this vital carbon store could potentially be converted from a net sink to a net source of atmospheric carbon – a net sink of carbon in peatlands can be a net source of some carbon species and already have an adverse impact upon greenhouse gas warming potential. With increasing temperature, rates of organic matter degradation increase, leading to increased release of CO_2 through soil respiration (e.g. McKenzie et al., 1998) Increasing drought (frequency and severity) leads to activation of new enzymic processes (Freeman et al., 2001); and increased atmospheric CO_2 could itself lead to increased carbon loss (e.g. Freeman et al., 2004). These climatic effects could be enhanced by other factors including changes in atmospheric deposition of S and N (eg. Silvola et al., 2003**)** or land management (eg. Clay et al., 2009). Indeed, inter-annual comparisons of net ecosystem exchange (NEE) have shown that during dry years a peatland can change from a net sink of carbon to a net source (Griffs et al., 2000; Alm et al., 1999). Equally, land management in peatlands has often meant draining of the peat with subsequent lowering of the average water table depth (Holden et al., 2011). The majority of carbon flux pathways to and from a peat soil can be related to the position of the water table. The greater the depth to the water table, the greater the oxidation of the peat profile which has been suggested to lead to: increased flux of dissolved CO_2 (Jones and Mulholland, 1998); increased soil CO_2 respiration (Glenn et al., 1993, Funk et al., 1994 and Bubier et al., 2003); and potentially increased losses of DOC (Mitchell and McDonald, 1995). Conversely, the shallower the water table, the lower is the ingress of oxidation; the greater extent of anaerobic decomposition of the peat leading to increased CH_4 production and decreased oxidation of the CH_4 being produced (Roulet et al., 1993, Levy et al. 2012).

Complete carbon budgets of peatlands are now common (e.g. Worrall et al., 2003, Billett et al., 2004, Roulet et al., 2007, Nilsson et al., 2008) and a number of studies have begun to explore the impact of climate change and other external drivers upon the carbon budget, eg. Clay et al., (2010). If carbon is being stored by peat accumulation, then peatlands are also stores of other important elements, eg. nitrogen (N). While studies of C budgets are common, studies of N budgets are rarer even though N_2O is powerful greenhouse gas (Hemond, 1983; Drever et al., 2010, Worrall et al., 2012) and only a few studies have considered fluvial budgets for a range of elements (Adamson et al., 2001).Understanding the impact of climate and land-use change on the water balance of a peatland is key to understanding the future potential of these ecosystems as a carbon store or ongoing greenhouse gas store sink. Over a given period, the water balance of a peatland is a balance of precipitation input and outputs of runoff pathways (surface and groundwater) and evaporation. Under climate change, it is expected that air temperatures will increase which could limit the potential for an ecosystem to dissipate its incident energy via sensible heat flux in favour of soil heat flux and evaporation. Several studies have measured evaporation from peatlands. For example, Campbell and Williamson (1997) measured Bowen ratios over a six month period at a 20 minute frequency and found Bowen ratios between 2 and 5, i.e. dominated by sensible heat flux. Similarly, for another New Zealand peat bog, Thompson et al. (1999) also found Bowen ratios that suggested dominance of sensible heat flux over evaporative flux. Conversely, Admiral et al. (2006) measured Bowen ratios over an Ontario bog and found values were typically below 1 for the snow-free season, similar to a Swedish Sphagnum mire (Kellner, 2001). It is clear, therefore, there is a range of behaviour within the diversity of peat bogs, this has contributed to diversity of methods for calculating evaporation from peatlands (Drexler et al., 2004) and attempts to understand the variation across space (Rouse et al., 2000). However, observations have always been restricted to only a few years which makes the assessment of long term changes in water and energy balances difficult.

A number of authors have extended the energy budget argument to consider the thermodynamics of ecosystems. Brunsell et al. (2010) have shown that the simplest way for an ecosystem to shed a change in incident energy is to increase evaporation as this is the most efficient means of diffusing entropy for a system that is thermodynamically "far-from-equilibrium" (Ozawa et al., 2003**).** However, this analysis and hypothesis has not been tested as long term energy balance data were not available. Alternatively, Addiscott (2010) has demonstrated that for a "near-equilibrium" system water loss would be minimised and changes in the amount of incident energy would be dissipated through sensible heat flux. Neither Brunsell et al. (2010) nor Addiscott (2010) had actually energy or water budget data upon which to test their model results. A simple test of the differences between these two system states would be to measure the sensitivity of evaporation to a change: if the change is absorbed by increasing evaporation then a system trying to maximise its entropy loss and is in a “far-from-equilibrium” state whereas if evaporation decreases in response to change then it is acting to minimise loss and is “near-equilibrium”.

Therefore, the purpose of this study is to estimate change in the long-term energy budget of a peat ecosystem as a test of how the environment may adapt to long term change.

Approach and Methodology

The energy budget of an ecosystem can be considered as:

$$R_n = H + G + \lambda E + P + e \quad \text{(i)}$$

Where: R_n = net radiation (Wm^{-2}); H – sensible heat flux (Wm^{-2}); G = soil heat flux (Wm^{-2}); λE – latent, or evaporative, heat flux (Wm^{-2}) where λ is the heat of vapourisation (2260 kJ kg^{-1}); P = primary production (Wm^{-2}); and e = residual error. The residual error term is included as there are other terms that cannot be estimated as they are often so small and these are assumed to be negligible in comparison, indeed P is often not included even when ecosystem energy budgets are considered (Kellner, 2001). The approach of this study was to estimate the components of Equation (i) for a single study over as long a period of years as possible.

Study site

Moor House and Upper Teesdale National Nature Reserve (NNR) is situated in the North Pennine upland region of the UK (Fig. 1). The Moor House NNR is a terrestrial and freshwater site within the UK Environmental Change Network (ECN). The ECN collects various hydrological and water quality data from the Trout Beck catchment that lies within the Moor House NNR. The Trout Beck catchment occurs mainly above 450 m O.D. with the highest point being the summit of Cross Fell at 893 m O.D (National Grid Reference NY 756326, N54^{o}41´18″ W2^{o}22´45″). The underlying geology is a succession of Carboniferous limestones, sands and shales with intrusions of the doleritic Whin Sill (Johnson and Dunham, 1963). The solid geology is covered by glacial till and colluvial material whose poor drainage qualities facilitated the development of blanket peat during the Holocene. Blanket peat covers 90% of Trout Beck catchment (Evans et al., 1999). The vegetation of the reserve is dominated by *Eriophorum sp*. (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum sp.* (moss). The mean annual temperature (1931 – 2006) was 5.31 ^{o}C. Air frosts were recorded on average on 99 days in a year (1991 – 2006, Holden and Rose, 2011). Mean annual precipitation (1953-1980, 1991-2006) was 2012 mm (Holden and Rose, 2011). An automatic weather station is situated within the catchment (Fig. 1) with hourly recording of rainfall by tipping bucket raingauge; the recording of air and soil temperature at 0, 10 and 30 cm below the soil surface; and solar radiation. In addition, a network of five piezometers has been monitored hourly for the depth to the water table, and manual calibrated weekly, since October 1994. Discharge has been measured from the catchment outlet on an hourly time scale since 1991. Note that there was only one automatic weather station in the catchment and only one network of piezometers. This monitoring was sited so as to be representative of the catchment but inevitably there will be heterogeneity and this has been considered in this catchment by Joyce et al. (2001). However, the approach of this study is to consider the energy budget at the monitored site and catchment data is only used to check water balances.

For reasons of the methodology used at study, i.e. it is not possible to estimate on days with snow cover, no term for the latent heat of fusion was included in Equation (i) was not considered in the study.

Net radiation (Rn)

The automatic weather station installed on the site has included the monitoring of net radiation (Kipp solarimeter – error of 1% at 1 Wm^{-2}) since 1992, but to complement the period of record of other data sets, the net radiation was summed on a daily basis from January 1995.

Evaporation (λE)

Evaporation was estimated using the method of White (1932), where the daily evaporation (E in mm) is estimated from change in water table depth:

$$E = S_y\left(d_1 + 24\frac{(d_5 - d_1)}{4}\right) \qquad \text{(ii)}$$

$$S_y = Ae^{B(d_{max} - d_1)} \qquad \text{(iii)}$$

Where: d_{max} = the maximum depth of the water table below the surface for the entire record (800 mm); d_x = the depth of the water above the maximum depth of the water table (mm) with x = 1 or 5 for water table depths at 1 am and 5 am respectively; S_y = the specific yield (dimensionless); and A, B = constants.

Hourly depth to water table measurements have been maintained for the site since October 1994 so that for complete calendar years records were available to this study from 1995 to 2012. The hourly depth to water table measurements from all five piezometers were averaged before applying White's method. White's method relies on the change in water table over a diurnal cycle being solely due to recharge and evaporation. The piezometers used in this study are situated on an interfluve and, to ensure that results were not affected by rainfall, only those days which were rain-free were considered; not only that but only days where the last 5 hours of the previous day were also rain-free. Unlike the original version of White's method, the approach used here was to allow the specific yield to vary with depth. There are no measurements of specific yield for this catchment but the form of specific yield function and initial values were selected from Price (1992). However, the form of the specific yield function was calibrated against the water balance for the catchment in 1995 which gave values of A = 0.00983, and B = 0.0054573, which means that the specific yield of the peat in this catchment varies from 0.78 at the surface to 0.009 at 800 mm depth – which is the base of the piezometers. As an alternative approach to estimate and check values of specific yield the daily water balance was considered. A simple daily water balance can be given as:

$$Q_d = rain_d - E_d - \Delta S_d \qquad \text{(iv)}$$

Where: Q_d = daily discharge from the catchment (mm/day); $rain_d$ = daily precipitation (mm/day); E_d = daily evaporation (mm/day); and ΔS_d = change in storage over the day (mm/day). Given the definition of change in storage and the Equation (ii) then it is possible to say that:

$$Q_D = rain_d - S_{yd}\left(d_1 + 24\frac{(d_5 - d_1)}{4}\right) - S_{yd}(d_{24} - d_1) \qquad \text{(v)}$$

Where: S_{yd} = the Specific yield averaged over a day. Given the hydrological data collected within the study catchment then Equation (v) can be solved to find S_{yd}. Note that this is only time in this study that data at the catchment scale is used in the context of the energy budget assessed at the point

Equation (ii) calculates evaporation as mm day^{-1} which is readily converted to an energy flux given 1 mm day^{-1} is 2.45 MJ day^{-1} or equivalent to 28.5 W m^{-2}.

Soil heat flux (G)

The soil heat flux was estimated on a daily basis using the approach of Sharratt et al. (1992). This approach used a 1D finite difference solution of the transient heat flux equation to give the heat flux density for each time interval (i) using Fourier's law:

$$\Delta G_i = -\frac{k_i \Delta T_i}{\Delta z_i} \qquad \text{(vi)}$$

Where: k_i = the thermal conductivity of the layer at time interval i (Wm^{-3}K^{-1}); ΔT_i = the average temperature difference across the layer at time interval i (K); and Δz_i = the thickness of the layer (m). In the case of this study temperatures at 0 cm depth and 10 cm depth were available at an hourly time step and ΔG_i was summed to a daily time step in line with the estimation of the other components of the energy balance. Equation (vi) required an estimate of the thermal conductivity of the layer in which the following was assumed:

$$k_i = \alpha k_{peat} + (1-\alpha) k_{air} \qquad \text{(vii)}$$

$$\alpha = \frac{(d_i - d_{max})}{(d_{max} - d_{min})} \qquad \text{(viii)}$$

Where: d_i = the water depth at time interval i (cm); d_{min} = the minimum water table recorded (cm). In effect, the hourly water table information was used to linearly adjust the thermal conductivity of the layer between that of dry air and that of water-saturated peat. The values of k_{peat} = 0.06 and k_{air} = 0.57 ($Wm^{-3}k^{-1}$ – Moore, 1987) were used.

Primary productivity (P)

The storage of energy in biomass and soil organic matter of a site are not commonly measured in energy balance studies as they are considered minor components on the short time scales normally considered. However, peat soils grow by accumulation of organic matter at rates typically on the order of 1 mm yr^{-1} (Borren et al., 2004). The accumulation of partly degraded organic matter represents a flux of energy into longer term storage. For this study site, there is an existing carbon budget (Worrall et al., 2009) which averages the carbon fluxes for the site over a 13 year period as:

$$100C_{pp} \Rightarrow 35C_R + 26C_{DOC} + 4C_{CH4} + 4C_{dissco2} + 9C_{POC} + 22C_{RES} \qquad \text{(ix)}$$

Where: C_x = carbon from the following uptake or release pathways, where x is: pp = primary productivity, R = net ecosystem respiration, DOC = dissolved organic carbon; CH4 = methane; $dissco_2$ = dissolved CO_2; POC = particulate organic carbon; and RES = residual carbon stored in the soil. Over the 13 years of study, the total carbon flux to the soils of the catchment (equivalent to C_{RES}) varied between -20 and -91 tonnes C km^{-2} yr^{-1} by far the biggest single component of the budget was the uptake of carbon by primary productivity (average across the study period of 176 tonnes C km^{-2} yr^{-1}). If the energy content of these flux pathways were known, then the flux due to primary production and long-term energy storage in the soil could be estimated.

The energy content of CO_2 and CH_4 were taken from standard values, ie. 0 and 54 MJ kg^{-1} respectively. For three, randomly-selected 0.5 x 0.5 m quadrats within the catchment, all the aboveground biomass was removed, dried at 105^{o}C and then homogenised first by food blender and secondly by Cryomill (Spex 6770 Freezer Mill). Peat cores to 1 m depth were taken in 3 locations in the catchment and divided into 2 cm sections to 10 cm; 5 cm sections from 10 to 50 cm depth, and then the base of the core at 90-100 cm depth. The peat sections were taken so that bulk density could be measured, dried to 105^{o}C, homogenised and ground in the cryomill. It was assumed that POC was eroded from throughout the peat profile, i.e. it was produced from either surface erosion of peat or from bank erosion alongside channels. The energy content of the DOC was analysed from 12 samples collected each month in 2012. A 25 litre sample of stream water was taken from a first-order peat-hosted stream within the catchment. The sample was stored upright and tapped off 5 cm above the base of the vessel so that any non-colloidal matter and suspended sediment settled out and only truly dissolved or colloidal was tapped off and evaporated to dryness at 40^{o}C with the residue ground for analysis.

The calorific value of the sampled organic matter was measured on a Parr 6200 bomb calorimeter. A sub-sample of known mass, typically 1g, had its moisture content raised back to approximately 4% by weight before being combusted in the bomb calorimeter. The 4% moisture does not detract from the calorific value but does aid the combustion process in the bomb and helps prevent sputtering of the sample during the ignition process. The bomb calorimeter was calibrated and standardised on each run of samples using benzoic acid. For the samples of DOC for which less than 0.5 g of sample was available, the sample was doped with a known amount of the benzoic acid standard so that a complete combustion was achieved. For both soil and vegetation samples the calorific value was measured in at least triplicate.

To relate the calorific values to the carbon flux, the carbon content of the samples was analysed on a Costech ECS 4010 elemental analyser with a pneumatic autosampler. Reactor 1 consisted of chromium (III) oxide/Silvered cobaltous-cobaltic oxide catalysts at a temperature of 995°C. Reactor 2 consisted of reduced high-purity copper at a temperature of 650°C. Helium was used as the carrier gas at a flow rate of 95 ml min^{-1} and the oxygen quantity for combustion was set at semi-micro. A packed (Porous polymer, HayeSep Q) 3m GC column was used for separation of CO_2 and N_2. The thermal conductivity detector (TCD) in the Costech instrument was used to calculate the signal of each sample; the software package used was Elemental Analysis Software Clarity. For the purposes of quality control, laboratory standards and repeats were included in each run. Calibration curves were based on regressions with an r^2 of 0.999 or better. The measured C concentrations were corrected for the ash content of the samples measured by loss on ignition at 550^{o}C overnight.

Sensible heat flux (H)

The sensible heat flux was not measured directly or estimated from the available long term data. Instead, the sensible heat flux was calculated to close Equation (i). However, in such an approach this means that the H value is in fact the H + e value, i.e. includes the residual error.

Bowen ratio

The Bowen ratio was calculated for each day with sufficient energy balance data, and the Bowen ratio is given as:

$$B = \frac{H}{\lambda E} \qquad \text{(x)}$$

Note that given the derivation of H used in this study then the residual error term is included in H.

Trend analysis

The time series of measured environmental variables and energy fluxes were considered as time series of two separable and analysable components – the trend and the seasonal variation (Worrall and Burt, 1998). Multiple linear regression was used comparing the response variable to the year in the time series (1994 as year 0) and the day of the year transformed as $sin\left(\frac{n\pi}{183}\right)$ and $cos\left(\frac{n\pi}{183}\right)$ where n is day number in the year with 1st January as day 1. Where possible and physically realistic, environmental variables and lagged variables were included in the multiple regression. When appropriate, response and descriptor variables were considered as both untransformed and log-transformed in the multiple regression. Furthermore, all appropriate variables were tested for normality using the Anderson-Darling test (Anderson and Darling, 1952) and, where the test was failed, the variable was log-transformed and retested – no further transformation proved necessary. For some variables it was not appropriate to consider log-transformation as they could have both negative and positive values, eg. net radiation (R_n) has positive or negative values depending upon whether the transfer was to or from the surface. Partial regression analysis was used to assess the proportion of variance explained by individual descriptors in multiple regression equations.

As an alternative approach, ANOVA was used to test for difference in evaporation between years. The ANOVA was conducted with two factors: the difference between the 12 months of the year; and the difference between the 19 years of the study (1994 – 2012). The advantage of an ANOVA approach over multiple regression is that ANOVA can find a significant change without an assumption of continuous change or an assumption of the nature of that change as is required in multiple regression. ANOVA was also performed using covariates to test whether the significant difference between years could be explained by changes in the available variables. The covariates considered were: air temperature, net radiation, depth to water table and the previous day's evaporation.

Results

Measured environmental variables

The time series of the measured variables at a monthly time step are shown in Figures 2a through 2d.

The median daily average temperature for the period 1994 to 2012 was 5.7 ^{o}C with an interquartile range of 2.3 to 9.6 ^{o}C. For the average daily temperature (T_j) the following was the best-fit equation:

$$T_j = 6.03 - 0.021year - 2.71sin\left(\frac{m\pi}{6}\right) - 2.83cos\left(\frac{m\pi}{6}\right) \quad \text{(xi)}$$

(0.09) (0.008) (0.05) (0.05)

$r^2 = 0.53$, n = 5757

Where: year = the year of the measurement with 1994 = 0 (year); m = month number with January = 1 to December = 12. Note that it was month number that was significant even though the time step of prediction was daily. Only variables that were found to be significantly different from zero at the 95% probability are included and the numbers in the brackets are the standard errors in the coefficient. Note that for this study site over the study period the average daily temperature showed a significant decrease.

Given the nature of daily rainfall totals, i.e. many at zero, the data were not normally distributed nor could they be readily transformed to a normal distribution and thus the analysis was performed on total monthly rainfalls over the period, here it can be taken that total monthly rainfall was total precipitation. For the monthly total rainfall, the median was 156 mm with an interquartile range of 92 to 215 mm. The best-fit equation for the log-transformed, monthly total rainfall ($rain_m$) was:

$$log_e rain_m = 5.08 + 0.11 sin\left(\frac{m\pi}{6}\right) + 0.21\cos\left(\frac{m\pi}{6}\right)) \qquad \text{(xii)}$$

(0.1) (0.05) (0.05)

$r^2 = 0.11$, n=183

There was no significant trend in the monthly rainfall over the period of the study at this site.

For water table depth, the median daily depth below the peat surface was 6.0 cm with an interquartile range of 4.3 and 8.9 cm below the surface. The best-fit equation for the water table depth below the peat surface was:

$$log_e d = 1.48 + 0.39 log_e year - 0.34 cos\left(\frac{n\pi}{183}\right) \qquad \text{(xiii)}$$

(0.02) (0.009) (0.02)

$r^2 = 0.22$, n=6415

Where all symbols are defined as above Therefore, the depth to the water table has increased over the course of the study, i.e. the water table has fallen further below the ground surface over the study period.

Stream runoff can be considered an integrating variable as it will depend on the interaction of rainfall, evaporation and changing storage. As for the rainfall data, stream runoff was assessed on monthly total runoff. The best-fit line for the monthly total runoff ($runoff_m$) was:

$$runoff_m = 19 + 1.4year + 30cos\left(\frac{m\pi}{6}\right) + 0.56rain_m \qquad \text{(xiv)}$$

$$\quad (7) \quad (0.5) \quad (4) \qquad (0.03)$$

$r^2 = 0.79$, n = 227

Therefore, there was a significant increase in monthly total runoff at a rate of 1.4 mm/yr.

As means of minimising the impact of changing storage and the impact of snow cover the water balance was then considered at an annual time step and on the basis of water years (1st October to 30th September) rather than calendar years, the best-fit comparison was:

$$runoff_a = 0.85rain_a \qquad \text{(xv)}$$

$$\quad (0.02)$$

$r^2 = 0.32$, n=19

Where: $runoff_a$ = the annual total runoff for a water year (mm); and $rain_a$ = the annual total rainfall for a water year (mm). Equation (xv) shows no significant role for time, but this does not mean that annual rainfall or annual runoff were not changing, rather that there was no significant change in the relationship between them at the annual time step. Indeed, when annual runoff and annual rainfall were tested separately against time, no significant relationships were found. Comparing the annual rainfall and runoff for each water year gives a median annual evaporation estimate as 517 mm with an inter-quartile range of 352 – 669 mm. Therefore, Equation (xv) suggests that the annual actual evaporation did not vary significantly over the period of the study either.

Net radiation

The time series of net radiation is shown in Figure 3. Over the period of study it was possible to measure a daily net radiation 6319 times. The distribution of net radiation is negatively skewed with a median of 30.6 Wm^{-2} and interquartile range between 3.0 and 73.8 Wm^{-2}, however, 19% of all daily values were below 0. The sign convention of Equation (i) means that net radiation is positive if it is a flux to the soil surface and negative if it is a flux from the soil surface. Median monthly values across the entire study period show that the minimum was in December with a peak in July, the months of December and January have median values below zero. The best-fit equation for the daily net radiation was:

$$R_n = 22.7 - 0.36year - 8.0sin\left(\frac{n\pi}{183}\right) - 22.9cos\left(\frac{n\pi}{183}\right) + 0.29R_{n-1} + 0.09R_{n-2} +$$

$$0.03R_{n-3} + 0.05R_{n-4} + 0.03R_{n-5} + 0.04R_{n-6} \qquad \text{(xvi)}$$

(1.1) (0.07) (0.5) (1.0) (0.01) (0.01)

(0.012) (0.01) (0.01) (0.01)

$r^2 = 0.66$, n=6319

Where: R_{n-x} = the daily net radiation for x days before the present (Wm^{-2}). The daily net radiation shows a significant decline over the period of the study at a rate of 0.36 $Wm^{-2}yr^{-1}$. Equation (xvi) shows that a significant relationship with previous day's net radiation up to six days previously with a declining influence over that period of six days – no significant relationship (at 95% probability) was found for further lagged daily values of R_n. It should be noted that the autoregressive effects of previous days' net radiation are all positive, i.e. negative net radiation on days before the present will suppress radiation for six subsequent days and vice versa, positive net radiation will enhance net radiation to the ground for six days afterwards. This autocorrelation effect may be a consequence of the pattern of weather at the site, i.e. net radiation is strongly governed by seasonality; day-to-day variation in net radiation is rarely so large that it swings from positive to negative; and net radiation may be steady for periods of a week at a time.

Evaporation

The best-fit of Equation (iii) upon calibration to the water balance in 1996 gave values of A = 0.005 and B = 0.001 and this gave an annual actual evaporation within 1 mm of an estimated 686 mm based upon the difference between annual runoff and annual total precipitation. When this calibration was compared to all other 18 years of data the following was the best fit equation:

$$E_{white} = \underset{(0.08)}{0.96} E_{water} \qquad \text{(xvii)}$$

n=19, r^2 = 0.89

Where: E_{white} = annual evaporation derived from White's method (mm); and E_{water} = annual evaporation derived from water balance at the catchment scale (mm). The comparison suggests that the estimates from White's method are on average 4% lower than those from an annual water balance. Further calibration of the White method result upon the basis of equation was not attempted as it was recognised that E_{water} itself has an uncertainty in its calculation and the comparison is between measurements made on two different scales. The specific yield (S_y) predicted by fitting Equations (ii) and (iii) was 0.77 at the peat surface and 0.01 at 80 cm water table depth. The daily average value of specific yield predicted by Equation (v) was 0.44 at 4 cm water table depth and 0.017 at 77 cm water table depth.

Given the criteria used to ensure that White's method was applicable, it was possible to calculate daily evaporation on 1662 days out of a possible 6514 days in the study period. For individual years the least return was for 1998 (12% of days) and the best return was for 2007 (56% of days). The month with the minimum amount of data was November (17% of possible days with a record) and the highest return was for May (33% of days). The estimated median evaporation, on rain-free days was 1.6 mm day^{-1} with an inter-quartile range of 0.8 to 2.8 mm day^{-1}. In terms of energy budget, the median energy flux was 44.8 Wm^{-2} with an inter-quartile range between 23.2 and 78.3 Wm^{-2} (Figure 4). By the sign convention of Equation (i) the energy flux is positive away from the surface. The best fit equation was:

$$log_e(E_n) = \underset{(1.8)}{10.3} log_e T_{ab} + \underset{(0.04)}{0.15} log_e year - \underset{(0.05)}{0.39} cos\left(\frac{n\pi}{183}\right) - \underset{(0.04)}{0.35} log_e d - \underset{(10)}{54} \quad \text{(xviii)}$$

r^2 = 0.18, n=1525

Where: d = average daily water depth from the surface (mm); and T_{ab} = the daily average absolute temperature (K). This confirms that, even having allowed for changes in external drivers, the evaporation from this site has increased with time – there is a positive relationship with the variable *year* in Equation (xviii). For Equation (xviii) the most important variable was the depth to water table (explaining 4.6% of the original variance) and unsurprisingly the evaporation declines with increasing depth of water table from the surface. The second most important variable was the seasonal cycle (explaining 3.8% of the original variance) with evaporation peaking in July and being at a minimum in December. Equally, it is unsurprising that the estimated daily evaporation increased with increasing temperature (temperature explained 2.6% of the original variance). The annual trend explained 1.4% of the regression.

As an alternative approach, analysis of variance (ANOVA) was used with month and year as factors and absolute temperature, net radiation, and depth to water table as covariates. Both factors, month and year, were significant when considered with or without covariates. Net radiation was not a significant covariate and, when covariates were included, the pattern across the year shows a sharp change between September and October that gives an asymmetry to the seasonal cycle. The year factor showed a significant decline from 1994 to 1996; a significant increase from 1996 to 2009; and then a significant decline from 2009 to 2012. With all covariates the r^2 of the ANOVA was 21%.

Soil heat flux

The estimated median soil heat flux was 0.7 Wm^{-2} and interquartile range between -3.5 and 5.2 Wm^{-2} (Figure 5). Again by the sign convention of Equation (i) a positive flux is a flux away from the soil surface and negative to the soil surface. The median soil heat flux was positive from April to August with a maximum in June and the flux was negative from September through March with its minimum in December. As with net radiation the direction of this flux, into or out of the soil, varies through the year and so the values were not log transformed. The best-fit equation was:

$$G = -879 + 1.8log_e year + 2.5sin\left(\frac{n\pi}{183}\right) - 4.8cos\left(\frac{n\pi}{183}\right) - 1.3log_e d + 156log_e T_{ab} \quad \text{(xix)}$$

(55) (0.2) (0.2) (0.3) (0.3) (9)

r^2= 0.45, n=1514

As with Equation (xviii), Equation (xix) show significant relationships with depth to water table and air temperature as expected. There was a significant increase in soil heat flux over the period of the study.

Sensible heat flux

The sensible heat flux was predicted to have a median of -0.79 Wm^{-2} and interquartile range between -33.4 and 42.2 Wm^{-2} (Figure 6) – by Equation (i) the sign convention would be that a positive value of sensible heat flux is an energy flux away from the surface, in this case the median sensible heat flux was an energy flux to the ecosystem. The presence of a heat sink in wetlands has been observed for boreal peatlands where Runkle et al. (2014) found that the ecosystem was a net heat sink between October and April, but this corresponded to the period of snow cover for their site. Equally, Huryna et al. (2013) found net monthly heat sinks even in summer for wetlands amongst farmland. In terms of monthly averages the value of H was less than zero from September through to February inclusive. The best-fit equation was:

$$H = 970 + 17cos\left(\frac{n\pi}{183}\right) - 2.4year + 3.6d + 1.04R_n - 3.7T_{ab} \quad \text{(xx)}$$

(180) (6) (0.5) (0.5) (0.06) (0.6)

$r^2 = 0.31$, n=1468

The sensible heat flux increased with increasing depth to water table, with increasing net radiation, but decreased with increasing air temperature. There was a significant decrease in the sensible heat flux over the time of the study. To understand the switch between positive and negative sensible heat flux, a logistic regression analysis was applied to the data in comparison with the available explanatory variables. The best-fit logistic regression equation was:

$$log_e\left(\frac{\theta}{1-\theta}\right) = 0.05T_{ab} - 0.06R_n - 0.8cos\left(\frac{m\pi}{6}\right) - 0.4sin\left(\frac{m\pi}{6}\right) - 11 \qquad \text{(xxi)}$$

` (0.02) (0.004) (0.2) (0.1) (6)

Where: θ = the probability of the sensible heat flux being negative, i.e. a flux into the surface. The equation is 92.3% concordant with the data, i.e. 92.3% of sensible heat flux observations were correctly classified by Equation (xxiix) and of the 1468 observations that could be used to calculate Equation (xxi) 45% of them were positive heat fluxes, i.e. there was not a distortion in the number of observations with H < 0 and those with H > 0. This equation can be readily simplified to give the inequality for a 50% probability that H is net sink to the surface:

$$8\left(2cos\left(\frac{m\pi}{6}\right) + sin\left(\frac{m\pi}{6}\right)\right) < T_c - R_n + 53.15 \qquad \text{(xvii)}$$

Where: T_c = daily average air temperature (^oC). The inequality in Equation (xxii) can be compared to average conditions of air temperature and net radiation (Figure 7) which shows that the system is likely to be a sensible heat sink throughout autumn and winter.

Bowen ratio

The median Bowen ratio was 0.11 with an inter-quartile range of -0.74 to 1.27 (Figure 8). The seasonal cycle in the Bowen ratio peaked in May and June with median values of the Bowen ratio greater than 1, i.e. dominated by sensible heat flux. For November through to March the median monthly Bowen ratio was negative representing the times of sensible heat sink while for all other months the median monthly Bowen ratio was between 0 and 1.

When compared to available drivers then the best-fit equation was:

$$B = 20 + 0.023R_n + 0.3sin\left(\frac{n\pi}{183}\right) - 0.07T_{ab} \qquad \text{(xxiii)}$$

(5) (0.002) (0.1) (0.002)

$r^2 = 0.18$, n=1278

Therefore, the Bowen ratio has not significantly changed over the course of this study but it is also clear that it is not an appropriate measure of the apportioning of energy within this system because the sensible heat flux is both positive and negative and the Bowen ratio therefore does not reflect the energy apportionment

Primary productivity

The aboveground biomass had a median gross heat value of 19.1 ± 1 MJ kg^{-1} where the variation is given as the inter-quartile range. The median carbon content of aboveground biomass was 47.5 ± 2.5 %. Given the reported primary productivity (176 gC $m^{-2}yr^{-1}$), then over the 13-year period the average energy uptake of 7.1 MJ $m^{-2}yr^{-1}$ is equivalent to an average P of 0.2 Wm^{-2}, considering that primary production will only occur in daylight and only during the growing season, then values of up to 4 times that high could be expected on sunny days in summer. The gross heat value of peat soil varied from 19.9 MJ kg^{-1} at the surface to a maximum of 21.2 MJ kg^{-1} at 1 m depth, a median for the profile was 19.9 MJ kg^{-1} - this value will be taken as the value for POC. The values of DOC varied between 7 and 13 MJ kg^{-1}. Given the stoichiometry expressed in Equation (ix), the energy budget shows that 7 MJ m^{-2} $yr^{=1}$ is absorbed as primary production, while 1.02±0.03 MJ m^{-2} $yr^{=1}$ was exported as DOC; 0.61 ± 0.02 MJ m^{-2} $yr^{=1}$ was exported as POC; and 0.39 ± 0.04 MJ m^{-2} $yr^{=1}$ was exported as CH_4. Balancing Equation (ix) shows that of 7.1 MJ $kg^{-1}yr^{-1}$ absorbed as primary production 2.0 MJ $kg^{-1}yr^{-1}$ was exported out of the ecosystem as DOC, POC or CH_4; 2.8 MJ $kg^{-1}yr^{-1}$ was returned as heat from the decay process and only 2.3 MJ kg^{-1} was held in long term storage which is 0.24% of the median net radiation. Although degradation processes will be faster in warm summer weather, it will continue during darkness and so at this site the amount of energy absorbed through primary production would be closer to 0.07 Wm^{-2}. It also means that an enthalpy can be given to Equation (ix), however, since Equation (ix) is not at equilibrium the enthalpy has no further thermodynamic interpretation. In effect Equation (ix) as viewed in Equation (xxiv) is an inefficient burning reaction with energy released as the vegetation is only partially converted back to CO_2.

$$100C_{pp} \xrightarrow{\Delta H = 813 kj/gC} 35C_{R} + 26C_{DOC} + 4C_{CH4} + 4C_{dissco2} + 9C_{POC} + 22C_{RES} \qquad \text{(xxiv)}$$

Discussion

Has this been an adequate method for the calculation of a long term evaporation and energy budget? There are a number of limitations to this approach. Firstly, the evaporation can only be calculated on days without rain which means that for a catchment such as the one studied the majority of the available data have to be sacrificed. The criterion that only rain-free days may be considered skews the sampling and, although over the period of the study all months had at least 95 observations, it does mean that the relationship with rainfall could not be examined and it had to be assumed that evaporation on rain-free days was representative of all days. Secondly, there are long term climate changes that would not necessarily be reflected in the variables available to this study, eg. wind speed. If wind speed and changed significantly over the period this would not well represented in changes in air temperature. Unfortunately, long term measures of wind speed were not available to this study. Thirdly, the common time step used in this study was daily and so it is possible the changes in the diurnal cycle of energy fluxes are being missed. Fourthly, the method relied on data from one site within the catchment and compared this to water balance across the whole catchment but this approach did calibrate and correlate between the two. Equally, it should be noted that the result for the catchment scale data showed an inter-annual increase in runoff from the catchment (Equation xiv) over a period when rainfall did not change (Equation xii) which therefore predicts that evaporation from the catchment does decline. It should be noted that, although there is a significant positive trend with time predicted by Equation (xviii), Equation (xviii) does not imply an ovcr all increase in evaporation as both air temperature declined and depth to the water table increased. However, Equation (xv) predicted no change in the relationship between rainfall and runoff at an annual time step over the course of the study.

Therefore, it could be suggested that Equations (xviii) and (xv) contradict but they are on different time steps and Equation (xvii) has to be considered alongside trends in two other environmental drivers and so we should be cautious about comparing trends between time steps and where magnitude of trends and the variables included differ.

The study has shown that there has been an increase in evaporation over the course of the study independent of changes in measured drivers or other environmental variables (Equation xviii). If the long term change in evaporation cannot be ascribed to changes in net radiation or air temperature, there are a number of possibilities. Firstly, the changes might be due changes in rainfall because evaporation could not be compared to this driver. A wet day prior to one that could be studied here may have led to increased evaporation above that which would be predicted from a consideration of the depth of the water table, for example the soil moisture may remain higher than would otherwise be considered. Secondly, the mathematical form of the functions used for each variable may be a simplification. Although variables were log-transformed and the normality of the distribution of each variable assessed and the study only proceeded once these criteria had been met, this approach may be adequate but may not be ideal. An examination of the variation of evaporation with depth to water table shows that, even when log transformed, the evaporation is higher at shallow water table depths than would be expected for the approaches used here. It is not only the form of the function used for each variable being considered but whether interaction terms should be considered as well as single variables. For example, we could hypothesize that the effect of temperature would vary with water table depth. Furthermore, as included in the trend analysis here evaporation is dependent upon water depth. However, for the study site the water depth is commonly very shallow with water table depths less than 15 cm, and so making capillary rise to the surface almost continuous and thus the water supply to the surface constant. If capillary rise can always supply water to the surface for evaporation then a slight increase in depth to the water table, but not to below the capillary fringe, may not limit evaporation. However, the trend analysis used here would not have been sensitive to such a threshold effect. Oversimplification in the empirical function used to model the time series of evaporation could give an apparent trend over time. However, it is unclear what such terms should be or whether the number of observations is sufficient to test for their significance. The purpose of this study was to consider how the ecosystem would adapt to change in driver variables (eg. air temperature) and how it would apportion that change in terms of energy balance (eg. increase evaporation or sensible heat flux). The study has shown that over a 19-year period in which temperature and net radiation decreased for this catchment, the evaporation significantly increased while the sensible heat flux and soil heat fluxes both significantly declined. However, the real question of this study is not whether significant changes occurred but rather did any of these energy dissipation pathways change disproportionately compared to the others. In this case a 29% decline in net radiation, coupled with a 0.06 K decline in air temperature, over the study period resulted in a 4% increase in evaporation, 60% decline in sensible heat flux and a 14% decline in soil heat flux. The Bowen ratio is unhelpful in this system because its variation is dominated by the switching of the sensible heat flux from sink or source with respect to the surface. The small magnitude of the change in evaporation relative to available drivers does suggest that evaporation is insensitive to change. In a system with a high evaporative demand, a reduction in energy input via radiation means that more energy is taken via sensible heat flux. Here evaporative demand is considered as the upper limit of the rate of evaporation created by the atmospheric driving forces (de Jager and van Zyl, 1989), and in a wetland the high evaporative demand will be due to large vapour pressure deficit between the often saturated peat surface and the atmosphere. If a high evaporation demand has to be met by energy from sensible heat flux then it is not surprising it declines (becoming more likely to be a sink rather than a source of sensible heat) and meaning that for this system sensible heat flux is more sensitive than other energy flux pathways. The relative insensitivity of evaporation compared to other energy fluxes is readily seen when comparing median monthly values across the year (Figure 9) – evaporation has a lower absolute range than other energy flux pathways.

The relative insensitivity of evaporation may help stabilise the water table in the peat soils and so help buffer changes in carbon fluxes. However, the depth to the water table has increased over the study period which would be expected to lead to increased carbon efflux from the catchment but because of reduced CH_4 flux with increased depth to water table leads to decreased fluxes of the more powerful greenhouse gas CH_4 (eg. Levy et al., 2013). But, the observation of this study does raise the possibility that, alongside being sinks or carbon and greenhouse gases, restored peatlands could also have the added benefit of being a sink of atmospheric heat. The large heat sink represented by this peat ecosystem is not unique and has been observed for other peat or wetland ecosystems (eg. Rejskova et al., 2010). If it is assumed that the study site acted as an evaporative cooler then for a median annual heat sink of -0.79 Wm^{-2} (the median value of the H estimated above) and given the median difference between the wet and dry bulb temperatures then this heat sink would cause a lowering of the air temperature by 0.5 K. Such a temperature effect is local and requires the export of the additional water vapour and assumes that the latent heat of vaporisation is released elsewhere. Ban-Weiss et al (2011) modelled a global change in land use that would result in an increase in latent heat flux by 1 Wm^{-2} and a sink of sensible heat of 1 Wm^{-2} and showed that this would result in an average temperature reduction of 0.54 K. Although it is neither possible to transform large areas into functioning peatlands or wetlands many UK peatlands are degraded where land management, wildfire, over-grazing, atmospheric pollution can have led to lowered water table and bare soils (Holden et al., 2007). Restoration of peatlands can readily revegetate and raise water tables which could lead to a shift in the partitioning of net radiation in favour of great latent heat export and even the creation of sensible heat sinks. Therefore, peatland restoration may have a climate mitigation effect not only due to changes in greenhouse gas fluxes but also in energy adsorption – it must be a future research question as to whether the sensible heat sink effect could ever be more important than the changes in the greenhouse gas warming potential?

The changes observed in the catchment could also be due to changes independent of the environmental variables considered here. For example, a change in the distribution of vegetation could cause a shift in water balance, i.e. a functional type with a deeper rooting depth over more of the area. Equally, there may be a change in the balance of flowpaths that means that runoff is preferred over retention and evaporation. Worrall et al. (2007) considered changes in runoff initiation for this catchment across the period of the severe drought in 1995 and showed that the catchment returned to pre-drought condition by the subsequent winter, i.e. long-term flowpath change was minimal. Grayson et al. (2010) showed that vegetation cover at this site had increased between 1970 and 1995 but actually decreased between 1995 and 2000 and that changing vegetation cover did affect runoff character. However, the study is based at one location and this location was chosen to be an interfluve plateau (i.e. flat) and so a good location to apply White's method but also an area of stable, climax, vegetation. Further, Holliday et al. (2008) showed through analysis of aerial photographs that vegetation change within the catchment has been focused in gullies and not interfluves.

Furthermore, the trends predicted in Equations (xiii) and (xviii) are log-transformed relationships with time and examination of these relationships shows that change was greatest earliest in the time series of the study. The year 1995 was a year of a severe drought across the UK and the severest over the period of the study within the study catchment, therefore it is possible that what is being observed here is dominated by recovery from a drought and indeed this is the detailed trend suggested by the *post hoc* analysis that the increase in evaporation occurred between 1996 and 2009..

One of the aims of this study was to test how a catchment would respond to change. Schneider and Kay (1994) have proposed that ecosystems are "far-from-equilibrium" systems that are energy- and entropy-dissipative and would maximise entropy production. A simple mechanism by which environments can maximise entropy production is by maximising evaporation and transpiration processes. Brunsell et al. (2010) have suggested that soil is a "far-from-equilibrium" system so that it will maximise entropy production by becoming vegetated which facilitates an increase in evaporation as means of dissipating energy. Addiscott (2010) has suggested that this is not true and that most soil-plant systems are designed to minimise water loss and might therefore be considered as "near-to-equilibrium" systems which would not maximise entropy production but would rather minimise entropy production, and therefore limit water losses. The site of this study was at a steady-state with respect to vegetation cover and has negligible bare soil area, i.e. the circumstances described for a "far from equilibrium" system do not occur at this site. This study showed that evaporation was well buffered against change and would take energy from both radiation and sensible heat, which is similar to a situation predicted by Addiscott (2010).

The study has shown that primary production is a negligible sink of energy within the catchment. Studies that have considered primary productivity as an energy sink have considered the energy flux on a short timescale since in an ecosystem that is at steady-state vegetation will not be accumulating dry matter and so any primary productivity is returned to the atmosphere and so the energy is also returned. Furthermore, primary productivity will consume incident radiation and act as an energy sink as it converts CO_2 and minerals to glucose. However, as glucose is converted into plant biomass there will be return of energy to the environment in the form of metabolic heat and also because the process will be somewhat inefficient (Loomis and Connor, 1992). Given the approach of Penning de Vries et al. (1974) it is possible to suggest that for a system reliant on using reduced forms N and S and one that produces 176 gC m^{-2} yr^{-1} as primary productivity, then 0.8 MJ $kg^{-1}yr^{-1}$ would be spent in metabolic heat rate. Although this return of metabolic heat from biosynthesis would not change the amount of energy sunk into the long term carbon store, it would mean that the primary production represents an even smaller sink of energy of 0.04 Wm^{-2}. Therefore, the energy converted into plant biomass is not the energy absorbed from incoming radiation, furthermore, for an ecosystem at steady state, i.e. no net accumulation of carbon or dry matter, the energy stored in the plant biomass will be returned as that material itself decays. Furthermore, the metabolic heat rate and the inefficiency in the metabolic process means that for non-accumulating ecosystems the primary productivity would be a small, net source of heat. The process of metabolic heat rate and inefficiency of conversion can be seen in equation for the conversion of plant biomass through the carbon cycle of the catchment (Equation viv and xxiii). On a peat soil there is long term storage of organic matter and so there is long term storage of energy in this study environment that represents a small but measurable proportion of the incoming energy.

Conclusions

The study has shown that there is long term (over 19 years) increase in evaporation for a catchment that is independent of changes in air temperature or net radiation. The study has shown that changes in evaporative energy flux are damped in comparison to other energy fluxes and that for much of the year the evaporative flux is driven by the absorption of sensible heat. The evaporative demand of the site means that much of the year the site is a net sink of sensible heat energy. The study suggests that the catchment is responding to change by limiting change in evaporation and this suggests the system is a “near-equilibrium” system.

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Figure 1. Location of the study site.

Figure 2. The trends in the measured variables; a) the monthly average air temperature; b) the monthly total rainfall; c) the monthly average depth to water table; and d) the monthly total runoff.

Figure 3. The time series of the net radiation where positive value is an input of energy into the ecosystem.

Figure 4. The whisker plot of the estimated time series of evaporation for the site. The whisker reprents the 5th to 95th percentile range and the dot is the median value.

Figure 5. The whisker plot of the calculated soil heat flux across the study period. Note that a positive soil heat flux is an energy flux away from the surface. The whisker reprents the 5th to 95th percentile range and the dot is the median value.

Figure 6. The whixker plot of the calculated sensible heat across the study period. Note that a positive value of sensible heat flux is an energy flux away from the surface. The whisker reprents the 5th to 95th percentile range and the dot is the median value.

Figure 7. Comparison of the difference between median monthly air temperature and median monthly net radiation in comparison to the 50% probability contour of the system being a net sensible heat sink.

Figure 8. The whisker plot of the estimated Bowen ratio over the time period of the study. The whisker reprents the 5th to 95th percentile range and the dot is the median value.

Figure 9. The monthly median energy fluxes from across the entire 19 year record in comparison to air temperature.