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Are peatlands in different states with respect to their thermodynamic behaviour? A simple test of peatland energy and entropy budgets.

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Abstract

Whilst all ecosystems must obey the second law of thermodynamics, these physical bounds and controls on ecosystem evolution and development are largely ignored across the ecohydrological literature. To unravel the importance of these underlying restraints on ecosystem form and function, and their power to inform our scientific understanding, we have

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calculated the entropy budget of a range of peat ecosystems. We hypothesise that less disturbed peatlands are “near equilibrium” with respect to the 2nd law of thermodynamics and thus respond to change by minimising entropy production. This “near equilibrium” state is best achieved by limiting evaporative losses. Alternatively, peatlands “far-from–equilibrium” respond to a change in energy inputs by maximising entropy production which is best achieved by increasing evapotranspiration. To test these alternatives this study examined the energy balance time series from seven peatlands across a disturbance gradient. We estimate the entropy budgets for each and determine how a change in net radiation (ΔR_n) was transferred to a change in latent heat flux ($\Delta\lambda E$). The study showed that:

i) The transfer of net radiation to latent heat differed significantly between peatlands. One group transferred up to 64% of the change in net radiation to a change in latent heat flux, while the second transferred as little as 27%.

ii) Sites that transferred the most energy to latent heat flux were those that produced the greatest entropy.

The study shows that an ecosystem could be “near equilibrium” rather than “far from equilibrium”.

Keywords: 2nd law of thermodynamics, evaporation, net radiation, peatland ecosystem, entropy, disturbance.

1. INTRODUCTION

An ecosystem’s energy budget must obey the 2nd law of thermodynamics even if it is an open system (Prigogin et al. 1972). Kleidon and Schymanski (2008) suggested that applying thermodynamic approaches to ecosystems was limited by the fact that they are open systems as they exchange energy and mass with their surroundings. Prigogine and Stengers (1984) have defined the possible states with respect to thermodynamics: thermostasis, linear non-equilibrium thermodynamics and "far from equilibrium" thermodynamics. Thermostasis equates with equilibrium thermodynamics that could exist in a closed system. Kleidon and Schymanski (2008) have assumed that since that thermodynamic equilibrium requires a closed system and ecosystems must be open systems then ecosystems must be "far from equilibrium". However, the other alternative is that an ecosystem obeys linear non-equilibrium thermodynamics.

Schneider and Kay (1994a & b) have proposed that a system "far from equilibrium" will always seek to maximise entropy production as the system responds in a non-linear fashion to the forces acting upon it where small changes in the driving forces can result in large changes in outputs and flows from the system. Addiscott (1994, 1995 and 2010) has criticised this concept that ecosystems were "far from equilibrium" as it did not seem to fit with his experience of soil-plant systems as they resisted change or perturbations, and minimised losses in response to external changes. Prigogine (1947) proposed a minimum entropy production principle, and Katachalsky and Curran (1965) suggested that natural systems, by the action of resisting perturbations, were acting as if they minimised entropy production and were therefore "near equilibrium". Onsager (1931) has described this "near equilibrium" case as linear, non-equilibrium thermodynamics because changes in forces are linearly related to changes in flows. However, more recently, analyses indicate that maximum and minimum entropy production are different ways of looking at the same system (Lucia 2012) or the result of over-specified boundary conditions (Kleidon & Lorenz 2005). That is minimum entropy production is more of a special case of maximum entropy production for systems that lack dynamic instability (Martyushev & Seleznev, 2006). Quijano & Lin (2014) have reviewed the alternative approaches to understanding entropy production in ecosystems.

Wang et al. (2007) proposed that one way for an ecosystem to maximise entropy production was to maximise water loss through evapotranspiration. Evidence for maximisation of entropy production via latent heat transfer (evapotranspiration) was given by Tesar et al. (2007) who compared net entropy production between a forested and a bare soil watershed and showed that the vegetated surface contributed higher entropy production than the bare soil which was due to an increase in transpiration flux as well as a reduction in temperature. Equally, Brunsell et al. (2011) used modelling to show that a vegetated land surface was thermodynamically favourable because an increased vegetation fraction maximised entropy production through increasing evapotranspiration. Further, through the use of a global circulation model, Kleidon (2007) showed that a vegetated surface had a higher entropy production than a non-vegetated surface. Holdaway et al. (2010) used eddy covariance data to show increased entropy production across a vegetation succession in the Amazon rainforest. Indeed, Schneider and Kay (1994a) said, "Much of the dissipation is accomplished by the plant kingdom (less than 1% through photosynthesis, with most of the dissipation occurring through evaporation and transpiration).", where vegetation increased entropy production because of latent heat flux. Alternatively, Addiscott (2010) concluded that water loss would be minimised for a "near equilibrium" system and changes in the amount of incident energy would be dissipated through sensible heat flux. To test between these two pathways and their implications (dissipation via sensible or latent heat fluxes), this study considers how the energy budgets respond to changes in incoming energy. Specifically, how a change in net radiation is transferred to a change in latent heat flux or to a change in sensible heat flux. An ecosystem maximising entropy production would transfer the majority of additional energy to latent heat. Alternatively, if a system was minimising its entropy production it would act to transfer additional energy to sensible heat. Several studies have sought to use a consideration of entropy to understand ecosystem energy budgets and more specifically evaporation. Although modelling approaches have been used to consider the thermodynamic behaviour of environments (Wang et al., 2007), no study has tested this thermodynamic behaviour or its implications based upon observations: maximum entropy production is a characteristic of ecosystems that are "far from equilibrium" and that this can be tested (Tesar et al., 2007; Holdaway et al., 2010). Although a number of studies have measured entropy budgets using field data (eg. Holdaaway et al., 2010; Brunsell et al., 2011; and Quijano & Lin, 2015), this study provides an alternative test by considering the behaviour of ecosystems relative to changing energy input.

This study tests the two thermodynamic extremes by considering the energy balance of peatlands. Within the terrestrial biosphere, northern peatlands are the most important terrestrial carbon (C) store. Despite only covering ~3% of Earth's total land area (Rydin and Jeghum, 2015), peatlands store large quantities of C. Northern peatlands store an estimated 500 ±100 GtC (Gorham, 1991; Yu et al, 2014; Loisel et al., 2014), which is equivalent to the total terrestrial vegetation store (IPCC, 2013), or the cumulative anthropogenic CO_2 emissions from fossil fuels, industry and land use change activities for the period 1870 – 2015 (Le Quere et al., 2016). Peatlands exist because at some stage in their development there was a positive C balance; an excess of C fixed via primary production that leads to organic matter accumulation over the release of C via a range of pathways (largely via respiration of CO_2). The classical explanation of the formation of peat (Belyea and Clymo, 2001) is that C is sequestered over long time-scales by submergence of organic matter. Therefore, understanding the impact of climate and land-use change on the peatland water balance is key to protect the future potential of these ecosystems as carbon stores.

Precipitation inputs are balanced against outputs of runoff (surface and groundwater), evapotranspiration and storage changes. Under climate change, it is expected that air temperatures will increase in northern latitudes 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. Peatland evapotranspiration has been widely measured. 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 evapotranspiration. Conversely, Admiral et al. (2006) measured Bowen ratios over an Ontario bog and found snow-free values typically below 1, similar to a Swedish *Sphagnum* mire (Kellner, 2001). A range of behaviour within the diversity of peat bogs is therefore clear and has contributed both to a diversity of methods for calculating evapotranspiration (Drexler et al., 2004) and attempts to understand this spatial variation (Rouse et al., 2000). Kettridge et al. (2016) proposed, based upon modelling peat soils with a range of hydraulic properties, that peat develops to maximise water use efficiency, which is behaviour that would equate with a system that was acting to minimise entropy production as predicted by Addiscott (2010).

A thermodynamic interpretation of the diverse rates of peatland evapotranspiration suggests increased water losses via evapotranspiration from systems “far from equilibrium” to maximise entropy production, and low evapotranspiration from peatlands “near equilibrium”, minimising water losses. A simple test of the differences between these two system states would be to measure the sensitivity of evaporation to a change in incoming energy. If the change in available incoming energy is absorbed by increasing evapotranspiration then a system is acting to maximise its entropy production. If the change is absorbed by exporting sensible heat then it is acting to minimise water loss and minimising entropy production. Furthermore, we would hypothesize that differences in entropy flux and production between peatlands may reflect differences in the health of peatlands and factors driving organic matter accumulation.

2. APPROACH & METHODOLOGY

This study considered seven peatland ecosystems across the UK with long term measurements of energy budget. These seven sites represent the diversity of peatlands across the UK including: upland and lowland sites; sites under intensive and extensive agriculture; and sites with differing nutrient status (Table 1, Figure 1). Energy budgets for each site were summarised to a common time step and the responses of latent flux to changes in net radiation were determined. However, by measuring across a range of peatlands sites we aim to interpret the presence or lack of contrast in the entropy budgets across a diversity of sites to give insight in to the controls on entropy flows for peatlands. However, the choice of sites was limited by the availability of suitable datasets and all those sites in the UK wtth the correct data at the time of writing were included. In addition, we test that a site "far from equilibrium" would flux and produce more entropy than a site "near equilibrium". Thus the entropy budget, including entropy production, was calculated for each site.

2.1 Measurement of Energy budget

The energy budget of an ecosystem can be considered as:

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

Where: R_n = net radiation (W/m^2); H = sensible heat flux (W/m^2); G = soil heat flux (W/m^2); λE = latent, or evaporative, heat flux (W/m^2) where λ is the latent heat of vapourisation (2260 kJ/kg); PP = primary production (W/m^2); and e = residual error. The residual error term is included as there are other smaller energy flux terms that are negligible compared to the other terms included. Indeed, PP is often excluded even when ecosystem energy budgets are considered (Kellner, 2001).

The net radiation can be defined as:

$$\mathrm{R_n} = (1-\alpha)Q_S^{in} + Q_L^{in} - Q_L^{out} \qquad \text{(ii)}$$

Where: Q_S^{in}= incoming short wave radiation (W/m^2); Q_L^x = the energy flux due to long wave radiation with x is either incoming long wave radiation (in) or outgoing long wave radiation (out) (W/m^2); and α = albedo (dimensionless).

At six sites the energy budget was measured by eddy covariance method, at the seventh site (Moor House - MH), the energy budget was determined from detailed hydrometeorological observations (Worrall et al., 2015).

2.2 Entropy production and budget

This study uses the method of Brunsell et al. (2011) where the total entropy budget at the land surface is:

$$\frac{dS}{dt} = J_{QL} + J_{QS} + J_H + J_{\lambda E} + J_G + \sigma_{QL} + \sigma_{QS} \qquad \text{(iii)}$$

Where: J_x = entropy flux (J/K /m^2/s) due to x; with x representing the long wave radiative flux (QL), the short wave radiative flux (QS), the sensible heat flux (H), latent heat flux (λE), soil heat flux (G); and σ_x = the entropy production (J/K /m^2/s) due to the short wave radiative flux (QS) and the long wave radiative flux (QL). Note in the sign convention of the system it would be expected that the budget would be negative. The entropy flux terms are expressed as the energy flux at their respective temperatures:

$$J_x = \frac{X}{T_{surf}} \tag{iv}$$

Where: X = energy flux as defined in equation (i), i.e. H, G, λE, and Q_S (J/m^2/s); and T_{surf} = the temperature at the soil surface (K). For long-wave radiation (J_{QL}):

$$J_{QL} = \frac{Q_L^{in}}{T_{air}} - \frac{Q_L^{out}}{T_{surf}} \tag{v}$$

Where: T_{air} = the air temperature (K); and other terms as defined above.

$$Q_L^{in} = 0.522 e_a^{1/7} s T_{air}^4 \tag{vi}$$

$$e_a = 2x10^{-8}\exp(0.0705 T_{air}) \tag{vii}$$

$$Q_L^{out} = 0.9 s T_{aero}^4 \tag{viii}$$

Where: e_a = actual vapour pressure (mbar or hPa); s = Stefan-Boltzmann constant (= 5.6697x10^{-8} W/m^2 K^4); and T_{aero} = the aerodynamic temperature (° K). Note that Equation (viii) assumes that the emissivity is 0.9 and assumes stable atmospheric conditions:

$$T_{aero} = T_{air} + \frac{H}{\kappa \rho c_p u_*}\left(ln\left(\frac{z-d}{z_m}\right) + 6\ln(1 + \frac{z}{O_L})\right) \tag{ix}$$

Where: κ = Von Karman' constant (0.4); ρ = air density (kg/m^3); c_p = specific heat capacity of air (J/kg/K); z = measurement height (m); d = displacement height (approximated as $^2/_3$ of the canopy height); z_m = aerodynamic roughness length ($^{1}/_{10}$ d m); O_L = Obukhov length (3 m); and u_* = air friction velocity (m/s).

The entropy production terms are:

$$\sigma_{QS} = Q_s\left(\frac{1}{T_{surf}} - \frac{1}{T_{sun}}\right) \qquad \text{(x)}$$

$$\sigma_{QL} = Q_L^{in}\left(\frac{1}{T_{surf}} - \frac{1}{T_{air}}\right) \qquad \text{(xi)}$$

From Equation (ii) and values of Q_L^{in} and Q_L^{out} from Equations (vi) and (viii):

$$Q_s = R_n + Q_L^{in} - Q_L^{out} \qquad \text{(xii)}$$

Where: T_{sun} = the temperature at the sun's surface (= 5780 K). Holdaway et al. (2010) provided an alternative approach to the calculation of Q_s based upon understanding the proportions of direct and diffuse components of the radiation, but the proportions have to be measured or assumed from empirical data, whereas the Equation (xii) requires only that the measurement of R_n.

Therefore, calculating the entropy budget and production requires additional measurement at the study sites, in particular the measurement of surface temperature as opposed to air temperature. For EFDA (Table 1) there were not sufficient measurements to perform the calculation of T_{aero} (Equation ix). For EFLN, EFEG, SLEG, AFHN and AFLN (Table 1) u_* was measured. For MH the value of u_* was calculated from the law of the wall (von Karman, 1930):

$$u_* = {}^{\kappa\bar{u}}\Big/_{\ln\left(\frac{z-d}{z_m}\right)} \qquad \text{(xiii)}$$

Surface temperature, when not measured, was calculated from the solution of the 1D heat equation for 0 cm depth (Sharratt et al., 1992). Sharratt et al. (1992) 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:

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

Where: k_i = the thermal conductivity of the layer at time interval I ($W/m^3/K^1$); ΔT_i = the temperature difference between the soil surface and measured soil temperature (K); and Δz_i = the distance between the surface and the measured soil temperature (m). When soil heat flux is known then surface temperature can be calculated. Values of k_i were taken from Moore (1987).

For EFLN and EFEG lack of sufficient soil temperature readings meant that use of Equation (xiv) was not feasible and so the assumption was made that surface temperatures could be estimated from calibration between air and surface temperatures from other sites. For all sites the measurement height (*z*) was taken as 1.5 m and canopy height was no greater than 30 cm for each site.

Equation (iii) relies on the estimation of the energy budget and would, therefore, be subject to any uncertainty in the energy balance and especially to uncertainty in the completeness (i.e. missing measurements) and closure (the expected zero sum of the measured components) of the energy budget. To understand the impact of lack of completeness and closure of the energy budgets, the energy budget of the site with the greatest imbalance in its energy budget was closed assuming that the sensible heat flux (H) closed the energy balance. Furthermore, the above approach has assumed values of constants. The emissivity (Equation viii) could vary with the type of surface cover. Wang et al. (2020) have modelled emissivity as varying between bare and vegetation soils with variation between approximately 0.8 and 0.98 and so although this study used a value of 0.9 for its emissivity, but the variation in emissivity was considered. Equally, Henderson-Sellers (1984) has shown that the latent heat of vapouriation (λ – Equation (i)) can be expected to decrease by 3% between 0 and 30 ^{o}C. To understand the influence of these sources of uncertainty the results for EFDA site were calculated allowing for 3% variation in λ and variation between 0.8 and 0.98 in emissivity.

2.3 Eddy covariance instrumentation

Eddy covariance fluxes were measured with open-path EC systems (Table 2). Two types of sonic anemometer-thermometers were used across the network. CSAT3 sonic anemometers (Campbell Scientific Inc. Logan Utah, USA) were used at EFEG, EFDA and the two AF sites. R3-50 sonic anemometers (Gill Instruments, Lymington, UK) were deployed at the other three flux tower locations. All sites (except MH) were equipped with either an LI-7500 IRGA (LI-COR Biosciences Ltd., Logan Utah, USA) or the more recent LI-7500A (LI-COR Biosciences Ltd., Logan Utah, USA). The measurement height at each location was set to at least two times the maximum canopy height (Table 2). The height of the sensors (Table 2) meant that the footprint of the EC system could be several hundred metres and in each case the EC system had been sited so that the footprint was within the peatland at each site. The exception was EFDA, where the tower was positioned at the edge of a field to sample fluxes from a single land parcel located to the south west of the flux tower. The EC sensors were scanned at a rate of 20 Hz and logged using either LI-COR Biosciences LI7550 (at EFLN, EFEG) or Campbell Scientific CR3000 dataloggers (all other sites).

A range of meteorological, energy balance and soil physics sensors were installed at each EC measurement site (Table 2). At most sites (excluding the two AF sites), the net radiation and its four components (incoming and outgoing short- and longwave radiation) were measured using four channel net radiometers. CNR1 net radiometers (Kipp & Zonen, Delft, The Netherlands) were installed at the majority of sites. A CNR4 net radiometer was installed at EFDA (Kipp & Zonen, Delft, The Netherlands). Single channel NR-lite radiometers (Kipp & Zonen, Delft, The Netherlands) were installed at AFHN and AFLN in combination with upward facing (shortwave) pyranometers (Didcot Instruments Ltd., Didcot, UK). HFP01 or HFP01-SC self-calibrating heat flux plates (Hukseflux Thermal Sensors B.V., Delft, The Netherlands) were installed below the soil surface to monitor the flux of heat into and out of the soil: all soil heat flux plates were installed at 10 cm depth. Air temperature and relative humidity were measured using HMP45 (Vaisala, Helsinki, Finland) probes at all sites. For these sites gap-filling was achieved using the method of Aubinet et al. (2003). In the raw data the proportion of readings requiring gap-filling was 38%, however, where data was missing for 12 hours or more then no daily average or sum was was calculated and so this mitigated against using gap-filled data.

2.4 Moor House (MH) energy balance

Moor House and Upper Teesdale National Nature Reserve (NNR) is situated in the North Pennine upland region of the UK (Figure 1). The 19-year long energy budget of the catchment has been calculated from an automatic weather station that is discussed in detail by Worrall et al. (2015). The automatic weather station situated within the Moor House catchment (Figure 1) includes 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. The station included the monitoring of net radiation (R_n - Kipp solarimeter – error of 1% at 1 Wm^{-2}). Discharge has been measured from the catchment outlet on an hourly time scale since 1991. Soil heat flux (G) was estimated on a daily basis using the approach of Sharratt et al. (1992) as described in Equation (xiv).

For the MH site, Worrall et al. (2015) estimated evapotranspiration using the method of White (1932). However, in this study the Penman-Grindley method was used for the estimation of evapotranspiration (Penman, 1949; Grindley, 1970). With this methodology. it is not possible to estimate on days with snow cover, no term for the latent heat of fusion was included. The Penman-Grindley method predicts actual evaporation (AET) based on rainfall totals and estimated potential evaporation (PET) for a given land use type. Potential evapotranspiration was calculated by the Priestley-Taylor method (Priestley and Taylor, 1972) based on Douglas et al. (2009), the PET (mm/day):

$$\lambda \rho_w PET = \alpha \frac{\Delta}{\Delta+\gamma}(R_n - G) \tag{xv}$$

$$\Delta = \frac{4098 e_s}{(237.3+T_{min})^2} \tag{xvi}$$

$$\lambda = 2.501 - 0.0002651 T_{avg} \tag{xvii}$$

$$\gamma = 0.001 \frac{c_p P}{\varepsilon \lambda} - 0.0016286 \frac{P}{\lambda} \tag{xviii}$$

$$e_s = 0.6108 exp\left(\frac{17.27 T_{min}}{237.3+T_{min}}\right) \tag{xix}$$

Where: ρ_w = density of water (kg/m^3); T_{avg} = average daily air temperature (^{o}C); e_s = saturated vapour pressure (kPa); c_p = specific heat capacity of air (1.013 kJ/kg/K); P = atmospheric pressure, taken as 101.3 kPa; T_{min} = minimum daily temperature (^{o}C); and a = constant (1.26). We made the assumption that the Penman-Grindley method was equally applicable across day and night time measurements.

Values of the root constants taken from monthly values reported by Lerner et al. (1990). The root constants were used as fitting parameter in this approach. Fitting was achieved by ensuring an annual water balance across the catchment assuming no long term change in water storage. The annual water balance was determined from rainfall and discharge measurements obtained within the catchment. Hourly rainfall was recorded by tipping bucket rain gauge and discharge has been measured from the catchment outlet on an hourly time scale since 1991.

The approach to calculating the energy balance at MH means that the energy balance time series could be summarised to a daily time step because of the nature of the latent heat flux calculation. However, most of the energy balance components at MH were based on hourly data recorded throughout each day from the weather station. The energy balance time series at MH and the varying time steps at the other sites meant that data from each study site were assessed on a common daily time step. 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). No gap filling was used on the MH dataset.

2.5 Statistical analysis

The difference between the Bowen ratio of the study sites was assessed using the Kruskal-Wallis test. The Kruskal Wallis test was used to assess the difference between sites and, separately, between months. A Kruskal Wallis test was used because the values of B were not normally distributed and could not be readily transformed to be normal.

The important test considered by this study was the change in latent heat flux (λE) in response to a change in net radiation (R_n), it is the time series of daily net radiation and net latent heat flux that need to be compared for the tests proposed by this study. The change in net radiation is taken as the difference between the total net radiation between one day and the next – where a day was a 24 hour period starting at midnight. Likewise, the change in latent heat flux was calculated as the difference between the total for one day and the next. This requirement to calculate change means that only successions of days for which complete net radiation and latent heat flux data were available could be used, i.e. days with gap-filled data were not used

To understand the response of the latent energy flux to a change in net radiation the equation was fitted to the data:

$$\Delta\lambda E = \phi\Delta R_n\left[1 - ksin\left(\frac{m\pi}{6}\right) - jcos\left(\frac{m\pi}{6}\right)\right] - \theta\Delta R_{n-1} + C \qquad \text{(xx)}$$

Where: m = month number (1 = January to 12 = December); $\Delta\lambda E$ = the change in daily latent heat flux between the previous and current day (W/m^2); ΔR_n = the change in net radiation flux between the previous and current day (W/m^2); ΔR_{n-1} = the change in net radiation flux between the previous day and the one prior to that (W/m^2); and ϕ, θ, k, j and C are constants. Equation (xx) was fitted to the data using a maximum likelihood approach (Minitab v17, State College, PA, USA). Given the study aim, ϕ is the important term which represents the proportion of change in net radiation that results in a change in latent heat flux over the same time period. In Equation (xx) we have recognised that a change in latent heat flux may result from a previous change in net radiation and so an autoregressive term ΔR_{n-1} was included. Only ΔR_{n-1} was considered and constant θ is the AR(1) process coefficient that represent the proportion of previous changes in net radiation that is contributing to current changes in latent heat flux. A physical interpretation of θ might be that it represents a contribution of changing soil heat flux to current latent heat flux. Further autoregressive components up to 5 days previously were considered but not found to be significant. The terms in k and j are set as a seasonal indices to allow for variation in the relationship between ΔR_n and $\Delta\lambda E$ so that the estimation of ϕ is an annual average. Note that in Equation (xix) a monthly time step has been used while R_n and λE were calculated on a daily time step. Seasonal, or intra-annual, adjustment based upon a daily time step would not have been possible as there were not enough measurements on each day of the year to given an estimate of a seasonal index to allow for calculating ϕ as an annual average. Based upon the fit of Equation (xix) it was possible to determine the mean and 95% confidence intervals of ϕ for each site and compare between sites using the Tukey test.

The second test is that $\frac{dS}{dt}$ (Equation (iii)) is greater for sites judged to be "far from equilibrium". That is, there is correspondence between ϕ and the entropy flux if the concept of maximum entropy production holds. Note that in the sign convention of the system an increase in entropy with time would be a loss from the ecosystem and so it would be expected that the budget would be negative. Significant differences in $\frac{dS}{dt}$ between sites was tested using ANOVA that included two factors. The two factors were considered (i) the difference between sites and; (ii) the difference between sampling month. The latter factor accounts for difference in sampling between sites and so gives a better comparison between sites. The variation between years could not be considered in the ANOVA as there was not a consistent set of years.

3. RESULTS

The summary of energy budgets and the Bowen ratio ($B = \frac{H}{\lambda E}$) are presented in Table 4. The incompleteness of the energy budgets varied from 4 to 24%, the budget for MH site was calculated by assuming energy balance. Bowen ratio peaks in April (median B = 0.6) with a minimum in December (median B = -1.57), and the months between October and February inclusive have $B < 0$, confirming that peat is a sink of sensible heat during winter months. Bowen ratio also varies considerably between sites, with some sites showing a large range in values (Figure 2). Negative values of B occur when sensible heat and latent heat fluxes are in opposite directions, i.e. the sensible heat flux is towards the soil. Median values of B for sites are very low, ranging from 0.00 to 1.6. The peculiar distribution of B resulting from its unbounded nature and values ranging to below zero means that it did not yield to ANOVA and so the Kruskal-Wallis test was used. The Kruskal-Wallis test did show that there were significant differences (at the 95% probability of not being zero) between sites and between months of the year. The value of B for the MH was significantly larger than that of the other sites, even though this site is an intact peatland the Bowen ratio implies the site is the most dominated by sensible heat fluxes. However, MH was also the only site where it was assumed that the energy budget could be closed by the specific heat flux. The site with the least closure was SL-EG and if the uncertainty of 24% was transferred to estimate H at MH then this would not be sufficient to alter the result that B is siginificantly higher at MH than all other sites.

3.1 Statistical analysis of ΔR_n and $\Delta\lambda E$

Statistically significant positive linear relationships between ΔR_n and $\Delta\lambda E$ were found for all sites (Table 5, Figure 3). Note that Figure 3 gives simple linear plots and does not adjust for seasonal effects as allowed for in Equation (xx). No site showed a significant sine term ($k = 0$ – Equation (xx)), but five sites did demonstrate a seasonal cycle marked by a significant cosine term ($j \neq 0$ – Equation (xx)). Thus, there is one seasonal cycle for those sites. That cycle peaks in June and has its minimum in December. The peak in June means that more of a change in R_n (a larger ΔR_n) is transferred to $\Delta\lambda E$. So for SLEG, the site with the strongest significant seasonal cycle, whilst annual average of ϕ was 0.42, in June it increased to 0.66 and was as low as 0.18 in December. Such a seasonal cycle follows day length but also is closely related to the annual cycles in a range of biophysical properties such as soil temperature or plant senescence. On the daily time step data used here, longer days mean that some sites convert more of a change in R_n in to a change in λE. The seasonal day length is a component included in the prediction of potential evaporation (eg. Thornthwaite equation - Thornthwaite, 1948).

For three sites there was a significant role for the previous days change in net radiation

(ΔR_{n-1}) on $\Delta\lambda E$ ($\theta \neq 0$ – Equation (xviii). In all three cases ΔR_{n-1} had a negative impact on $\Delta\lambda E$ (Table 5). In this way the significant autoregressive component in Equation (xx) could be seen as variation in supply of energy from another heat sink and could be analogous to the soil heat flux (G). It should be noted that a significant autoregressive component was only observed for East Anglian fen sites (EFLN, EFEG and EFDA).

The average ΔR_{n-1} that was transferred to $\Delta\lambda E$ (ϕ; Equation (xx)) for each study site varied from 0.27 to 0.64 (27 to 64% - Figure 4). That is, some sites transferred the majority of change in energy input to latent heat while others transferred the majority to sensible heat. Sites fell in to three statistically different groups based on ϕ (at 95% probability of greater than zero; post hoc analysis, via a Tukey test). In the higher group ϕ averaged between 0.55 and 0.64 and represents exclusively East Anglian Fen sites. The next highest, but still significantly different group, is the Somerset Level site (SLEG). ϕ is lowest for sites MH, AFLN and AFHN. The site judged, *a priori*, to be the most intact site (MH - Moor House, North Pennines) was the site with the lowest annual average ϕ.

The assumption about the nature of incompleteness, or imbalance, within the energy budget, i.e. that H is adjusted to complete the energy budget as was necessary for the MH site, would have no impact on this calculation of ϕ. The impact of allowing the value of λ to decrease with increasing air temperature (Henderson-Sellers, 1984) acted to reduce the value of ϕ by 1.5% as large positive values of ΔR_n were generally at the higher air temperatures when λ was lower. Allowing for the variation in λ did not change the significance of the relationships between ΔR_n and $\Delta\lambda E$.

3.2 Entropy budgets

The entropy flux was estimated on 1142 days across six of the seven sites (Figure 5 – note the sign convention that negative is a production of entropy from the ecosystem). Both site and month factors were significant, although the proportion of overall variance explained by the ANOVA was only 22%. Site factor showed that four sites were not significantly different from each other (MH, SLEG, AFHN and AFLN) while sites EFEG and EFHN were significantly different both from this group of four and each other. The group of four sites had a lower entropy flux than EFEG and EFHN. This pattern corresponds to that hypothesised from the observations of ϕ. EFEG and EFHN produce more entropy and show a greater responsiveness to changes in incident net radiation (i.e. greater values of ϕ – Figure 4) suggesting they were indeed "far from equilibrium". The MH site had a significantly higher value of B than any other site, but this relatively large value of B does not give a distinct and significantly different entropy budget (Figure 2). Furthermore, sites with the lowest responsiveness (ϕ) are also those which have the lowest $\frac{dS}{dt}$. However, it should be noted that EFEG has only 5 observations of entropy flux.

There is a significant linear relationship between mean ϕ and mean $\frac{dS}{dt}$ for each site (Figure 6):

$$\frac{ds}{dt} = -7.1\phi \quad n = 6, r^2 = 0.72 \qquad \text{(xxi)}$$

(2.2)

The term in the bracket beneath Equation (xxi) is the standard error in the coefficient. Note there is no significant constant term in this equation. Note in the sign convention of the system an increase in entropy would be a loss from the ecosystem and so it would be expected that the budget would be negative, i.e. in Equation (xxi) $\frac{dS}{dt} < 0$. Given that by definition $0 \leq \phi \leq 1$ then $\frac{dS}{dt}$ cannot be greater than 0 (given the sign convention of this system) as it is consistent with the second law of thermodynamics. Conversely, given the allowable range of ϕ, Equation

(xxi) predicts a maximum value of $\frac{dS}{dt}$ which has no physical meaning.

The above calculation was based on the energy balance as it presented. For the site with the most unbalanced energy balance (SLEG – Table 4) the energy budget was balanced using the same assumption as for MH (i.e. energy budget closed by changing H) and the entropy budget recalculated (SLEGadj – Figure 5). The uncertainty in the energy budget made a approximately 20% difference, which transferred to the entropy budget, but a large percentage change in a small number is still a small number and there was no statistical difference in entropy budgets by including SLEGadj. Therefore, this approach and result is not sensitive to assumptions of the energy balance. Inclusion of the variation in the value of emissivity for different surfaces (Wang et al., 2020) for the EFDA site made only a difference in the sixth significant figure of the value of $\frac{dS}{dt}$ and so this source of variation was not considered further.

4. Discussion

This study shows that peatlands can be significantly differentiated by their response to changes in net radiation and that, at least relative to other peatlands, some peatlands minimise entropy production. The tests applied are not sufficient to test whether peatlands are "near equilibrium" or "far from equilibrium" since the value of ϕ that represents either state is not known, nor was the value of ϕ such that any change in R_n is transferred exclusively to a change in either sensible heat or latent heat (i.e. ϕ was never found to be equal to either 0 or 1). However, we can show that peatlands significantly differ in their value of ϕ, with some responding to changes in energy input by shifting the majority of that energy into latent heat flux while others shift the majority to sensible heat. Therefore, we show that some peatlands respond by increasing entropy flux relative to other sites. This contrast between peatlands as to how they respond to changes in incident energy is that expected if ecosystems were in different states with respect to their thermodynamic behaviour. The primary measure used (relationship between ΔR_n and $\Delta\lambda E$) may reflect different processes with distinct thermodynamic consequences and interpretations. A positive value of ΔR_n could be due to a number of different factors, as can be seen from Equation (ii), e.g., increased Q_S^{in} or Q_L^{in} or decreased Q_L^{out}. Similarly, a negative value of ΔR_n could result from the converse changes in the components of R_n (eg. decreased Q_S^{in}). From Equations (ii) and (iv) it can be seen that the same magnitude of change in Q_S^{in}, Q_L^{in} or Q_L^{out} are very different in terms of J_x (entropy flux due to x – Equation (iv)) because the temperature at which each of these energy fluxes is occurring is quite different. Therefore, it is difficult to give a direct or linear relationship between ΔR_n, $\Delta\lambda E$ and $\frac{dS}{dt}$.

The test proposed by this study did not include or rely on a contrast in behaviour between sites within the same type of ecosystem. Therefore, a common behaviour for peatlands is difficult to describe. But peatlands show a range of behaviours. This difference raises the question, what is the physical basis or explanation of the observed differences? Differences cannot be due to seasonality or temporal changes as the data sets were gathered across complete years and for different years of data, and indeed, Equation (xx) considered seasonality as a separate control. Differences between sites could be due to a north-west to south-east split with the higher values of φ to the south-east and lower values to the north-west. This north-west to south-east contrast could be due to climatic differences as this contrast represents both a rainfall and a temperature gradient across the UK – average annual rainfall for EFLN – 553 mm compared to 2100 mm at MH. Contrast could be between peatland types, with the lowest values for the most intact and upland peat (MH) and the highest values for former fen peats (EFLN). Highly altered fenland peatlands might be expected to have lower average water table depths than semi-natural and intact sites. Relatively high water tables might be expected to increase water available to supply evaporation at its potential rate. Indeed, this was observed at MH (Worrall et al., 2015). If water was available then it might be expected that changes in input energy could be readily transferred to a change in latent heat flux: but the reverse might appear to be the case where the drier East Anglian sites (EFEG, EFHN and EFDA) have higher values of φ (Figure 4). However, it should be noted that ϕ is a relative and not an absolute change in energy fluxes. There are a number of other differences that might be expected for highly disturbed peatlands that have a higher magnitude entropy flux. The highly disturbed sites in this study are less likely to have continuous vegetation cover that is continuous in both time and space, i.e. bare soil is more likely to exist and vegetation cover may be seasonal. For sites such as MH the vegetation cover is well developed with mature *Calluna vulgaris* and an understorey of *Sphagnum spp*. A continuous vegetation layer may buffer against changes in net radiation (ΔR_n). The presence of *Sphagnum spp.* at MH may also be a source of the difference between the study sites. *Sphagnum spp.*, probably the most important peat-forming plant genus, is non-vascular and as such does not so much transpire as other plants do but instead transmit water by capillary action and so creates a layer that may act to limit evaporation (Waddington et al., 2015). Furthermore, Equation (xx) was formulated to give a single value of ϕ and any possibility of seasonal differences in ϕ was removed. If vegetation cover was seasonal then ϕ might be as well. In the fits of Equation (xx) those sites with the significantly higher ϕ were also the only sites where there was a significant value of θ (Table 5) and all other sites did not have significant values of θ. This study has interpreted θ as a role for soil heat flux and those sites with either a greater proportion of bare soil across the site and across the year might have greater soil heating especially given the low value of albedo for bare peat soil compared to vegetated peat. The aerodynamic resistance of a site will control the latent and sensible heat fluxes and this could be controlled by vegetation height (Lhomme et al., 1988; Allen etal., 1998). However, Kellner (2001) and Van de Greind and Owe (1994) have shown that for vegetated peatlands the aerodynamic resistance is dominantly controlled by the vapour pressure deficit and not the water table nor vegetation properties. Conversely, Peichl et al.

(2013) did confirm that, over a boreal mire, the aerodynamic resistance was controlled by vapour pressure deficit, but that a drop in the water table from the surface to 25 cm depth did lead to a threefold change in aerodynamic resistance. Therefore, the height of vegetation and vapour pressure deficit across sites could lead to changing proportions of energy fluxes and their responsiveness. Ultimately, there are just seven sites and so proving the cause of the contrast can be no more than descriptive or speculative.

To further test the thermodynamic state of an ecosystem the entropy budget of these sites was calculated. Indeed, sites do significantly differ in the amount of entropy they produce and those sites with the largest values of ϕ do produce the most entropy.

Addiscott (2010) suggested that plant soil systems are "near equilibrium" because plants act to limit transpiration. This necessary link between the ordering processes of primary production compared to the disordering and dissipative process of transpiration has long been recognised in the transpiration efficiency of plants, i.e. how much primary production is achieved for how much water is transpired (Loomis and Connor, 1992). Peatland ecosystems used in this study have two further complexities compared to other plant ecosystems. Firstly, peatlands are often dominated by sphagnum mosses which are non-vascular platns and so do not transpire in the manner of vascular plants but rather work through capillary action. Secondly, soils in a peat environment 'grow' as they accumulate organic matter. Mineral soils may turn over the organic matter derived from primary productivity but the amount of organic matter is at steady-state with respect to constant external drivers (Bell et al., 2011). However, a peat soil, with constant external drivers can go on accumulating and thus acts to accumulate rather than return to the atmosphere the products of primary productivity – this would be a decrease in entropy relative to most ecosystems that return all products of primary production, for example release of CO_2 to the atmosphere. Therefore, to not breach the second law of thermodynamics there must be additional dissipative, i.e. entropy producing structures in peat ecosystems that more than balance the organic matter accumulation. As for plant systems, the most efficient way to counter-balance the process of organic matter accumulation in a growing peat soil is to evaporate or transpire more water. Therefore, we would expect growing peat soils to be necessarily wetter than mineral soils simply because of the 2nd law of thermodynamics. Independent evidence for intact peatland being "near equilibrium" comes from Kettridge et al. (2016) who showed that a peat develops to maximise water use efficiency. Water use efficiency would equate to a peat that, in response to change, would minimise water losses just as demonstrated here for sites where the value of φ is low. Indeed, the site which transforms only 27% of change in incoming energy to evapotranspiration is the most intact of the study sites, and has been so for many decades. From this study we cannot identify what would cause a peatland to transition between the states of "near equilibrium" or "far from equilibrium" but we can speculate that restoration of peatland vegetation and wet conditions may lead to sites that are "near equilibrium". It should be noted that the only other field-based entropy budget (Holdaway et al., 2010) found the opposite for Amazon rainforest, where the intact ecosystem when compared to a damaged ecosystem maximised entropy production.

5. CONCLUSIONS

This study proposed that peatlands could be considered "near equilibrium" and not the "far from equilibrium" systems that they have been proposed to be. Furthemore, this study showed that these two states could be distinguished by how sites partitioned changes in net radiation and their rates of entropy production. The study showed that peatland sites did significantly differ in their response to changes in net radiation with one study site transferring 64% of a change in net radiation to latent heat flux, while another site transferred only 27% of change in net radiation to latent heat. Those sites transferring the most energy to latent heat flux are those sites producing the most entropy. This study concludes that peatlands can be distinguished between sites "far from equilibrium" where evaporative losses are maximised and those "near equilibrium" where evaporative losses are minimised.

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DATA AVAILABILITY STATEMENT

Data available within the supporting information.

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Figure 1. Location map of the seven sites used in this study. Note that the study included three sites in the East Anglian Fens and two on the Anglian Fens.

Figure 2. Comparison of Bowen ratios (B) between study sites. The lines represent range and the dot marks the median value although for comparative purposes the entire range of B may not be shown for every site.

Figure 3. The comparison of ΔR_n and $\Delta\lambda E$ for all study sites. As part of this study a significant straight line is expected, with or without seasonal adjustment (Equation (xix)) for this graph for each study site and the gradient of this line is measure of the responsiveness and entropy shedding of the site.

Figure 4. The least squares mean and 95% confidence interval of ϕ ($\Delta\lambda E/\Delta R_n$) for each study site.

Figure 5. The least squares mean and 95% confidence interval of $\frac{dS}{dt}$, the entropy flux, for each study site. Note that by sign convention of this study the greatest production of entropy will be the largest negative value.

Figure 6. Comparison of the mean ϕ and mean $\frac{dS}{dt}$ for each of the study sites for which $\frac{dS}{dt}$ could be estimated. Error bars are given as the mean percentage 95th percentile range of the values.

Table 1. Details of sites included in this study.

Region	Site	Site type	Code
North Pennines	Moor House	Upland blanket bog	MH
East Anglia	Wicken Fen	Low nutrient semi-natural	EF-LN
	Bakers fen	Extensive grassland	EF-EG
	Rosedene Fm	Arable on deep peat	EF-DA
Somerset Levels	Tadham Moor	Extensive grassland	SL-EG
Anglesey Fen	Cors Erddreiniog	Low nutrient semi-natural	AF-LN
	Cors Erddreiniog	High nutrient semi-natural	AF-HN

Table 2. The type of equipment used at each site, where IRGA = infra-red gas analyser; RH = relative humidity; and other symbols are as defined in Equation (i).

Code	Measurement ht (m)	IRGA	R_n	G	RH
MH	1.3				
EFLN	3.9	LI7500A	CNR1	HFP01	HMP45
EFEG	2.4	LI7500A	CNR1	HFP01-SC	HMP45
EFDA	1.6	LI7500	CNR4	HFP01-SC	HMP45
SLEG	2.8	LI7500	CNR1	HFP01	HMP45
AFLN	2.5	LI7500	NR-LITE	HFP01	HMP45
AFHN	3.4	LI7500	NR-LITE	HFP01	HMP45

Table 3. Details of the records considered within the study. The sample size (n) is given as the sample size for $\Delta\lambda E$ and ΔR_n in Equation (xviii).

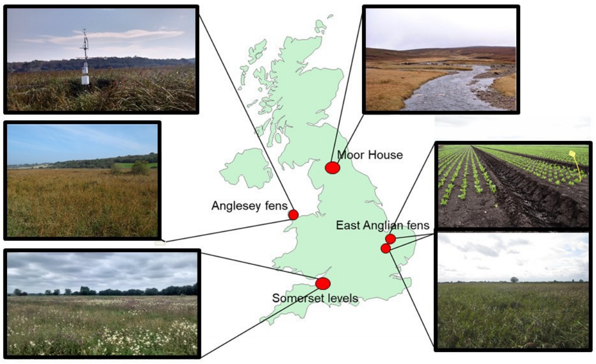
Site	Code	Period of record	n
Moor House	MH	2004 - 2006	1012
Wicken Fen	EFLN	2015	176
Bakers fen	EFEG	2013 - 2015	743
Rosedene Fm	EFDA	2012 – 2015	1027
Tadham Moor	SLEG	2013 - 2015	851
Cors Erddreiniog	AFLN	2014 - 2016	376
Cors Erddreiniog	AFHN	2014 - 2015	249

Table 4. Median values of the daily average energy flux components and the Bowen ratio for the days of data that contribute to calculation of $\Delta\lambda E$ and ΔR_n in Equation (xviii). The closure of the energy is expressed as a percentage of the R_n.

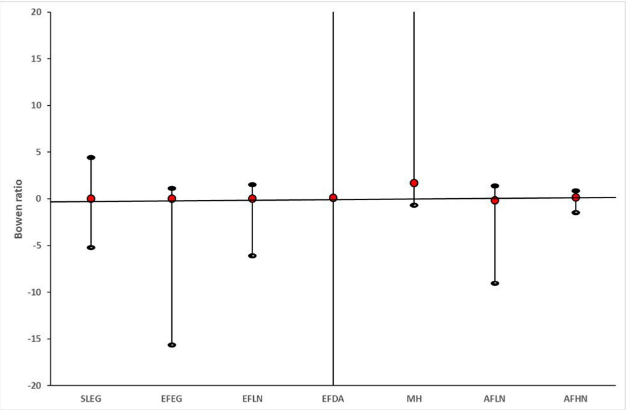
Site		R_n (W/m^2)	H (W/m^2)	G (W/m^2)	λE (W/m^2)	B	Closure (%)
Moor House	MH	28.2	17.5	-0.05	9.2	1.7	0
Wicken Fen	EFLN	-32.7	-28.7	-7.3	9.9	0.02	16
Bakers Fen	EFEG	-26.7	-15.6	0.4	6.4	0.12	16
Rosedene Fm	EFDA	60.9	6.7	-1.6	43.9	0.09	5
Tadham Moor	SLEG	43.3	10.5	-5.6	77.9	0.00	24
Cors Erddreiniog	AFLN	34.1	29.9	-13.9	11.3	0.16	4
Cors Erddreiniog	AFHN	45.9	6.8	-0.7	42.1	0.15	5

Table 5. Details of the records considered within the study

Code	ϕ	k	j	θ	C	R^2
MH	0.27	0	0	0	0	0.74
EFLN	0.64	0	0	0.38	351	0.34
EFEG	0.55	0	0.51	0.08	0	0.77
EFDA	0.55	0	0.23	0.03	0	0.55
SLEG	0.42	0	0.56	0	0	0.80
AFLN	0.30	0	0.24	0	0	0.60
AFHN	0.27	0	0.05	0	0	0.55



HYP_14431_entropybudgetfig1300.jpg



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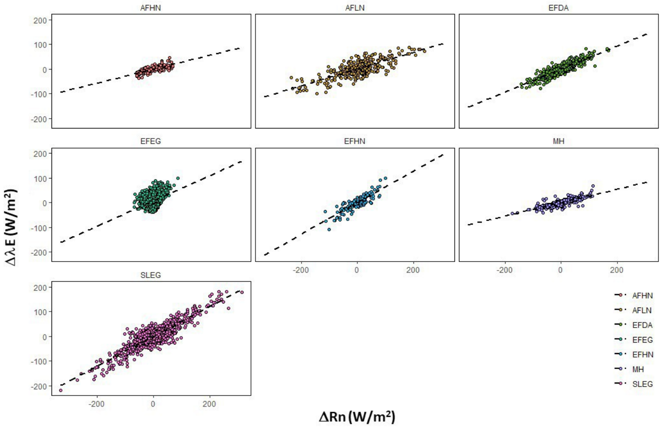

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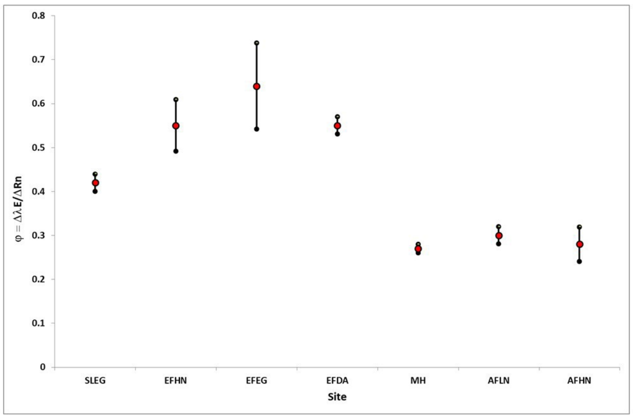
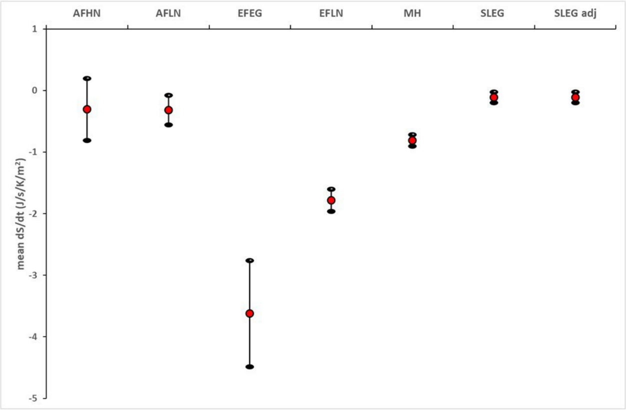
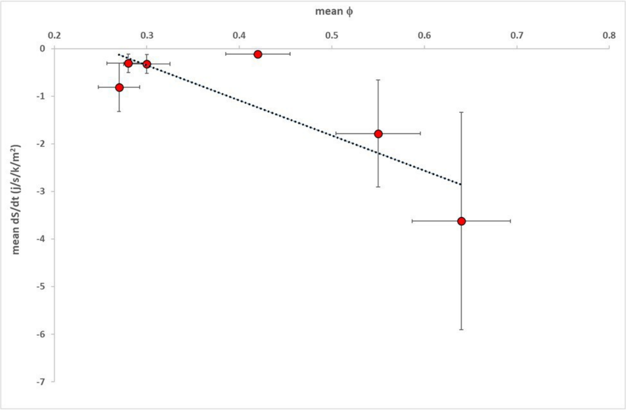


HYP_14431_entropybudgetfig4300.jpg



HYP_14431_entropybudgetfig5300.jpg



HYP_14431_entropybudgetfig6300.jpg