Controls on Carbon Cycling in Upland Blanket Peat Soils

DIXON, SIMON,DAVID

DIXON, SIMON,DAVID (2012) *Controls on Carbon Cycling in Upland Blanket Peat Soils*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/3641/

“When one tugs at a single thing in Nature, he finds it attached to the rest of the world.”

- John Muir (1838 - 1914)

Controls on Carbon Cycling in Upland Blanket Peat Soils

Simon David Dixon

Department of Earth Sciences
Durham University

One Volume

This thesis is submitted in accordance with the regulations for the degree of Doctor of Philosophy in the University of Durham, Department of Earth Sciences, 2012

Simon David Dixon

Controls on Carbon Cycling in Upland Blanket Peat Soils

Abstract

Peatlands are a globally important, terrestrial store of carbon and the UK is recognised as an internationally significant holder of peatlands. Of all the kinds of peatland found in the UK, blanket bogs are dominant, representing 87% of the UK's peatland area. The UK's peatlands, in contrast to many other areas of boreal/temperate peat, are relatively accessible and as such have been subject to land-management pressures for many thousands of years. These management pressures have led to the deterioration of many peatlands in the UK, with only 1% of England's peatlands being considered 'pristine' in a Natural England report (Natural England, 2010).

Climate change and increasing land-use pressures are predicted to affect all UK peatlands in coming years. As such, studies of the drivers of carbon cycling on UK peatlands are being undertaken in order to help in the construction of models to predict the dynamics of peatland carbon balance. These models will subsequently enable land-managers and policy makers to take informed decisions regarding peatland management and carbon storage. One such model of peatland carbon balance is the Durham Carbon Model, which uses a mass balance between fluxes of carbon in and out of a peatland in order to estimate its net carbon budget. While the Durham Carbon Model is able to deal with the effects of some aspects of land-management on peatland carbon balance, there remain a number of important drivers as yet unaccounted for in the model.

As such, the remit of this thesis was to conduct in-situ, experiments in order to provide additional data on peatland carbon cycling with a view to incorporating these drivers into the model. Specifically, this research examines three areas as yet unaccounted for in the Durham Carbon Model: altitude, vegetation and diurnal processes. These factors are considered relative to CO_2 flux and, in some cases, soil pore water dissolved organic carbon concentration. Additional experiments were also performed to determine whether empirical models of CO_2 flux can be physically interpretable.

Results obtained for this thesis suggest that the most important factor in predicting CO_2 flux on blanket peat soils is vegetation type and vegetation mediated processes, i.e. photosynthetic controls on respiration. Moreover, the relationship between respiration and photosynthesis was found across a range of other factors and temporal scales. In addition to vegetation, altitude was found to significantly affect CO_2 for some vegetation types. Therefore, both of these factors are to be incorporated into the Durham Carbon Model. Experiments suggested that empirical models of CO_2 flux can be physically interpretable. The results of the diurnal experiment gave evidence to support the hypothesis that some component of the relationship between photosynthesis and respiration is temporally lagged, perhaps by 3 hours. However, the results were not unequivocal and thus further work is needed to fully examine some of the results presented herein.

Declaration and Copyright

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any university. Where relevant, material from the work of others has been acknowledged.

Signed:

Date:

Acknowledgements

The biggest thank-you has to go to my first supervisor, Fred Worrall. None of the work in this thesis would have been possible without your guidance, patience and time, thank you!

Being a member of the Carbon, Waste and Water research group has been hugely beneficial for me as a person and a scientist. I am particularly grateful to my (unofficial) third supervisor, James Rowson. Thank you for helping me to find my feet and giving me the confidence to get to this point. Big thank-yous also to Chris Ottley, Darren Grockë, Neil Gray, Madeleine Bell, Kate Turner, Gareth Clay, Ian Boothroyd, Ben Franklin and Rachel Bullock for assistance in the field and laboratories. Moreover, thank-yous to Suzie Qassim, Cat Moody, Emma Christie, Helen Foster and Iona Macintosh for all of the Environmental Bay banter that has kept me (relatively) sane throughout.

The next group of thank-yous go to all the people in the Department of Earth Sciences that made these past few years so interesting. Whether it’s my; surfing buddies, Viv Cumming, Alan Rooney, Isobel Yeo and Dave Ashby; my ladies-what-lunch; Amy Clarke, Niamh Monaghan and Sarah Porter; my Great North Run comrades; Harriet Ridley, Ben Hedley and Claire McLeod; my ‘isn’t-life-rubbish-so-lets-just-have-a-baked-potato’ friend Kathy Mather or my housemates; Hannah Walter, Madeleine Bell and Rich Walker, it’s been a lot of fun, so thank you, one and all.

Thank you to my all my friends and family. To Mum and Dad. To Claire and Charlie. To Dan and Melissa. To Izzy and Lizzie and Thomas. To Ceri. You’ve all helped me reach this point. To Ben Franklin, thank-you for making me laugh so much. And finally, thank-you, to you, for reading this thesis.

Table of Contents

List of Figures

List of Tables

1 – Introduction

1.1– Blanket Peatlands: An Overview

An informative place to begin any piece of academic endeavour is to define what it is that is being investigated. In essence, a peatland is defined as an ecosystem where the accumulation of organic matter is greater than the rate of decay, i.e. the value of A in equation 1.1.1 is greater than zero. This process, over time, leads to the formation of a soil, peat, which is predominantly organic carbon. In the UK a peat soil is defined (Avery, 1980, pp 38) as having: "more than 40 cm of organic (O horizon) material within the upper 80 cm, excluding fresh litter (L) and living moss". Where the peat soil rests directly on bedrock or drift the organic (O) horizon must be in excess of 30 cm deep and there must be no overlying non-humose mineral horizon that has a colour value in excess of four extending below 30 cm (Avery, 1980, pp 38). For a peat soil to accumulate, the productivity and thus the biomass flux into the soil from the plants present must be greater than that of the soil and litter heterotrophs. In northern peatlands it has been estimated that the average rate of carbon accumulation is 29 g C m^{-2} y^{-1} representing some 10% of average net primary production (Gorham, 1991). Peatland dry matter accumulation has been modelled and is given below (equation 1.1.1; Clymo, 1984):

$$\mathrm{A} = \mathrm{L}e^{-\mathrm{kt}}$$ *Equation 1.1.1*

where; A is the rate of dry mass peat accumulation, L is the rate of dry matter input (i.e. litter fall, rhizodeposition etc.), k is the dry matter decay coefficient as a proportion of time (i.e. in units of t^{-1}) and t is time.

The activity of soil and litter heterotrophs, i.e. the decay rate of organic matter, in peatlands is, in the first instance, a function of soil moisture conditions (Charman, 2002, pp 73). Peatlands, including blanket peatlands, tend to begin formation in topographic hollows where standing water tables are near the surface with little annual variability (Moore and Bellamy, 1974, pp 9-10). This ‘primary’ peat with its high standing water table tends to be oxygen poor and acidic, which serves to reduce the activity of heterotrophs causing the rate of decay to fall below that of the rate of deposition of organic matter (Charman, 2002, Chapter 5). The combination of waterlogging and acidity is also a feature of the secondary and tertiary peats that grow out from the initial primary deposits (Moore and Bellamy, 1974, Chapters 1-4). So, peatlands accumulate carbon not because they are highly productive environments, but rather that they have suppressed rates of organic matter decomposition.

Blanket peatlands are distinguished from other peatlands by the fact that they are not confined to topographic troughs but instead are ‘blanketed’ across the landscape and thus span a range of altitudinal (i.e. vertical distance from sea level) and topographic gradients. It is typical to find blanket peat deposits occurring on slopes between 0 – 10°. Infrequently blanket peats are found at slope angles of up to 18° and very rarely they have been reported on slopes approaching 25° (Moore and Bellamy, 1974, pp 29). Two primary factors have to coincide for blanket peat formation to become favourable; firstly, the climate needs to be ‘hyper-oceanic’ (Charman, 2002, pp 8) and the underlying substrate needs to be impermeable (e.g. Doyle, 1997; Martini and Glooschenko, 1985). These features combined allow the peatland to maintain near-surface water tables, despite lying on topographic gradients of up to 20° (e.g. Charman, 2002; Doyle, 1997). When discussing the formation of the ‘Flow Country’ of northwest Scotland Lindsay et al. (1988) described the annual climatic conditions (i.e. hyper-oceanic) needed to sustain actively accumulating blanket peatlands as; (i) a minimum of 1000 mm rainfall, (ii) a minimum of 160 wet days, (iii) a mean temperature of < 15°C for the warmest month and (iv) only ‘minor’ seasonal temperature fluctuations.

Given the impermeable strata found beneath blanket peatlands, they tend to be hydrologically isolated from groundwater within the underlying geology. Peatlands can be categorised by their hydrology, with ‘primary’ peat systems occurring inside basins or depressions. ‘Secondary’ peat systems remain hydrologically connected to the primary system they grew out from but can be found outside the limits of the basin or depression confining the primary peat. ‘Tertiary’ peat systems do not have to be hydrologically connected to primary systems and form a perched water table by retaining inputs directly from precipitation. Thus blanket peatlands are defined as tertiary peat deposits as they contain perched water tables and do not always connect to other primary or secondary peat systems (Moore and Bellamy, 1974, pp 10). The effect of this hydrological isolation from mineral-rich groundwater means that they receive almost all of their nutrients from precipitation and as such they are classified as ombrotrophic (e.g. Charman, 2002, 6-10). Receiving nutrient inputs only from precipitation leads to them being relatively nutrient poor with respect to groundwater-fed peatlands (Charman, 2002, pp 8). The peatland categorisation given to a nutrient poor peatland is a ‘bog’, whereas, a ‘fen’ is the nutrient-rich equivalent (Charman, 2002, pp 4).

1.2 – Peatlands and the Global Carbon Cycle

Estimating the total amount of carbon stored in peat soils at present from a regional to global scale has received much attention in the literature. Immirzi et al. (1992) estimated that 200-500 Gt C were stored in peatlands globally; this figure was then refined to 357 Gt C by Eswaran et al. (1993). More recently a review of national databases from peat-holding nations by Joosten (2009) suggested that around 446 Gt C were stored in peatlands globally. These estimates are, however, subject to very large errors (often not formally stated) as there are numerous deficiencies in the data used to calculate them. The most important factors affecting accurate measurement of peatland carbon stocks are uncertainties in the quantification of the depth, aerial extent and carbon density of peat.

The uncertainties in measurement of these factors tend to suggest that the current values are underestimates.

Net ecosystem production in peatland ecosystems is similarly difficult to estimate accurately but is thought to be around 100-200 Mt C annually (e.g. Charman, 2002, pp 92-94). This is relatively low when compared with the average annual net fluxes into global forests estimated to be 900 Mt C annually (Dixon et al., 1994). However, despite the low productivity of peatland ecosystems, low degradation rates within the soil mean that carbon stored there can have a residence time of thousands of years (e.g. Doyle 1997; Gorham et al., 2007; Tallis, 1998a). It is the longevity and density of the carbon store in peatlands that gives them their importance in the global carbon cycle.

The expansion of peatlands, tropical (e.g. Blunier et al., 1995) and northern (e.g. MacDonald et al., 2006), since the last deglaciation, has been associated with rapid increases in atmospheric methane concentrations, especially during the ‘explosion’ in peatland initiation around 12-8 ka before present (e.g. Gorham et al., 2007). However, these correlations are not without controversy, with Reyes and Cooke (2011) suggesting that peatland initiation lagged atmospheric methane increases, implying that peatland initiation might not have been the primary driver. Nonetheless, peatlands are thought to have played an important role in regulating atmospheric C levels during the early Holocene (e.g. Yu, 2011) and could have continued to do so if not for anthropogenic modifications of the land surface, in the first instance forest clearing and early progress towards agriculture and at present with industrialisation, overprinting these effects (e.g. Kaplan et al., 2011). As such, peatlands have the potential to be both sinks and sources of C with respect to the atmosphere and understanding the processes that underpin carbon cycling within these systems is important in order to predict their future behaviour in the carbon cycle.

1.3 – The Peatland Resources of the United Kingdom

The UK is an internationally significant holder of peatlands. Montanarella et al. (2006) estimate that the UK has 14.8% of the land area of Western Europe covered by soils with greater than 25% organic carbon in their upper most 30 cm. This contribution puts the UK in third place in Western Europe in terms of area of soils with high organic carbon concentrations, behind Finland and Sweden. Of these peatlands, blanket bogs are by far the most extensive in the UK. Lindsay (1995) estimated that of the 1,645,970 ha of peatlands in the UK 1,429,106 ha (i.e. 87%) are blanket bogs. Peatlands are latitudinally constrained, with their occurrence increasing with increasing latitude, mainly due to changing water balance (e.g. O'Connell, 1990; Evans and Warburton, 2007, pp 7). Indeed, of the total peatland area in the UK, 66% is found in Scotland (Lindsay, 1995) and the majority of peatlands in England and Wales are found in the uplands (Bradley et al., 2005), commonly at greater than 500 m above sea level (Evans and Warburton, 2007, pp 7).

The peatlands of the UK have been estimated to hold 1.75 Gt C (15th largest national stock globally), which is thought to be an underestimate due to a lack of data pertaining to the depths of Scottish blanket peatlands (Joosten, 2009). Despite this relatively large stock, there is evidence that the peatlands of the UK are becoming sources of carbon to the environment, with Janssens et al., (2005) inferring that the UK is losing 27 g C m^{-2} peatland y^{-1}. Janssens et al., (2005) attribute this loss mainly to the effects of anthropogenic interference, particularly peatland drainage.

1.3.1 – The State of English Blanket Peatlands

Much work has been carried out to assess the state of peatlands in England. Currently the most comprehensive review in this area is a government funded report (Natural England, 2010) looking into England's peatlands' role as carbon stores and centres of greenhouse gas flux. Natural England (2010) report that of the 3,553 km^2 of blanket bogs in England only 35 km^2 (i.e. 1 %) are in an 'undamaged' state. The following degradational conditions were mapped by Natural England (2010) as affecting English blanket bogs: management for semi-natural vegetation not suited to carbon sequestration (51% of blanket peat area), overgrazing (9%), rotational moorland burning (30%), artificial drainage (21%), drainage by gully incision (14%), afforestation (7%), degradation that has left only bare peat (1%). These values are not mutually exclusive, i.e. an individual peatland area may be affected by one or more of these factors and as such the percentages are not additive.

Combining these mapped areas with data regarding the greenhouse gas effects of these treatments suggested that English blanket bogs emit 0.89 Mt CO_2-equivalents annually with rotational burning being the largest emitter at 0.26 Mt CO_2-e y^{-1}. These estimates, in the Natural England (2010) report, are given, however, without errors and have not been peer reviewed, thus the results should be viewed with caution. Nevertheless, the report reflects the conclusions of published peer-reviewed studies (e.g. Bellamy et al., 2005; Janssens et al., 2005) that concur in the assertion that blanket peatlands in England are generally a source, not sink, of carbon to the environment.

The Natural England (2010) report highlighted the issue of bare peat. This, quite simply, is peat where the surface layers of vegetation and litter have been removed. On blanket peatlands in England the drivers contributing to the creation of bare surfaces include: wind erosion (e.g. Warburton, 2003), wildfire (e.g. Rothwell et al., 2007), overgrazing (Rawes, 1983) and gully erosion (e.g. Bower, 1961; Evans and Warburton, 2005; Rothwell et al., 2007). Bare peat areas are particularly large sources of carbon from peatlands to the environment as they contain no vegetative layer to draw down CO_2. Moreover, without vegetation and seeking the path of least resistance, erosion of blanket peat will tend to localise in these areas (e.g. Evans and Lindsay, 2010b).

1.3.1.1 – Restoration of the Peak District Blanket Bogs

The part of the England with the largest amount of bare peat is the Peak District (Natural England, 2010). Initiation of peatland formation in the Southern Pennines (including the Peak District) spanned a 4,500 year period from 9,000 to 5,500 years BP and was controlled by climatic and anthropogenic drivers (Tallis, 1991). Erosion of Peak District blanket bogs began approximately 1,200-1,000 years ago when peat slides initiated the formation of dendritic gully drainage systems, controlled to some extent by pre-glacial geomorphology (Tallis, 1985). These systems continued to propagate, showing a rapid extension in gullying after 1770 (Tallis, 1965), with the extent of gullying being controlled by elevation, gradient (Bower, 1961), climate and anthropogenic effects (Tallis, 1985). In addition to gully incision, wildfire has been a major driver of the creation of bare peat in the Peak District (Bonn et al., 2008, pp 405-408). In a single wildfire event approximately 844 ha of peatland on Bleaklow Plateau (Peak District) was scorched leaving nothing but a bare, charred soil surface behind (McMorrow et al., 2006).

Palaeoecological studies of peatland stratigraphy (e.g. Tallis, 1985; Tallis 1991) in the Peak District have shown that carbon accumulation has been highly variable and natural revegetation following climate-induced erosional periods has been identified (Tallis, 1985). This natural revegetation, in gully systems, has also been observed in modern times (e.g. Evans et al., 2006; Crowe et al., 2008) and has been shown to reduce sediment loads (i.e. particulate organic carbon fluxes) leaving gullied catchments (Evans et al., 2006). Noting the success of natural revegetation in slowing down/reversing degradation of blanket peatlands in the past; land managers, conservationists and scientists have been working together to artificially revegetate large areas of bare/degraded blanket bog in the Peak District under the umbrella of the Moors for the Future partnership (MftFP).

Founded in 2003 the MftFP aims: "(i) to raise awareness of why the moors are valuable…, (ii) to restore and conserve important recreational and natural moorland resources…, (iii) to develop expertise on how to protect and manage the moors sustainably". Following these objectives the MftFP has embarked on a number of connected projects to restore areas of bare peat and gully erosion. One such project involved blocking water flow in gullies in order to re-establish water tables in the surrounding peatlands and reduce sediment loads leaving upland catchments. A desk study to optimise the locations of the gully blocks was carried out prior to installation of the blocks (Evans et al., 2005). Following on from this bare peat stabilisation (employing heather mulch and/or geojute netting), surface revegetation with grass seed sowing and *Sphagnum* spp. propagation was carried out.

These projects are still ongoing and results concerning their effectiveness are only just starting to be published. Allott et al. (2009) reported that revegetation alone appears to have raised water tables relative to areas of bare peat, however, there were too few sites used to make the results statistically significant. Worrall et al. (2011) reported that revegetation of bare peat in the Peak District has caused a decrease in carbon losses relative to bare peat controls. Moreover, one of the restored sites investigated appeared to have a more favourable carbon budget than the vegetated control sites. Preliminary *Sphagnum* spp. propagation results suggested that the *Sphagnum* spp. is taking to the bare peat, especially in wetter, more sheltered areas; however, it appears not to do well when the plants sown alongside approach 100% ground cover (Hinde et al., 2010). While these results are encouraging, they are only preliminary and more research is needed to properly demonstrate the effectiveness of the peatland restoration from a carbon perspective. An important tool in this endeavour is creating models of peatland carbon balance which can forecast accurately how effective these treatments will be and where these treatments are most likely to have the biggest effects.

1.4 – Carbon Budgets and Modelling of Peatlands

Estimating the net carbon budget, i.e. the total net ecosystem uptake or loss of carbon for a given area has become an important area of environmental science, particularly with respect to forecasting future changes in carbon stocks. A common method to estimate carbon balance on a national/international scale is to use temporal changes in national inventories of soil carbon (e.g. Bellamy et al., 2005), coupled with estimates of the effects of land-use/climatic/vegetational changes on the system (e.g. Janssens et al., 2005; Joosten, 2009; Armentano and Menges, 1986). This approach is limited primarily by the quality of the data (e.g. resolution, comprehensiveness etc.), flux estimates (e.g. comprehensiveness, suitability) and conceptual model(s) available. For example, Armentano and Menges (1986) estimated changes in temperate zone peatland carbon stocks, using a deterministic empirical model. However, the model had a number of assumptions that were verifiably false. They assumed, for instance, that only drained peatlands would export DOC, whereas DOC is lost from pristine peatlands (e.g. Worrall and Burt., 2005) as well as drained ones (e.g. Wilson et al., 2011), and DOC typically represents 10% of carbon released from peat (e.g. Holden, 2005b). The results and estimates of the Armentano and Menges (1986) study were used, in part, for Janssens et al. (2005) the UK carbon balance study. In addition to the errors introduced by Armentano and Menges (1986), Janssens et al. (2005) is limited by the fact that it considers only peatland drainage for arable or forestry, rather than peatland drainage for heathland, which is the most common reason for peatland drainage in the UK (Holden et al., 2007). As such, Janssens et al. (2005) could be underestimating carbon losses from peatland drainage, while their use of estimates from Armentano and Menges, (1986) means they may also be underestimating losses of carbon as DOC from pristine peatlands.

Another approach to estimating the carbon balance of peatlands is to use a process based model (e.g. ECOSSE, MILLENIA etc.) which uses historic or projected climatic and/or land use and/or peat depth data in order to predict the carbon balance of peatlands. These types of model predict the net carbon balance of a given ecosystem by attempting to simulate the biological, chemical and physical reactions and interactions taking place. These models' main limitation is that as they become more complex their input data requirements can become burdensome and expensive to obtain. Examples of two well known, peat centric, process-based net carbon balance models are given below.

The MILLENIA model (Heinemeyer et al., 2010) was constructed to improve on previous peat decomposition models (e.g. Clymo, 1984; Frolking et al., 2001), which did not take into account annual litter cohorts or actual evapotranspiration-driven net primary production. The Estimator of Carbon in Organic Soils – Sequestration and Emission (ECOSSE) model (e.g. Smith et al., 2007) is a process-based model which estimates the net decay of soil organic matter within a number of conceptual pools. Decomposition is described by first order kinetics and the rates of decay are modified to account for climatic, soil-chemical, land management and biological factors.

The predictions of these models of peatland carbon balance were compared by Clark et al. (2010) across four monitoring sites where large amounts of carbon flux data have been gathered. Clark et al, (2010) compared the two process-based models above, to the 'semi-empirical' Durham Carbon Model (DCM, e.g. Worrall et al., 2009a; 2009b) and nine separate bioclimatic envelope models. The results of this study showed that in terms of carbon budget magnitude MILLENNIA and ECOSSE were comparable. However, whilst predicting similar magnitude carbon balances, MILLENNIA and ECOSSE predicted different trends in UK peatland carbon budgets over the coming century where; MILLENNIA predicts a slight net increase in the size of the net C sink, whereas ECOSSE predicts a shift to a net source by the end of the century.

The differences between the modelled trends were ascribed by Clark et al., (2010) to the differing processes and process sensitivities considered within the models. In the case of MILLENNIA, the authors (Heinemeyer et al., 2010) considered the interaction between changing plant functional type, water table and net primary production, which suggested a vegetative shift that would lead to more decay-resistant litter, and thus increased carbon accumulation. The ECOSSE model did not consider functional group and, on the other hand, was more sensitive to temperature than water table and thus predicted a net source of C to the environment with the projected increase in temperature.

As well as inventory estimates and process-based modelling, the carbon balance of peatlands in the UK has been predicted using a third approach, the mass balance model. This approach is relatively simple in conception, with the carbon budget of a peatland simply being the difference between fluxes of carbon in to fluxes of carbon out of the peatland, and thus does not specifically consider pre-existing carbon stocks. These fluxes are either measured directly or estimated from existing published models and/or values. This approach has been applied on a number of temporal scales, with Cannell and Milne (1995) estimating the long term average net carbon CO_2 balance of forested peatlands over the life cycles of forest plantations and Anderson, (2002) determining the long-term carbon accumulation rate since initiation at three different peat bogs in North-west Scotland. On a different time scale, Billett et al. (2004) estimated the actual (i.e. present day) annual carbon balance of a lowland peat system in central Scotland, assuming a mass balance between net primary production and downstream fluvial losses.

Despite the popularity of the technique, Lindsay (2010) cautions that mass balance approaches to modelling have tended to be on a catchment by catchment basis. This, the author contends, means that the modelled peatlands are ‘fragmented’ into several, partial peatland systems, rather than being considered as a whole integrated system. The benefit of a whole system approach would be that it includes all spatial, geomorphological and environmental controls on the peatland system dynamics. To get around the supposed limitations imposed by individual catchment analyses, the author suggests that mass balance studies focus on entire peatlands (i.e. macrotopes) rather than just the peat lying within a given catchment. This argument may be somewhat unrealistic as the additional resources required to monitor carbon fluxes from an entire peatland system, given that many individual peatlands can cover hundreds of square kilometres. However, the logic underpinning the argument has merit. Essentially, Lindsay, (2010) is saying that in order to fully understand the dynamics of a peatland it is necessary to investigate a representative sample of the peatland's surface, sampling the range of conditions that affect carbon cycling that the peatland finds itself in (i.e. altitude, vegetation, slope, aspect, surface microtopography, land-use etc.). An example of a mass balance model that is attempting to sample the range of conditions that Pennine blanket peat bogs are subject to is the Durham Carbon Model (DCM). As work done in this thesis is to be incorporated into the DCM, a case study about this model is given in the next section.

1.4.1 – The Durham Carbon Model (DCM)

The Durham Carbon Model (DCM) is something of an evolving concept. First published in Worrall et al. (2003), it was initially intended to produce a reliable estimate of the net carbon budget for a British upland blanket peat covered catchment, Trout Beck in the Moor House National Nature Reserve in the North Pennines. The model considered the carbon balance of a peatland as a mass balance between input and export fluxes of carbon (equation 1.4.1.1); this equation is based on the schematic model of the peatland carbon budget given in Worrall et al. (2003) and remains in this format throughout all of the uses of the DCM regardless of area studied or scale. This mass balance took into account the following inputs: net primary production of CO_2, dissolved organic (DOC) and inorganic carbon (DIC) from rainfall and weathering of the underlying strata transporting dissolved (DIC) and inorganic carbon (PIC) into the soil. The output fluxes included CO_2 via ecosystem respiration, CH_4 emission from methanogenesis, DOC, POC and DIC as a fluvial flux from surface erosion, runoff and through-flow leaving the catchment. The data used to power the model were different for different fluxes, but included weekly water table depth (CH_4), weekly stream-water quality samples (DOC, DIC) and periodic storm-flow samples and event analysis (DOC, POC). The mass balance equation used by the DCM is given in equation 1.4.1.1. . On this occasion the DCM suggested that for the year 1999 the catchment was a net sink of 15.4 ± 11.9 g C m^{-2} y^{-1}.

$$\mathrm{C_{Total}} = \mathrm{C_{NEE}} + \mathrm{C_{Rain}} + \mathrm{C_{Weathering}} - \mathrm{C_{Methane}} - \mathrm{C_{Respiration}} - \mathrm{C_{DOC}} - \mathrm{C_{DIC}} - \mathrm{C_{POC}}$$

Equation 1.4.1.1

where: C_{Total} = the total C balance, C_{NEE} = the total amount of C gained or lost by net ecosystem exchange (NEE) of CO_2, C_{Rain} = the total amount of carbon gained from rainfall, $C_{Weathering}$ = the total amount of C gained from weathering of the underlying strata, C_{DOC} = the total amount of C lost as DOC, C_{DIC} = the total amount of carbon lost as dissolved CO_2 and C_{POC} = the total amount of C lost as POC.

The DCM was used again on the Trout Beck catchment in Worrall et al., (2007). This time all fluxes were modelled relative to two driving variables: temperature and rainfall. These variables, coupled with measured water table depths, were used to produce a water balance model for the catchment which predicts depth to water table, actual evaporation and runoff production within the catchment. The hydrological predictions are then linked back to the main carbon fluxes in order to estimate the total carbon balance for the year. The mass balance equation in Worrall et al. (2007) remains the same as Worrall et al. (2003), however, the methods used to determine the flux values differ. Carbon dioxide flux is estimated by predicting both gross primary productivity (P_g) and net ecosystem respiration (R_{eco}) with published models (R_{eco} via Lloyd and Taylor, 1994 and P_g via Leigh, 1975) and then taking the difference. Dissolved organic carbon, POC and DIC fluxes are calculated with updated methods. However, CH_4 and rain-based DOC and DIC inputs were estimated in the same way as Worrall et al. (2003). Arguably the most important change to the model in Worrall et al. (2007) is the addition of a methodology for predicting future changes in the carbon fluxes and thus the carbon budget of the catchment, employing the approach of Worrall and Burt (1998). Worrall et al. (2007) estimated that the catchment was a net source of carbon of between 11.2 to 20.9 g C m^{-2} y^{-1} this is in contrast to the net sink of an equivalent magnitude determined in Worrall et al. (2003). Worrall et al. (2007) further estimates that the catchment would become a larger magnitude net source of carbon over the decade 2003-2012. In addition, the catchment is likely to become a net source of carbon gases (CO_2 and CH_4) by 2034, if the trends found in the time series analysis hold steady.

The third use of the DCM on the Trout Beck catchment was by Worrall et al. (2009a). This paper used the same mass balance equation as Worrall et al. (2003; 2007) but its method for estimating flux values differed slightly from both. For example, CO_2 flux was directly measured in this study, and the results of these observations were used to create an empirical model of R_{eco} and were used to calibrate the model of P_g. In fact, in contrast to Worrall et al. (2003; 2007), Worrall et al. (2009a) directly measured all of the fluxes of C in the mass balance equation apart from methane. By doing this, it was found that the estimates of primary productivity were much higher, in the range -151.4 to -189.1 g C m^{-2} y^{-1}, compared to those in Worrall et al. (2007), which were in the range -123.3 to -134.3 g C m^{-2} y^{-1}. Moreover, ecosystem respiration, as predicted by the empirical model derived from the observed data, was in the range 49.1 – 58.2 g C m^{-2} y^{-1} in Worrall et al. (2009a) which is much lower than the range predicted in Worrall et al. (2007), 107.1 – 109.8 g C m^{-2} y^{-1}. These differences resulted in a big increase in the estimated total magnitude of net ecosystem exchange of CO_2. Thus, the overall carbon budget of the Trout Beck catchment modelled by Worrall et al. (2009a) varied between a net sink of -20 to -91 g C m^{-2} y^{-1} over the 13-year (1993-2005) study period. This sink is far in excess of anything predicted by the previous mass balance models on the catchment. As Worrall et al. (2009a) used observed data from the catchment being studied, it is likely that this model is more accurate than previous models based on non-locally calibrated models. This, therefore, demonstrates the importance of model calibration with 'real-world' data in order to produce realistic models of carbon balance.

Having refined the process of carbon budget modelling in the Trout Beck catchment, the DCM was next employed at a different scale, the blanket peat of the Peak District, in order to determine whether carbon offsetting could pay for upland restoration in the area (Worrall et al. 2009b). This study, however, is a slight step back when compared with Worrall et al. (2009a) as it reverts to using Lloyd and Taylor's (1994) approach to predicting ecosystem respiration, rather than the Trout Beck calibrated empirical model in Worrall et al. (2009a). However, Worrall et al. (2009b) did calibrate many of the modelled fluxes, including CO_2, against data from within the Peak District. In order to upscale the previously catchment scale DCM to a more regional scale, a cumulative approach was taken. The Peak District was "discretised" into 1 km^2 boxes and the DCM was applied at to each box that had a surface area of peat in excess of 10% of the total surface area of the box. The value for each box was the DCM estimate weighted by the proportion of peat within the box in question. These individual box budgets (including zero values from boxes without peat) were then summed in order to give the estimated value for the Peak District as a whole. Overall, the model found that the blanket peat bogs of the Peak District were a net sink of carbon of around -82 g C m^{-2} y^{-1}. This figure is similar to the estimate of Worrall et al. (2009a) from the Trout Beck catchment. Furthermore, the authors reported that, assuming that the DEFRA shadow carbon price range (£13-39 per tonne C) was enforced that over a 30-year period, 51% of the areas targeted for restoration would show a profit, by sequestering more carbon. Moreover, it is noted that this additional sequestration should carry on in perpetuity as pristine peat bogs are perpetual sinks of carbon. It is important to note that of the models considered thus far in this introduction, only the DCM is currently able to consider the effects of land-management on carbon balance.

Ultimately the DCM works at a catchment scale, with some of the gas flux models calibrated at the plot scale, with the assumption being made that they are sufficiently well replicated to be representative of the catchment as a whole. When moving between localities or when the data become available, it is routine to re-calibrate sub-models within the mass balance equation with direct measurements from the area of interest (i.e. Worrall et al. 2007; 2009a; 2009b). The model can be upscaled through a process of discretisation (i.e. splitting into 1 km^2 boxes) and summation over the land area in question, using the % of peatland cover in the discrete boxes as the weighting factor (Worrall et al., 2009b). On some occasions, where the data are available, new empirical models of CO_2 (Worrall et al., 2009a) and POC flux (Worrall et al., 2007) are created. Where direct measurements for calibration are not available, widely-applicable literature-derived models (i.e. Lloyd and Taylor, 1994) are used (Worrall et al., 2003). By applying the model to large, catchment scale and higher areas, the assumption is (inexplicitly) made that factors not considered within the model (i.e. changing vegetation, altitude etc.) will not affect the model output. However, spatial variation in many of the these factors, for instance in vegetation type due to management and/or soil hydro-bio-chemo-physical factors, can be expected to affect carbon cycling (i.e. Leppälä et al., 2008; Trinder et al., 2008; Ward et al, 2009). As such, the DCM in its current form is incomplete and further work is required to allow the DCM to account for potentially confounding spatially-varying factors.

1.5 – Motivation for Thesis

The case study above has shown how the DCM has evolved over time and how it has been put into practical use. While the model has, so far, yielded some important results, there is more work to be done in order to refine it further. As such, the remit of this thesis is to study the dynamics of carbon cycling on upland peatlands in order to provide insights into how the DCM might be made more accurate and representative of a wider range of conditions found on the catchments it is applied to.

There are a number of important factors that affect carbon fluxes on peat bogs that have not explicitly been considered in the DCM. Perhaps most noteworthy is the absence of vegetation type in the model. The MILLENNIA model (Heinemeyer et al., 2010) takes this into account, and as a result finds a different long-term C balance trend for the coming century across the UK than either the ECOSSE (Smith et al., 2007) or DCM (Worrall et al., 2003;2007;2009a;2009b) models. Therefore, in order to improve the spatial applicability of the DCM, an in situ, longitudinal study of the effects of common upland vegetation on carbon flux will be undertaken in this thesis. Differences found between vegetation types could potentially be used to construct vegetation specific sub-models of CO_2 flux, DOC etc. which will enable the DCM to deal with varying vegetation type within a catchment. However, the actual incorporation of these sub-models into the DCM is not an aim of this research.

The effects of altitude (above sea level) are considered in the DCM only with respect to their effects on environmental drivers. No investigation has so far been conducted to measure the direct effects of altitude on blanket peatland carbon flux, despite the fact that individual blanket peatlands can cover a relatively wide range of altitude when compared to other common peatland types. Given the fact that altitude data, for the purposes of modelling, are easily and inexpensively obtainable, the direct role of altitude on blanket peat carbon flux will be investigated in this thesis. If a relationship is found to exist this could be incorporated into sub-models of the main model with little additional resource or effort.

Finally, the DCM in its construction has employed empirical sub-models of various carbon fluxes, including CH_4 and CO_2. These sub-models have been created using individual or multiple linear regressions (see chapter 2) between response and predictor variables obtained from direct, in-field monitoring without consideration of site-specific categorical factors. This technique is to be employed extensively in this thesis and has been employed in other published research (e.g. Brook et al., 1983; Buffam et al., 2010; Lee, 2010; Clay et al., 2012) and in other doctoral theses from this research group (e.g. Rowson, 2007). However, the assumption is being made that these models, derived from purely empirical relationships between field derived datasets, are physically interpretable, i.e. that they can be said to accurately represent the physical, chemical and/or biological processes ongoing within the peat soils. While necessary, this assumption should be investigated. As such, experimental manipulations of the carbon cycle will be undertaken in this thesis to determine whether the changes in the peatland carbon cycle post manipulation are evident in the differences in MLR coefficients between the control and manipulated plots.

1.6 – Structure of Thesis

This thesis follows a conventional structure being made up of this introduction, a methodology chapter, four experimental chapters, a conclusions and further work chapter and appendices. More detail regarding each chapter is given below:

- Methodology – the field, laboratory and statistical analyses used throughout this thesis are given in this chapter. The reason for this is that in order to maximise comparability of results between chapters, the data were gathered and analysed using predefined standard protocols. As such, it makes sense to state them once in a methodology chapter rather than repeating them in each experimental chapter as the methods employed do not tend to differ between experiments. In cases where new methods, experimental designs or analytical techniques are employed or the standard protocols given in the methodology are changed, these amendments are stated separately within the experimental design sections of each experimental chapter.
- The Role of Altitude – this chapter investigates whether altitude (above sea level) leads to any predictable changes in carbon fluxes, other than those changes that can be accounted for by the other covariates measured.
- The Role of Vegetation – this chapter investigates the comparative effects of vegetation type on carbon flux. Moreover, the effects of differing canopy heights of *Calluna vulgaris* on carbon flux are analysed, in order that the DCM can take these management induced modifications to *C. vulgaris* into account. Finally, this chapter deals with the effects of vegetation on the structure and predictive ability of common literature and empirically derived models of ecosystem respiration.

- The Role of Diurnal Processes – this chapter tests the hypothesis that a lag exists between the cessation of photosynthesis and the subsequent decrease in the magnitude of ecosystem respiration. In addition, the day time and night time rates of CO_2 flux are compared in order to determine whether whole diurnal cycle CO_2 fluxes can be reliably estimated from daytime only readings.
- Manipulation Trials – this chapter is really two separate experiments, one on a short time scale (58 days) with twice-daily resolution sampling for the first 14 days and the other on an annual timescale with twice-monthly resolution sampling. However, the goal of both experiments is to manipulate the carbon cycle in order to investigate the assumption that empirical models of carbon flux can be physically interpretable.
- Conclusions and Further Work – this chapter provides of summary of the key findings of each experimental chapter and provides a commentary on areas for further investigation highlighted by the research carried out in this thesis.
- Bibliography – provides a list of all of the sources cited in this thesis.
- Appendix - provides the raw data compilations used for the analyses, by experimental chapter.

2 – Methodology

2.1 – Study Sites

All data gathered for this thesis were collected from a number of sites distributed on the blanket peatlands of the Peak District National Park and the South Pennines. Data collected on the first of these sites began in October 2006 and many of the sites referenced in this thesis are still under active monitoring at the time of writing. Prior to stating where these sites were and how they were installed and used, it is important to consider what is meant by the term ‘site’.

In the case of this research, a site is considered to be a collection of replicate gas and water sampling apparatus, located in close proximity (within 2-3 m) to their replicates sampling a specific factor (e.g. vegetation, restoration or management type). As such, site is the smallest spatial unit of this study, above this there are localities. These are larger geographical units containing a number of sites, where it is possible to walk between the sites within minutes. Next there are areas, which are large geographical units containing a number of sites (and possibly localities) such that walking between all the sites in the area would be difficult. Finally, there are regions which are very large units containing all the other sub-divisions. A map showing the distribution of the main study areas is given in figure 2.1.1.

The data contained in this thesis were not obtained exclusively for the research presented herein, as such, the sites used were (i) begun at different times (ii) set up with specific research intentions, that were not always related to those of this thesis, and (iii) on some occasions were retired. These facts pose limitations on the extent to which certain attributes of the datasets (e.g. considering the effects of specific years) can be analysed with the statistical methods available.

While there are those three major differences to bear in mind when considering the data gathered in this study, the sites used also have a number of important similarities which makes data gathered from them readily comparable. Firstly, all sites were instrumented in the same fashion and with the same materials (described in section 2.2). All sites contain a minimum of three replicate sets of equipment; most commonly sites would contain six replicates. Sites with six replicates were preferred as they offer a good balance between replication and time/resource allocation to fieldwork. All sites were left for a minimum of four weeks, after initial instrumentation, before any measurements were taken to allow carbon cycling processes disrupted by site instrumentation to re-equilibrate. Standard data acquisition procedures (section 2.2) were followed, using the same equipment and all sites were sampled monthly.

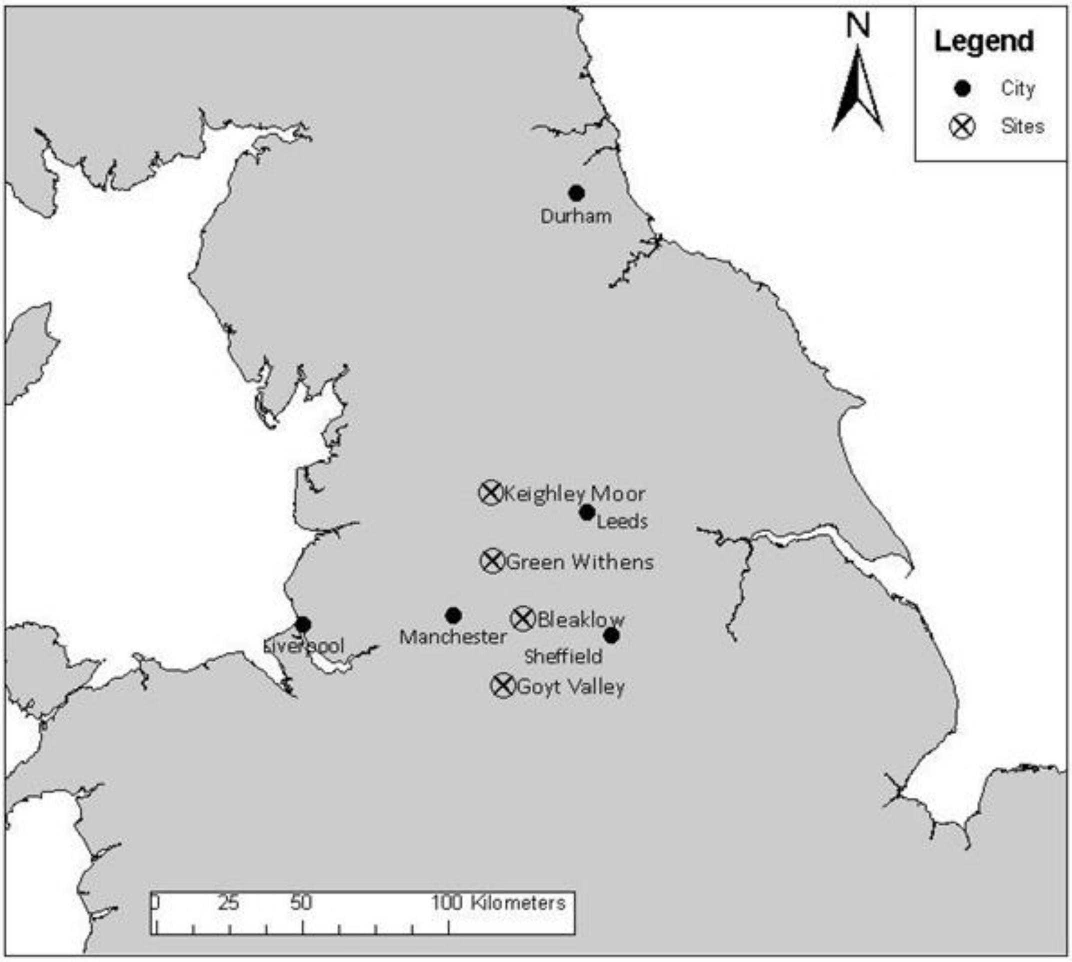


Figure 2.1.1 – Map Showing the Locations of the Study Areas

2.1.1 – Bleaklow Plateau

The Bleaklow Plateau (SK 0961 9695) is a raised topographic plateau between the cities of Manchester, to the west, and Sheffield, to the south-east. It has a maximum elevation of 633 m above sea level (asl) and is covered in blanket peat bogs, of ca. 2 m depth, from the summit to an elevation of ca. 500 m asl. It has an annual precipitation in excess of 1400 mm a year (Evans, 2011, personal communication). The blanket peat is underlain by periglacial deposits with Millstone Grit bedrock (Evans and Lindsay, 2010a). The presence of an impermeable, laterally-extensive, periglacial surface stratum created conditions of poor drainage which led to plaudification and thus formation of the blanket peat observed today. Initiation of blanket peat formation on the plateau is thought to have begun in the range of 7500 to 5400 years BP (Tallis and Switsur, 1991).

There are a number of carbon cycling projects that have been and/or still are being undertaken by the Carbon, Waste and Water Research Group of Durham University on Bleaklow Plateau. As such, the following list gives details of all sites from which data have been gathered for some and/or all of the following experimental chapters of this thesis. A map showing the distribution of the sites is given in figure 2.1.1.1. Each entry in the list starts with the site name followed by its two/three letter acronym.

- *Baskerville Drift (BVD)* − is a 2.5 m deep gully, trending south east, incised into the peat (SK 10864 93922; 521 m asl, 5.7° slope, 225° aspect) which is naturally re-vegetating its gully floor and, to a more limited extent, its gully walls. The main groups colonising the gully are *Eriophorum vaginatum* and *Sphagnum* spp. with a large carpet of *Sphagnum* spp. forming in a hollow protected from the abrasive action of the gully stream by a perimeter of *E. vaginatum*. This site has nine replicate plots, with the first six spanning two parallel perpendicular transects from interfluve to gully floor and the final three being situated in the *Sphagnum* lawn. The site was first sampled in December 2007 and is still in operation at the time of writing.

- *Joseph's Patch Gully (JPG)* – is a 2.5 m deep gully, trending south west, incised into the peat (SK 08781 96156; 568 m asl, 7.9° slope, 270° aspect) which has been re-vegetated by means of seeding with a lawn grass seed mix (i.e. *Dechampsia* spp. and *Festuca* spp.) and had its slopes stabilised with biodegradable geojute netting. The site contains six replicate dip-well and gas collar pairings, which are situated from on a line perpendicular to the gully with the interfluve, gully walls and floors all being sampled twice. The site was instrumented November 2006 and remains active at the time of writing.
- *Oriental (ORI)* – is a 2 m deep gully incised into an area of bare peat (SK 09635 95601; 613 m asl, 3.2° slope, 210° aspect), trending south east, that has some limited natural re-vegetation with *Eriophorum vaginatum*. In addition, the gully itself has been blocked with plastic sheet-piling dams at 3 m intervals in the vicinity of the site in order to restore the water table. As this is a gully site it follows the plot layout of JPG. Data gathering began on this site in November 2006 and ceased January 2009.
- *Penguin's Drift (PEN)* – is a site adjacent to the A57 (SK 09054 93154; 507 m asl, 5.4° slope, 146° aspect) which is covered with *E. angustifolium* and *E. vaginatum* moorland with a small stream (flowing to the south-east), containing a V-notch weir plate, passing through the centre of the site. This site is instrumented with six replicate dip-wells and gas collars and has been active since October 2006. As of the time of writing the site is still being used for data collection purposes.
- *Tubby East (TE)* – is an area of bare peat (SK 09588 95663; 617 m asl, 5.1° slope, 191° aspect) which has been re-vegetated with the same lawn grass seed mix as JPG, but without slope stabilisation measures. It is obvious that, with five collars out of six containing bare peat the restoration interventions made on this site have not been successful. Data gathering on this site began in November 2006 and is still active at the time of writing.
- *Trenches North (TN)* – is an area of completely bare peat (SK 09359 96549; 608 m asl,

1.4° slope, 278° aspect) which has had no management restorative interventions in the vicinity of Bleaklow Summit. The plots are installed in two sets of three on either side of a minor (i.e. < 1 m deep, south westerly flowing, drainage gully). Data gathering on the site began in November 2006 and the site is still active at the time of writing.

- *Trenches South (TS)* – is a 3 m deep gully incised into an area of completely bare peat near to Bleaklow Summit (SK 09402 96384; 614 m asl, 5.2° slope, 329° aspect) which has had no management or restorative interventions. The 6 plots that make up this site are laid out in a similar fashion to JPG with two transects across the gully from interfluve to interfluve perpendicular to the stream direction. Data gathering began on this site in November 2006 and is still active at the time of writing.
- *Tubby West (TW)* – is a 2 m deep gully incised into the peat (SK 09309 95778; 618 m asl, 1.0° slope, 180° aspect) which has been re-vegetated with the same lawn grass seed mix as the JPG with slope stabilisation by means of the application of a layer of heather mulch (i.e. heather branches) on to the peat surface. The site is instrumented in a similar fashion to JPG with plots forming a transect across the gully from interfluve to interfluve. Data gathering on this site began in November 2006 and is still active at the time of writing.
- *Woodhead Mature (WM)* – is an area blanket peat with a thick canopy of mature (i.e. > 30 cm canopy height) *Calluna vulgaris*, with some infrequent *Vaccinium* spp. (SK 12348 98619; 468 m asl, 10.8° slope, 315° aspect). The site is instrumented as two sets of three plots in parallel rows with one row at a slightly higher (i.e. < 2 m) elevation than the other. This site had not been managed by burning for at least five years prior to data gathering, which started in July 2007. Data gathering on this site ceased in March 2009.
- *Woodhead Recent (WR)* – is an area of peat covered with non-*Sphagnum* mosses and juvenile (i.e. canopy height < 10 cm) *C. vulgaris* (SK 12348 98619; 468 m asl, 10.8° slope, 315° aspect). The site was burnt within twelve months prior to data gathering, which began in July

2007 and ceased March 2009.

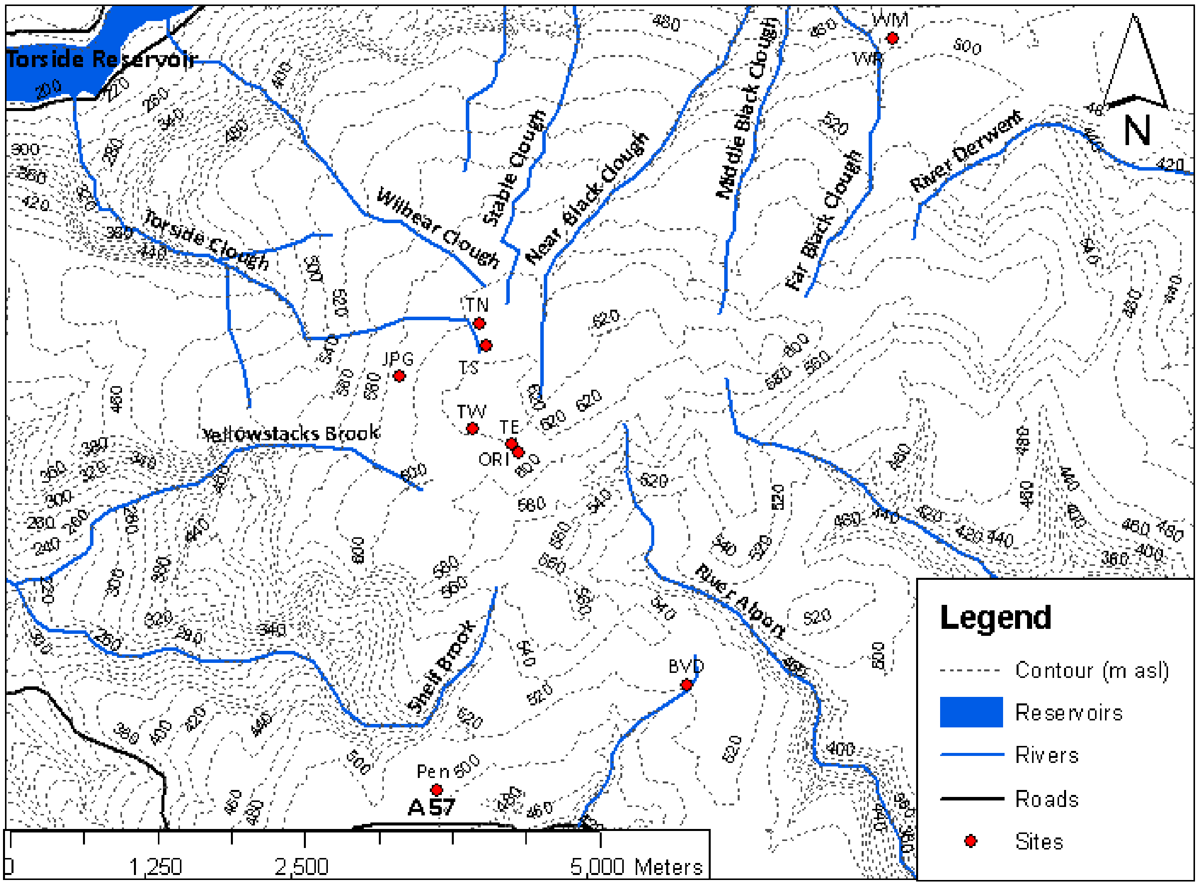


Figure 2.1.1.1 **–** Map Showing the Spatial Distribution of the Bleaklow Sites

2.1.2 – Goyt Valley

The Goyt Valley is a valley cut by headwaters of the River Goyt, which flows to the north and, eventually west, to meet the River Etherow, finally joining the River Mersey near Stockport. The valley lies 4 km to the west of the town of Buxton in the Peak District. The eastern flank of the north-south trending valley is covered in blanket peat bogs from its summit at ~500 m asl to ~350 m asl, receiving in excess of 1300 mm of rainfall annually. The geology underlying the peat deposits is capped by periglacial clay deposits underlain by bedded carboniferous sediments (shales grading to grit-stones) (Cope, 1998) with thinly bedded coal measures, which outcrop near the car park at Ravenslow (see section 2.1.2.2) (author's observation). The blanket peat in the Goyt Valley area has been studied at two primary localities in this thesis, which are described in more detail below. A map showing the locations of all the Goyt Valley sites is given in figure 2.1.2.1.

2.1.2.1 – Big Moor

Laying on the north eastern slope of the Goyt Valley the locality, known in this study as Big Moor (SK 0199 7393), is an extensive area of heavily managed heather moorland underlain by blanket peat deposits of a depth >1 m on all sites. This locality was instrumented in order to study the comparative effects of cutting versus burning of *C. vulgaris* in a dry heath setting. The sites of this locality sample areas of land that have been burned or cut, at differing times, in order to assess the temporal manifestation of effects on carbon cycling. A complete list of sites and their attributes is given below:

- *Bottle (B N/S)* – split into two, adjacent, sub-sites of three plots a piece (Bottle North (BN) – SK02027 74012; 432 m asl, 6.1° slope, 305° aspect; and Bottle South (BS) – SK 02088 73969; 442 m asl, 6.5° slope, 8° aspect), this site samples an area of blanket peat that had its *C. vulgaris* burned one year before the site was instrumented. The site was first sampled in July 2008 and is still being sampled at the time of writing.
- *Bendigo (Ben)* – is a site containing only three plots, sampling an area of blanket peat upon which the *C. vulgaris* had been cut a year prior to instrumentation (SK 02013 74076; 430 m asl, 8.0° slope, 315° aspect). This site was first sampled in July 2008 and is still active at the time of writing.
- *Goodship 1 (GS1)* – is a site (SK 02140 73707; 451 m asl, 4.0° slope, 45° aspect) containing six replicate plots sampling an area of blanket peat upon which the *C. vulgaris* had been burnt a month prior to site instrumentation. This site was first sampled in June 2008 and is still active at the time of writing.
- *Goodship 3 (GS3)* – is a site (SK 02052 73795; 449 m asl, 8.5° slope, 270° aspect) with three replication plots, that samples blanket peat where the *C. vulgaris* had been cut one

year prior to site instrumentation. This site was first sampled in June 2008 and is currently active at the time of writing.

- $Mossad\ (Moss)$ – is a site (SK 02331 73460; 449 m asl, 5.9° slope, 26° aspect) of six replicate plots sampling an area of blanket peat upon which the *C. vulgaris* had been cut one month prior to site instrumentation. The first samples were collected from this site in June 2008 and the site was retired in March 2010.
- $Otterbox\ (OB)$ – is a site (SK 02164 72600; 430 m asl, 5.0° slope, 21° aspect) consisting of six replicate plots sampling an area of blanket peat upon which the *C. vulgaris* had been burned one month prior to the site being instrumented. The first samples were collected from this site in June 2008 and the site is still in operation at the time of writing
- $Patang\ (Pat)$ – is a site (SK 02052 73818; 448 m asl, 6.5° slope, 276° aspect) consisting of six replicate plots sampling an area of mixed *C. vulgaris* and *Vaccinium* spp. heather that has not been managed by cutting, burning or grazing for at least five years prior to site instrumentation. The site was sampled first in June 2008 and the site is still in operation at the time of writing.
- $Prometheus\ (Prom)$ – is a site (SK 02204 73528; 456 m asl, 7.1° slope, 71° aspect) with six replicate plots sampling *C. vulgaris* that was burnt five years prior to site instrumentation. The site was first sampled in June 2008 and the site was retired in March 2010.

2.1.2.2 – Ravenslow

Ravenslow lies about 2.5 km to the south of Big Moor (SK 0214 7179), still on the eastern flank of the Goyt Valley and as such is subject to similar prevailing conditions and underlying geology. This locality is part of the same observational study as Big Moor, studying the impacts of heather burning (there are no cut sites on Ravenslow) on blanket peat carbon cycling. However, this locality is a wet heath setting (i.e. relatively shallow water tables) primarily due to its gentler slopes, which enables the burning study to control for any differing effects on wet versus dry burned heathlands. The sites on Ravenslow used in this study are as follows:

- *Dory (Dory)* – is a flat site (SK 02152 71800; 441 m asl, 2.0° slope, 180° aspect) centred on an area of hummock and hollow microtopography that was instrumented with three replicate plots to sample the *Sphagnum* spp. found in the hollows. These plots were sampled in order to increase the number of plots sampling *Sphagnum* spp. thus increasing the dataset size for the vegetation study (Chapter 4). The site was first sampled in December 2008 and was retired after January 2010.
- *Kraken (Kra)* – is a flat site (SK 02020 72170; 431 m asl, 1.0° slope, 90° aspect) of six replicate plots sampling an area of *C. vulgaris* that had not been managed by burning for at least five years prior to site instrumentation. The site was first sampled in June 2008 and remains active at the time of writing.
- *Nemo (Nemo)* – is a flat site (SK 02166 71840, 431 m asl, 2.0° slope, 290° aspect) of three replicate plots sampling an area of *Sphagnum* spp. lawn near a pond. This site was set up with the same intention as Dory, i.e. in order to better sample *Sphagnum* spp. for the vegetation study (Chapter 4). The site was first sampled in December 2008 and was retired after January 2010.
- *Neptune (Nep)* – is a flat site (SK 02125 71859; 435 m asl, 2.3° slope, 315° aspect) of six replicate plots sampling an area of *C. vulgaris* that was burned within 1 < burn age < 5 years prior to site instrumentation. The site was first sampled in June 2008 and remains active at the time of writing.
- *Poseidon (Pos)* – is a site of two sets of three replicates (SK 02165 71850; 430 m asl, 2.2° slope, 225° aspect and SK 02075 72155; 436 m asl, 0° slope, 45° aspect) approximately 500 m apart sampling areas of *C. vulgaris* topped blanket peat that were burned one month prior to

site instrumentation. The site was first sampled in June 2008 and remains active at the time of writing.

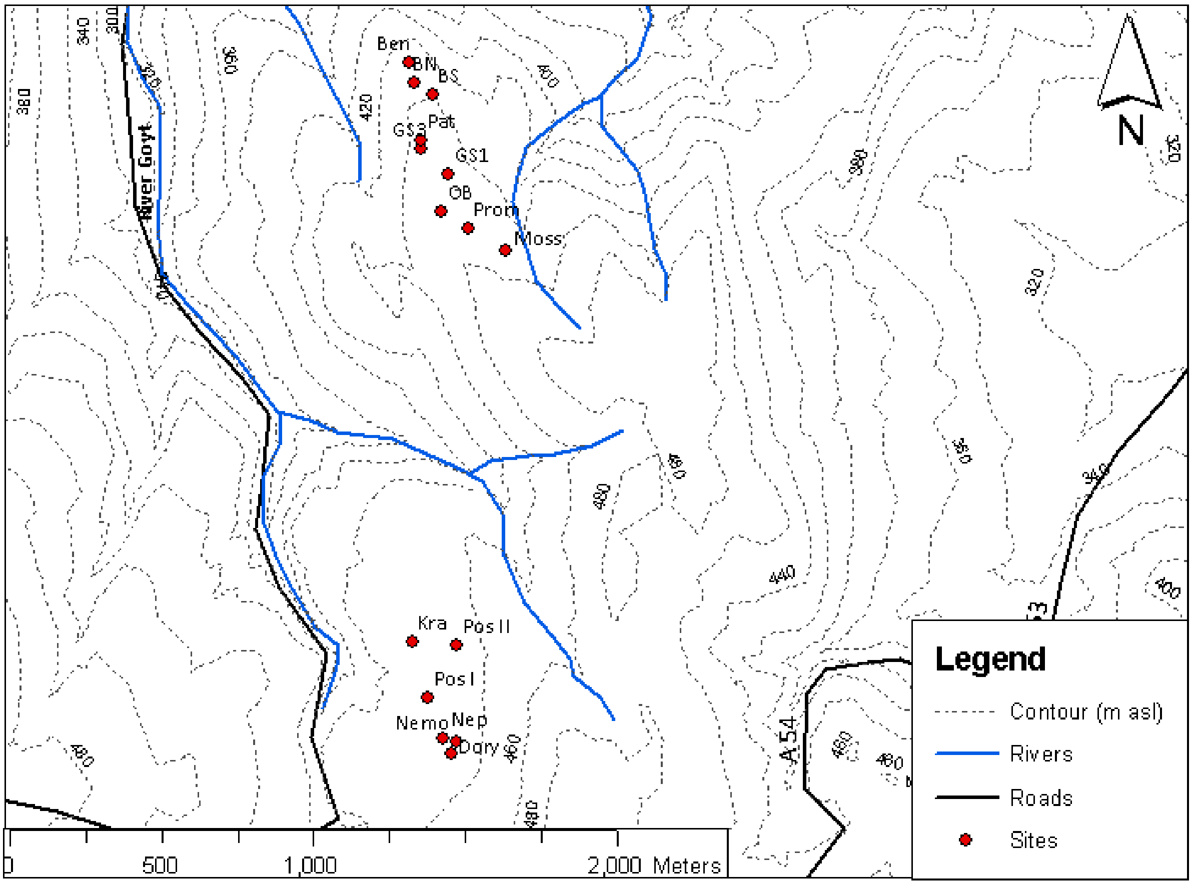


Figure 2.1.2.1 **–** Map Showing the Distribution of the Goyt Valley Sites

2.1.3 – Green Withens Reservoir

This reservoir lies in the South Pennines (SD 9892 1629), close to junction 22 of the M62, between the cities of Manchester and Leeds and is a drinking water supply reservoir. The sites installed in this area were specifically set up in order to sample *Molinia caerulea*, which was poorly sampled on the existing sites in the Peak District, but is dominant on the northern shore of this reservoir.

The two sites were installed on the banks of two streams, gently sloping, which drained into the northern shore of the reservoir. Stream 2 (SD 9877 1661) had four sub-sites (S2:a-d), with three replicates a piece and Steam 4 (SD 9852 1642) had three sub-sites (S4:a-c) with three replicates a piece, see table 2.1.4.1 for details of each sub-site location. All of the collars were installed in blanket peat dominated by *M. caerulea*. The entire locality was instrumented on the same day and the first samples were taken April 2009 with the final readings being recorded in March 2010 when the locality was decommissioned. A map showing the spatial distribution of the Green Withens sites is given in figure 2.1.3.1.

Table 2.1.3.1 – Locations of Green Withens Sites (S2 slope 1.1°, aspect 113° and S4 slope 5.1°, aspect 125°)

Site Name	Grid Reference	Altitude (m asl)
S2:a	SD 98771 16611	364
S2:b	SD 98751 16643	366
S2:c	SD 98765 16685	368
S2:d	SD 98705 16712	374
S4:a	SD 98520 16429	366
S4:b	SD 98483 16471	368
S4:c	SD 98427 16506	373

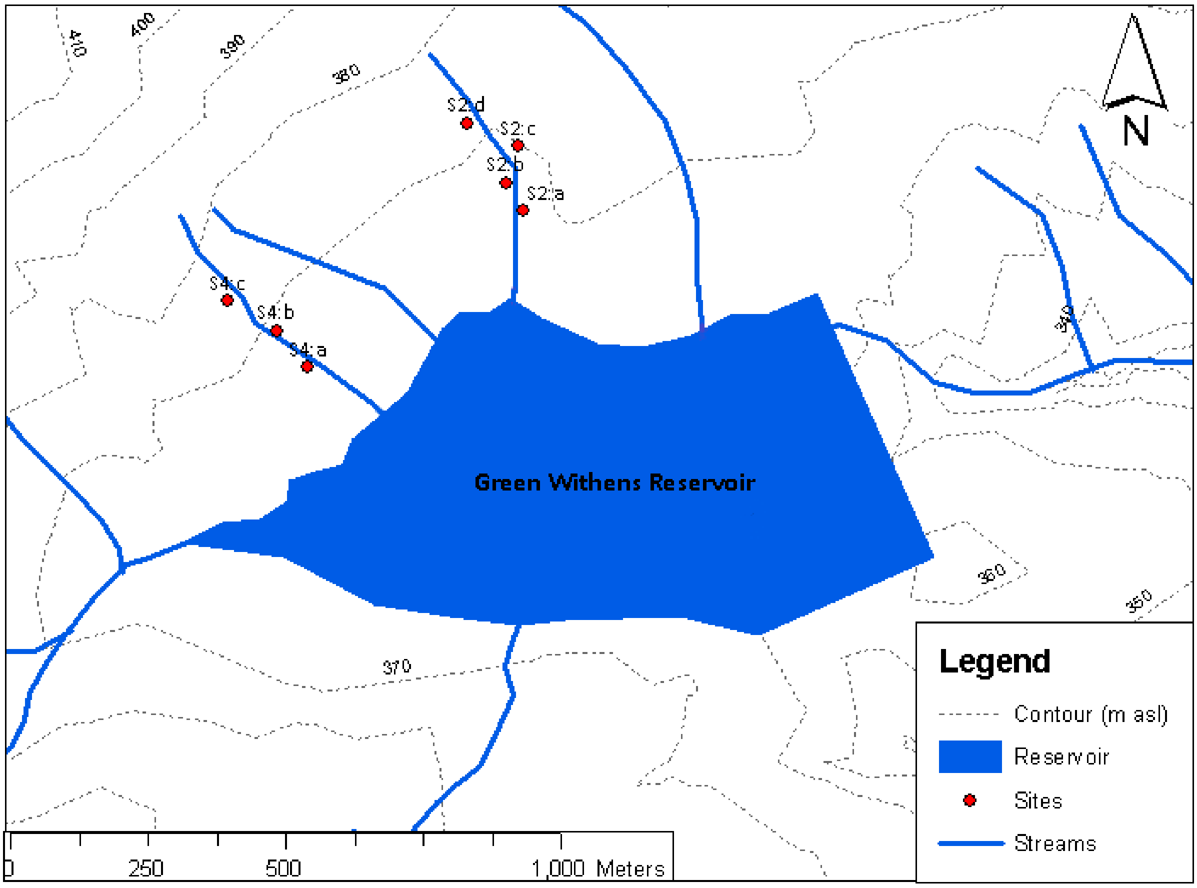


Figure 2.1.3.1 **–** Map Showing the Distribution of the Green Withens Sites

2.1.4 – Keighley Moor Reservoir

This reservoir lies 5 km to the west of Keighley in the South Pennines (SD 9871 3942) and like Green Withens, is a drinking water supply reservoir. The reservoir in this area is surrounded by a large amount of heavily managed (i.e. burned) heathland. The sites set up in this area were installed with the intention of increasing the number plots sampling burned *C. vulgaris* and *Sphagnum* spp. As such, there were three primary sites instrumented in this area; Burn A (BA), Burn B (BB) and *Sphagnum* (S).

For both of the 'Burn' sites there were four sub-sites with three replicate plots a piece, lettered a-d respectively. For the *Sphagnum* site there were two sub-sites with three replicates a piece, lettered A and B. The sites were first sampled in March 2009 and were retired in March 2010 when the area was decommissioned. Table 2.4.1 gives the locations and altitudes of the individual sub-sites in this area and figure 2.4.1 shows the geographical distribution of the sites.

Table 2.4.1 – Locations of Keighley Moor Sites (BA slope 4.2°, aspect 45°; BB slope 3.0°, aspect 135°; SA slope 5.8°, aspect 59° and SB slope 5.2°, aspect 90°)

Site Name	Grid Reference	Altitude (m asl)
BA:a	SD 98041 39720	417
BA:b	SD 98088 39740	411
BA:c	SD 98158 39749	406
BA:d	SD 98196 39619	396
BB:a	SD 97797 39621	425
BB:b	SD 97863 39525	414
BB:c	SD 97919 39525	413
BB:d	SD 97986 39486	413
SA	SD 98224 39723	404
SB	SD 98247 39713	391

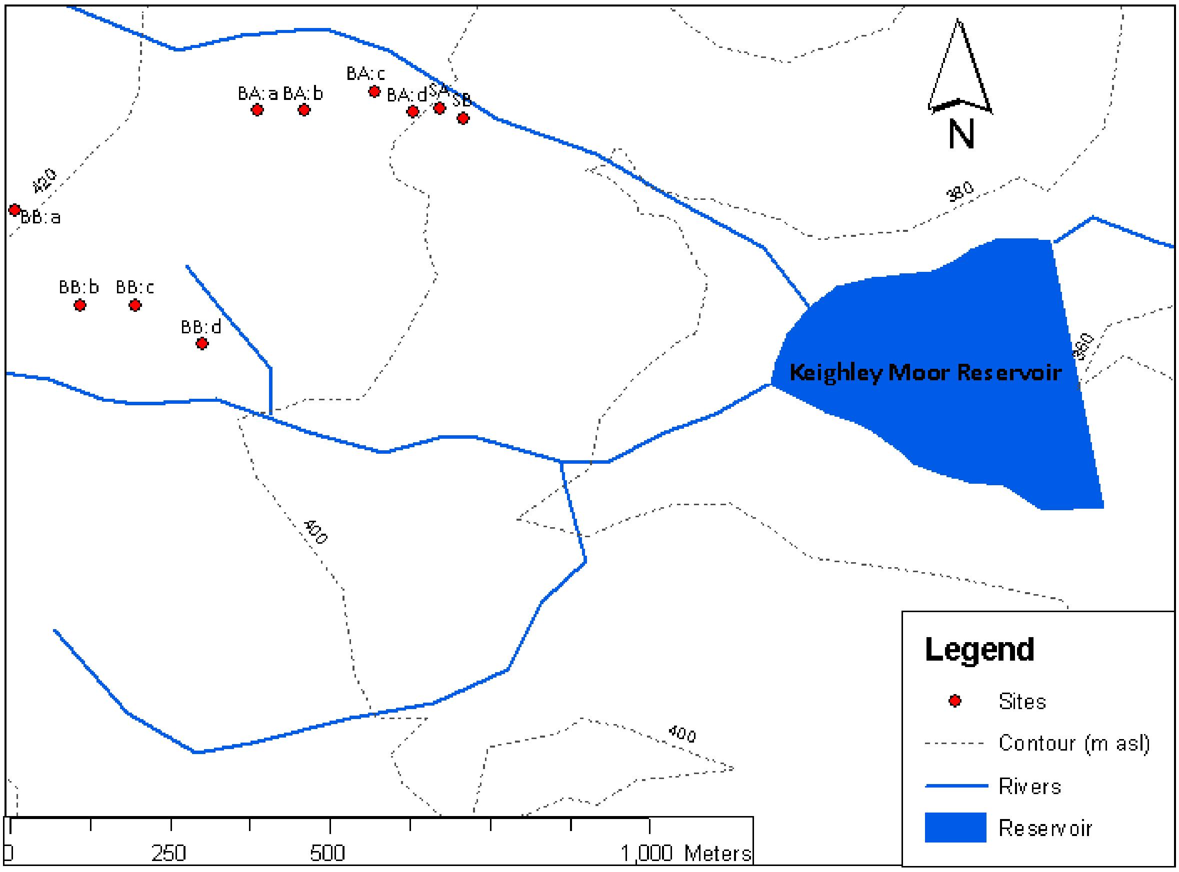


Figure 2.4.1 **–** Map Showing the Distribution of the Keighley Moor Sites

2.1.5 – Summary

Table 2.1.5 summaries the key site information given in section 2.1 of this thesis.

Table 2.1.5 – Site Characteristics and Factor Level Distribution (relevant to chapters 3 and 4)

Region	Locality	Site	Plots	Vegetation								Morphology	Altitude	Slope	Aspect	Treatment	Time Since Treament	Time Series
				Bare	Bilb	CG	Hea	LG	Mol	NS	Spg		(m asl)	(o)	(o)		(years)	
PD	BP	BVD	9	1	1	4	-	-	-	-	3	Gully	521	5.7	225	-	-	Dec 07 - Jan 10
		JPG	6	1	-	-	-	5	-	-	-	Gully	568	7.9	270	Restored	< 1	Dec 06 - Jan 10
		ORI	6	-	-	6	-	-	-	-	-	Gully	613	3.2	210	Restored	< 1	Nov 06 - Jan 10
		PEN	6	-	-	6	-	-	-	-	-	Stream	507	5.4	146	-	-	Nov 06 - Jan 10
		TE	6	5	-	-	-	1	-	-	-	Flat	617	5.1	191	Restored	< 1	Nov 06 - Jan 10
		TN	6	6	-	-	-	-	-	-	-	Flat	608	1.4	278	-	-	Nov 06 - Jan 10
		TS	6	6	-	-	-	-	-	-	-	Gully	614	5.2	329	-	-	Nov 06 - Jan 10
		TW	6	-	-	-	-	6	-	-	-	Gully	618	1	180	Restored	< 1	Nov 06 - Jan 10
		WM	6	-	1	-	5	-	-	-	-	Flat	468	10.8	315	Burned	> 5	July 07 - Mar 09
		WR	6	-	1	-	5	-	-	-	-	Flat	468	10.8	315	Burned	< 1	July 07 - Mar 09
	GV	B(N)	3	-	-	-	2	-	-	1	-	Flat	432	6.1	305	Burned	1	Jul 08 - Jan 10
		B(S)	3	-	-	-	3	-	-	-	-	Flat	442	6.5	8	Burned	1	Jul 08 - Jan 10
		Ben	3	-	-	1	1	-	-	-	-	Flat	430	8	315	Cut	1	Jul 08 - Jan 10
		GS1	6	-	-	1	-	-	-	5	-	Flat	451	4	45	Burned	< 1	Jun 08 - Jan 10
		GS3	3	-	2	-	-	-	-	1	-	Flat	449	8.5	270	Cut	1	Jun 08 - Jan 10
		Moss	6	1	1	2	-	-	-	2	-	Flat	449	5.9	26	Cut	< 1	Jun 08 - Jan 10
		OB	6	1*	-	-	5	-	-	-	-	Flat	430	5	21	Burned	< 1	Jun 08 - Jan 10
		Pat	6	1*	3	1	-	-	-	1	-	Flat	448	6.5	276	-	-	Jun 08 - Jan 10
		Prom	6	2*	-	-	4	-	-	-	-	Flat	456	7.1	71	Burned	5	Jun 08 - Jan 10
		Dory	3	-	-	-	-	-	-	-	3	Flat	441	2	180	-	-	Dec 08 - Jan 10
		Kra	6	-	-	2	1	-	-	3	-	Flat	431	1	90	-	-	Jun 08 - Jan 10
		Nemo	3	-	-	-	-	-	-	-	3	Flat	441	2	290	-	-	Dec 08 - Jan 10
		Nep	6	-	-	4	1	-	-	-	1	Flat	435	2.3	315	Burned	1<age<5	Jun 08 - Jan 10
		Pos (I)	3	-	-	2	-	-	1	-	-	Flat	430	2.2	275	Burned	< 1	Jun 08 - Jan 10
		Pos (II)	3	-	-	1	-	-	2	-	-	Flat	436	0	45	Burned	< 1	Jun 08 - Jan 10
SP	GW	S2	12	3	-	-	-	-	9	-	-	Stream	368	1.1	113	-	-	Apr 09 - Mar 10
		S4	9	-	-	-	-	-	9	-	-	Stream	369	5.1	125	-	-	Apr 09 - Mar 10
	KM	BA	12	5*	-	-	7	-	-	-	-	Flat	410	4.2	45	Burned	1<age<5	Mar 09 - Feb 10
		BB	12	1	1	2	7	-	-	-	1	Flat	415	3	135	Burned	1<age<5	Mar 09 - Feb 10
		S(A)	3	-	-	-	-	-	-	-	3	Stream	404	5.8	59	-	-	Mar 09 - Feb 10
		S(B)	3	-	-	1	-	-	-	-	2	Stream	391	5.2	90	-	-	Mar 09 - Feb 10

* denotes that not all collars listed under 'bare' were used in the bare dataset due to large amounts of surface litter, see experimental designs in following chapters

Abbreviations - PD = Peak District, SP = South Pennines, BP = Bleaklow Plateau, GV = Goyt Valley, GW = Green Withens, KM = Keighley Moor, Sites = as per section 2.1

Morphology - Flat = site on a peat surface devoid of streams or gully channels, Gully = site samples transects in a dendritic gully, Stream = site within 3 m of a stream

Treament - see section 2.1 within the entry for each site for details

Slope and Aspect - values estimated from 1:10,000 resolution DTMs from Digimap analysed in ArcGIS

2.2 – Field Data Gathering

2.2.1 – Water Table Depth and Soil Pore Water Sampling

In order to access the saturated zone and thus be able to measure the water table depth and take a soil pore water sample, each replicate plot on a site was instrumented with dip well. A dip well is a one meter length of five centimetre diameter PVC pipe, along which openings have been drilled at ten centimetre intervals and left open at the base. Once sunk into the peat, these openings create a pressure gradient which is corrected by water from the saturated peat flowing into the pipe. Once the pressure inside and outside the pipe is in equilibrium the distance between the soil surface and the water level in the pipe represents the depth of the water table below the soil surface.

It is difficult when measuring water table depth to take the measurement relative to the soil surface, which is the standard datum. A more convenient datum for the purposes of accurate measurement is the top of the dip well (i.e. the dip-well aperture). As such, all measured water table depths have to be corrected by subtracting the height of the dip well above the soil surface from the measurement taken in order to state the reading relative to the standard datum.

To accurately measure the depth of the water table a conductivity probe was employed. This tool is a 1.5 m pole that has a tape measure along its whole length, with zero at the end that comes into contact with the water. This end of the pole, housing two electrodes, is pushed into the dip well until the end contacts the water surface. Once this happens, the intrinsic conductivity of the water completes a circuit within the system and an LED at the top end of the pole illuminates. At this point a reading is taken from the tape measure of what depth, below the dip well aperture, the light illuminated at.

The next step of the process is to take a soil pore water sample from the dip well. This is achieved by means of a dip-probe, which is simply a length of bamboo cane with a 30 ml steralin (see section 2.3) attached to the bottom. The benefit of this tool is that it takes a standard volume of sample at each dip well, is easy and cheap to manufacture, it requires little/no maintenance and it is lightweight and thus easy to transport. It was important to always take a water sample after the water table depth measurement as sampling soil pore water will, temporarily, draw down the water table. The dip probe also meant that water was not collected unless there was at least 10 cm depth of water in the dipwell this helped prevent the collection of peat sludge. This protocol was obeyed on all sampling occasions, at all sites.

2.2.2 – Carbon Dioxide Flux Sampling

The gross fluxes of CO_2 into and out of blanket peat and the net balance of these two fluxes were important variables to be analysed in this study. The process to assess CO_2 flux is more complex than for measuring the water table and a description and discussion of the procedures followed is given below.

Soil surface fluxes of CO_2 can be measured using various devices and techniques, each with their own strengths and limitations. The oldest (e.g. Lundegaardh, 1927), and at present, least commonly used technique is known as alkali titration. In this method a container, usually a circular disc containing a known volume and concentration of K or NaOH is applied in a sealed chamber to the soil surface. This trap will be left on the soil for a set amount of time (typically 1 to 24 hours). After this the alkali is taken to a laboratory where it is titrated, with an acid, commonly HCl, to a predetermined pH level (e.g. from pH 8.3 to pH 3.7; Jensen et al., 1996). The flux value (i.e. the concentration of CO_2 absorbed by the alkali trap over time) is then corrected for the effects of ambient CO_2 concentrations by subtracting the value obtained from a control trap, not exposed to the soil surface.

The benefits of this method are that it can be used to determine fluxes of CO_2 over long time intervals and as such can be representative of average daily fluxes etc. Moreover, the method is cheap to set up and carry out and thus can generate large amounts of data over large areas. However, there also are some limitations to this method. Firstly, the alkali titration method over estimates small fluxes (< 100 mg CO_2-C m^{-2} h^{-1}) by ~12 % and underestimates large fluxes (> 100 mg CO_2-C m^{-2} h^{-1}) by "a large amount" (Jensen et al., 1996) relative to an infra-red gas analyser (described later in this section). These errors are due to alteration of the diffusive gradient in the chamber head space relative to the ambient conditions. Furthermore, alkali traps can only deal with net or gross soil release of CO_2 (i.e. source behaviour) and will not record soil sinks. This makes it impossible to measure NEE or P_g with this method.

The alkali titration method is known as a closed chamber method due to it making use of a sealed chamber. Additionally, as there is nothing circulating the gases within the chamber it is defined as a static method. The next technique for measuring CO_2 flux from soil discussed is also a closed chamber technique, but in this method the gases are actively agitated and circulated to a detector with a system of pumps and fans, and as such the method is known as a dynamic closed chamber technique. In essence, the starting point of this approach is the same as the alkali titration where an air tight chamber is sealed to the soil surface. However, in this case the gases within the chamber are mixed by a fan, to prevent gas stratification, and thus minimise chamber impacts on the diffusive gradient. The gas within the chamber is sampled by being pumped into a detector unit external to the chamber by means of gas tight hoses and an air pump. In the detector unit, a known quanta of infra-red radiation is released in a range (i.e. mid-range 4000 – 400 cm^{-1}) of wavelengths known to be absorbed by CO_2. This beam passes through the chamber air sample and any absorption of infra-red radiation due CO_2 is registered as a smaller amount of radiation entering the detector than was known to have been emitted. From this difference in radiation emitted/detected the concentration of CO_2 in the chamber can be calculated. This reading is only an instantaneous concentration, and to produce a flux a series of these readings are taken, at a regular sampling interval, with the flux of CO_2 being defined as the gradient of the best fit linear regression fitted to the concentration data over time.

The system described above is known as a dynamic, closed chamber (CC), infra-red gas analyser (IRGA) system and has become a very popular way of monitoring CO_2 flux from soils in situ. Its main benefits are that, like the alkali trap method, the system is portable and can be used to take a large number of readings over a large area. Moreover, the IRGA system can detect increasing or decreasing trends in CO_2 flux from the soil and as such is capable of measuring both R_{eco} and NEE from which the rate of P_g can be estimated. This method is less labour intensive that the alkali trap method as no additional laboratory titrations or gas chromatography is required to calculate the flux of CO_2. It only needs a short period of time and thus has minimal impacts on the diffusive gradient between soil pores and air.

There are also, however, limitations to this system. Firstly, CC-IRGA methods tend to alter the pressure gradient between the air and the soil surface within the chamber, which with increasing internal chamber wind speeds (generated by the fan) can increase the rate of CO_2 flux from the soil surface into the chamber, relative the rate outside the chamber (Le Dantect et al., 1999). This effect was shown by the same study to be adequately dealt with by using fan speeds under 0.4 m s^{-1} and the flux is measured as it passes through ambient. Secondly, this method requires the installation of gas collars into the soil surface in order to provide an air tight coupling for the chamber. Soil respiration of CO_2 has been shown to decrease with increasing depths of collar insertion, this thought to be due to shutdown of autotrophic respiration from severed roots (Wang et al., 2005). As such, in order to minimise this effect it is important to insert collars no deeper than ~5 cm into the soil surface. Moreover, it is also important to leave the plots with inserted collars to re-equilibrate after collar insertion to allow the any short term disturbances in the carbon cycle to settle.

In addition to the limitations above, all closed chamber methods are subject to limitations concerning the greenhouse and PAR reducing effects of their chamber walls which will, over time, warm the chamber air and soil surface more than the surrounding areas and reduce the amount of photosynthetically active radiation reaching chamber vegetation. These effects are known to interact enhancing R_{eco} and reducing NEE. To overcome these effects acrylic or Teflon is used for the chamber walls which minimises the PAR reducing effects, in some cases to less than 10% (e.g. Burrows et al., 2005). Furthermore, shorter flux measurement durations are used (< 5 min) in order to prevent significant increases in chamber temperature relative to external temperatures.

As well as the CC-IRGA method another dynamic-IRGA method has been developed known as the open path (OP) IRGA system. This arrangement uses a chamber that is not sealed but instead actively draws external air in, to be circulated through the chamber and then released through the opposite side. Instead of measuring the increase or decrease in chamber CO_2 concentrations to calculate a flux, the OP-IRGA system measures the flux of CO_2 by the difference in the concentration of CO_2 entering and leaving the chamber. In situ use of this method is limited by the size of the hardware and power supplies needed, making portability an issue. However, an in situ and laboratory study by Bekku et al., (1995) showed that there were no significant differences between CC- and OP-IRGA methods for estimating soil respiration.

The final common method for calculating CO_2 flux is known as the micro-meteorological approach, or eddy-covariance technique. This technique works by installing a tower (typically 2-3 m in height) on an area of flat ground. The tower houses instruments to measure: CO_2 concentrations (usually using an IRGA); air temperature and pressure; solar radiation/PAR; wind speed and direction; and relative humidity. These recorded data are subsequently analysed to provide high frequency net CO_2 flux rates integrated over the ‘footprint’ area upwind of the tower. The main benefit of eddy covariance methods is that they are high frequency with long temporal coverage meaning accurate daily, weekly etc. fluxes can be calculated from them. There are, however, a number of limitations of this scheme, the most relevant being that it can only measure net flux and thus gross component fluxes have to be modelled and/or estimated (e.g. Reichstein et al., 2005). Moreover, it will only record flux over a large (relative to the chamber plots) area, the location and size of which is subject to wind direction. As such, it is not amenable to sub-ecosystem scale studies of factors that vary on a small spatial scale, e.g. individual vegetation types, heterogeneous land management variation on a small spatial scale (i.e. heather canopy height mosaics from cutting/burning).

It can be seen from the discussion above that a number of different methods/approaches exist for measuring CO_2 flux from soil and that the selection of an appropriate method relies on the requirements of the analysis to be undertaken. As this study is concerned with the variation of CO_2 flux in factors that vary on small spatial scales (e.g. vegetation), requiring large numbers of replicate readings being taken in situ, it was decided that the CC-IRGA method was the most appropriate technique for measuring the CO_2 data gathered. Therefore, the next section of this chapter describes the specific protocol observed for obtaining CO_2 flux data by the CC-IRGA method.

2.2.2.1 – Site Instrumentation

In order to seal the CPY-2 (PP-Systems, Hitchin) chambers to the soil surface, 15 cm diameter uPVC gas collars were inserted into the peat surface to no deeper than 5 cm, to minimise root disturbance. These collars were then left in place for the duration of a site's lifespan, with the first set of readings being taken only after a re-equilibration time of four weeks had elapsed. Each plot on each site contained a gas collar and dip well pairing in this study. The gas collars were installed in close proximity to the dip-well (typically within 10-20 cm) so that the water table measurement taken was as close as possible to the water table beneath the gas collar. A seal was created between the chamber and gas collar by means of a tapering metal skirt on the bottom rim of the chamber which is inserted into the collar until it is firmly in place. See figure 2.2.2.1.1 for an overview of a plot layout.

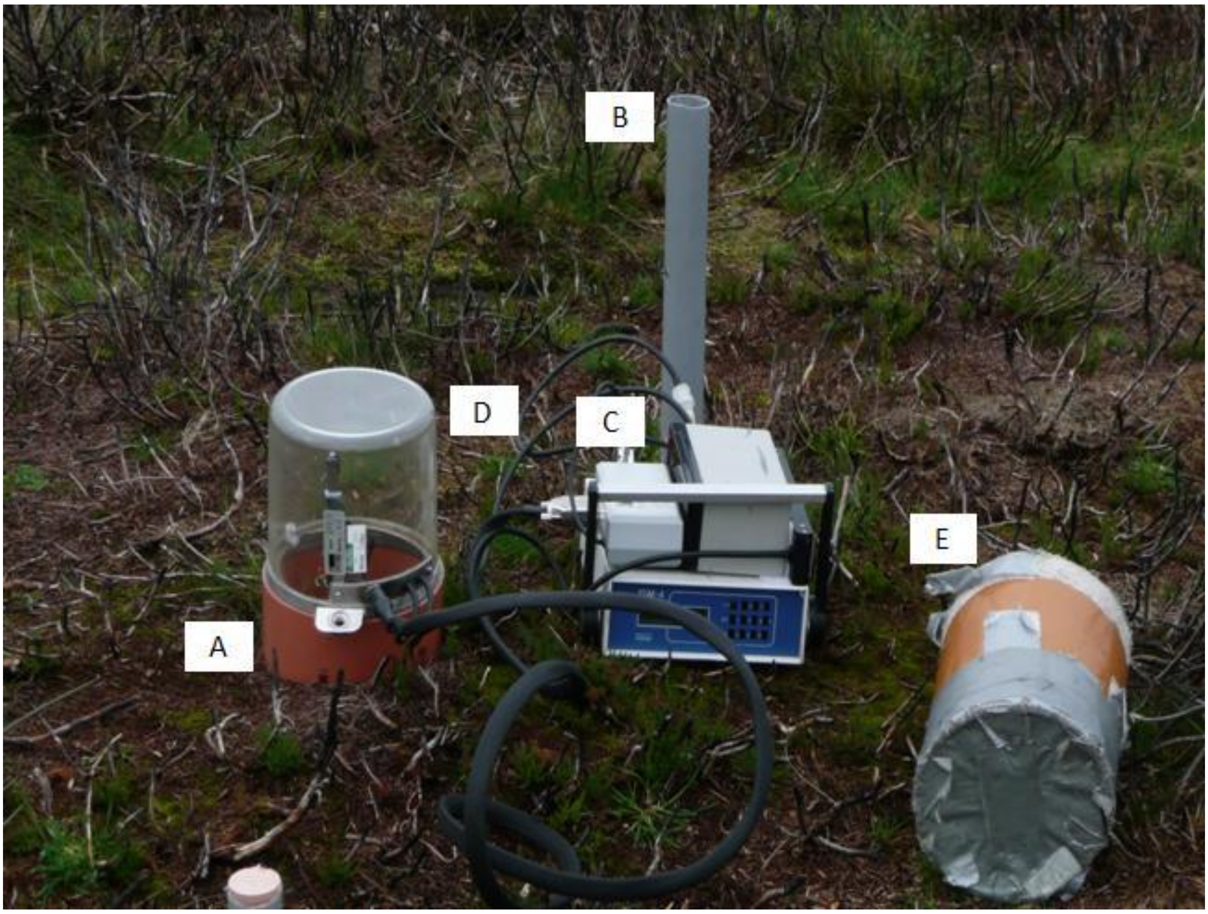


***Figure 2.2.2.1.1* –** This image shows the following features of a standard plot used in this thesis. (A) shows the PVC gas collar, inserted to circa five centimetres depth, (B) shows the end of the dip-well visible above the peat surface, (C) shows the main detector housing and power supply for the EGM-4 IRGA system, (D) shows the CPY-2 closed acrylic chamber (with an internal thermocouple and PAR gauge) in NEE measurement configuration and (E) shows the PVC cover that would be placed over the CPY-2 chamber to cut out daylight and measure R_{eco}.

2.2.2.2 – Infrared Gas Analysis

Once the sites were instrumented correctly and the re-equilibration time had passed measurements of CO_2 flux were taken by the following protocol. Firstly, the EGM-4 (PP-Systems, Hitchin) IRGA was turned on and allowed to reach its operating temperature of 55°C. Once complete the device performed an automated internal calibration which included purging the detector of CO_2 by running the sampled air through soda lime granules and thus taking a zero CO_2 blank reading (this process repeats at a regular interval of once every ten measurement runs).

At this point the device is ready to use for CO_2 flux measurements. The first measurement taken at all plots is the R_{eco} reading. To do this the clear acrylic CPY-2 chamber is covered by a tightly fitting opaque PVC cover in order to block out all sunlight, thus cutting off PAR. This prevented the plants photosynthesising and hence the only flux of CO_2 occurring should have been respiratory in nature.

The dark reading was taken first as the chamber cover minimised the greenhouse effects on soil surface and chamber air temperature increases. The reading was taken by purging the chamber and detector to ambient CO_2 concentrations by running the fan and air pump on a fast setting for 15 seconds, while holding the chamber away from sources of CO_2. Once complete the chamber was sealed to the collar, covered by the PVC sleeve and the device run started. During the run the device recorded the concentration of CO_2 reaching the detector at four second intervals for two minutes after an initial equilibration delay of ten seconds. The concentration data were converted to a flux by means of the gradient of the linear regression with respect to time. All fluxes reported in this study are temporally and spatially upscaled to units of g CO_2 m^{-2} h^{-1}.

After a dark (i.e. R_{eco}) reading is taken, the chamber is removed from the ground and purged to ambient CO_2 concentrations, in the same way as previously. During this time the surface of the plot is exposed to the air and any greenhouse warming of the surface should reduce or dissipate entirely during this time. Following on from purging the PVC cover is removed from the chamber and the chamber is reintroduced to the gas collar. The device is run once again for the same measurement interval with the same equilibration time and sampling interval as for the dark reading. With light now entering the chamber the vegetation inside will be able to photosynthesise and as such this reading will represent the NEE flux as both photosynthesis and ecosystem respiration are on-going. During both readings, light and dark, the PAR and air temperature gauges located within the CPY-2 chamber were active and readings were recorded from these at the same sampling frequency as CO_2 concentration readings.

It is not possible to prevent respiration from occurring; consequently, it is not possible to directly measure P_g however P_g can be estimated from the difference between the R_{eco} and NEE fluxes given equation 2.2.2.2.1. This thesis employs the following sign convention when reporting CO_2 flux; that all CO_2 fluxes are stated relative to the atmospheric pool of CO_2. Accordingly, a net sink of CO_2 into peat has a negative sign as it represents of loss from the atmospheric pool, vice versa for a source.

$$\mathrm{Pg{=}NEE{-}Reco} \qquad \textbf{Equation 2.2.2.2.1}$$

When estimating P_g in this fashion and then regressing these values against R_{eco} or NEE, it is important to note the potential for self-correlation. A self-correlation occurs when two variables are correlated when they both contain a shared component. For example, suppose we wish to correlate A to B, where A = x and B = x + y obviously in this case both A and B contain the component x, thus some of the magnitude of the correlation found could be due to this shared component. Kenney (1982) used this hypothetical example to show how this self-correlation comes about mathematically. Kenney (1982) demonstrated that if you take two variables and then perform a regression between x (A) and x + y (B) that the coefficient of correlation between r_{AB} is given by equation 2.2.2.2.2:

$$\boldsymbol{r_{AB}} = \frac{\boldsymbol{1+r_{xy}(S_y/S_x)}}{\sqrt{\{\boldsymbol{1+(S_y/S_x)^2}\}}} \qquad \textbf{Equation 2.2.2.2.2}$$

where: r_{AB} is the coefficient of correlation between A and B, S_x and S_y are the standard deviations of x and y respectively and r_{xy} is the coefficient of correlation between x and y.

As x and y are totally independent, $r_{xy} = 0$. Substituting this into the equation and reducing accordingly yields the following relationship (equation 2.2.2.2.3):

$$r_{AB} = \frac{1}{\sqrt{\left\{1+\left(S_y/S_x\right)^2\right\}}}$$ **Equation 2.2.2.2.3**

As such, it can now be seen that for the case where $r_{xy} = 0$, that the coefficient of correlation between A and B is determined by the variance in x and y and will thus yield a non-zero result even if A and B are totally independent. This is the mathematical determination of self-correlation. It can be seen that where $S_x = S_y$ then $r_{AB} = 0.71$ and that as $Sy/Sx0$ then $R_{AB} \rightarrow 0$, i.e. that the magnitude of the variance in the shared term, x, relative to y is the most important feature determining the size of the artificial correlation.

In the work of Kenney (1982) this type of self-correlation was described as “spurious self-correlation” as it was the author’s contention that the entire magnitude of any correlation found in these circumstances is meaningless. However, this position was challenged by Prairie and Bird (1989). Their suggestion was illustrated with an example from anatomy. Suppose, that A is the weight of someone’s liver and B is their total body weight it follows that y = A – B, i.e. body weight minus liver weight. They assert that “…common sense would suggest that there is nothing wrong with examining the relationship between liver and body weight directly as they are the variables of interest”. This is because the relationship they are looking at can logically be expected to exist and that the problem of self-correlation is really a problem of errors. If both sides of a regression equation contain the same term then they will also contain the same measurement error term, which will correlate to itself and thus induce the observed self-correlation. However, despite this, some of the overall correlation magnitude will be ‘real’ and thus observed correlations between variables of this kind should not be dismissed too hastily. Instead they propose that three rules should be observed when performing regressions of this kind, they are; “1) they satisfy the assumptions of correlation analysis, 2) the variables are meaningful, that is, they represent the concepts of interest and not just a component of them, and 3) the variables do not share a large measurement error term”.

Kenney (1982) responded to Prairie and Bird (1989) suggesting that they had not addressed the mathematical necessity of self-correlation, but merely sidestepped the issue (Kenney, 1991). This argument was then addressed by Vickers et al. (2009) who proposed a method to separate the ‘real’ and artificial magnitudes of the correlation coefficients. Their method involved taking NEE and R_{eco} readings from an eddy covariance flux system and using the data to generate artificial, random R_{eco} values from a normal distribution, then applying equation 2.2.2.2.1 in order to estimate P_g. This estimate of P_g should be entirely random because the input data used to calculate it was randomised. This random P_g dataset was then correlated to the original R_{eco} dataset. Given the randomisation, the magnitude of any relationship found should, they contend, reflect the magnitude of the self-correlation. After estimating the size of the self-correlation a proper regression between the original R_{eco} and P_g datasets was carried out. The authors then took the correlation coefficient from the ‘random’ regression from the ‘real’ regression. This difference was then said to be the actual magnitude of correlation between the R_{eco} and P_g. Their results showed that self-correlation was significantly greater than zero on all occasions but that the magnitude of self-correlation was reduced by using independent measures of R_{eco} and P_g. They went on to conclude that there was no evidence in their study to refute the “strong causal relationship between assimilation and respiration”.

Lasslop et al., (2010), while agreeing that self-correlation is an important consideration, disagreed with Vickers et al.'s (2009) conception of the problem with respect to R_{eco} and P_g. They pointed out that P_g = NEE – R_{eco}, and thus R_{eco} is not a shared variable inside P_g, instead the measurement error on R_{eco} has been transferred from R_{eco} to P_g. They concluded that a better way to deal with self-correlation in the context of R_{eco} to P_g relationships would be to take independent measures of R_{eco} and NEE. Vickers et al. (2009) and Lasslop et al. (2010) were discussing eddy covariance CO_2 flux systems, where R_{eco} and NEE are not always independently measured. This problem is also an issue for the close chamber IRGA approach taken in this thesis. However, it is the measurement error on R_{eco} that causes the self-correlation. It is important to remember that a large part of measurement error is systematic (i.e. constant) and thus will not contribute to dataset variability. Therefore, these effects will not be manifest in the gradient of the linear equation but will instead affect the constant (i.e. intercept) term. However, a portion of the error on the R_{eco} reading will be random error, i.e. error that is not systematic. The magnitude of random error is difficult to characterise and thus no estimate can be given as to its size in the datasets presented in this thesis. Nonetheless, the standardised procedures employed to gather the data should minimise the potential for large errors in the data. Moreover, a number of data quality control techniques are employed in this thesis to reduce the potential size of dataset error further. The first such method is to remove outlying data points (descibed in section 2.4.1) which are most likely to be subject to large magnitude (relative to overall dataset variability) errors. The second method is removal of logically inconsistent data potins. This means that if a data point is either measured (e.g. R_{eco}, DOC) or estimated (e.g. P_g) with a sign (-/+) that is logically inconsistent with the sign convention adopted for that variable (i.e. getting a negative value of R_{eco}) then the data point is removed. This is because it is logically impossible for such a data point to be accurate and as such it is unambigously subject to some degree of error. Therefore, by removing such logically inconsistent datapoints, a large source of potential error is removed from the dataset.

In summary, it is acknowledged and highlighted that self-correlation is an issue when interpreting the results of R_{eco} to P_g regressions in this thesis. However, as the same measurement system and protocols were observed when determining R_{eco} and NEE fluxes, the size of the error of R_{eco} should be similar in magnitude to the size of the error of NEE, which was shown above to minimise self-correlation. In addition the 'worst case' scenario outlined by Kenney (1982) (equation 2.2.2.2.3) does not apply in this context as $r_{RecoNEE} \neq 0$. Thus while self-correlation remains a problem in this thesis, as it does in all other studies examining the relationship between R_{eco} and P_g when measured as a residual, the methodological set up and subsequent data quality controls have been designed to minimise this effect.

2.2.3 – Methane Flux Sampling

Methane fluxes were sampled on three occasions: January 2009, September 2009 and January 2010. On all occasions the following field procedures were followed.

Methane flux was sampled using a static closed chamber method similar to McNamara et al. 2008 and Wilson et al. 2009. In this method an opaque PVC chamber 30 cm in height and 15 cm in diameter was sealed to an existing gas collar by means of a rubber band fastening (15 cm diameter, 10 cm length), to ensure a gas tight seal. The chamber is then left for 40 minutes. During this time five, 20 ml, air samples were extracted from the chamber using a gas tight glass syringe (Hamilton 1010 10 ml gas tight syringe) via a self-sealing rubber septum (subaseal®), located in the centre of the top panel of the chamber, at regular ten minute intervals. This gas was immediately injected into a, pre-evacuated, gas tight air sample vial (VWR 20 ml clear glass gas vial) through a silicone septum (VWR 20 mm silicone septum).

2.3 – Laboratory Analyses

Most laboratory analysis undertaken in this study was on soil pore water samples as such a standard protocol was developed for the analysis of water samples. All water samples gathered were stored in 30 ml sterile containers (steralins; Greiner-Bio One 30 ml polypropylene steralin) and were kept refrigerated at less than 5°C until analysis. Prior to analysis samples were centrifuged (ALC PK121 Multispeed Centrifuge) for 10 min, at 4000 rotations per minute, to aid the settling of sediment.

Samples were then filtered, via either a Buchner funnel through 0.8 µm filter paper or a 0.45 µm syringe filter prior to pH/conductivity analysis (see section 2.3.4.1). After this any extract taken from a sample not filtered to 0.45 µm for any other analysis was filtered through a 0.45 µm syringe filter. These filtering procedures were undertaken so that all analyses on 0.45 µm filtered samples can be considered to represent an analysis of dissolved and colloidal material only. Indeed, Thurman (1985, pp 64) defines colloidal organic carbon as anything between 0.45 µm and 1.5 nm in size.

2.3.1 – Basic Water Quality Measurements

Prior to undertaking any analysis all water samples were centrifuged and filtered in the manner given above. After this the first, basic water quality measurements are taken. Details of this three stage process are given below.

2.3.1.1 – pH/Conductivity Measurement

Firstly, a conductivity reading is taken using a Hanna Instruments Multi-Range Conductivity meter (model number 9033). The probe is bathed in de-ionised water between and prior to taking readings. Once placed into the sample the probe is given time to equilibrate, with a reading only being recorded once the value given has been stable for at least 2 min.

Following the conductivity reading a similar process is employed to measure the sample's pH with a Hanna Instruments pH meter (model number 9025). Again, the probe is bathed in de-ionised water between and prior to taking readings. An equivalent equilibration time is observed with this probe also.

In order to ensure the accuracy of the results obtained both the conductivity and pH probes were periodically (typically every week) calibrated in manufacturer supplied buffer solutions. Moreover, both probes were bathed in hydrogen peroxide (H_2O_2) on a monthly basis in order to remove any build-up of organic material which may affect the accuracy of the results obtained.

2.3.1.2 – UV-Visible Spectrum Absorbance Readings

After pH and conductivity analysis had been performed, a suite of UV-Visible spectrum readings were taken using a spectrophotometer (Jenway 6505 UV/Vis. Spectrophotometer). These readings were conducted at the following wavelengths: 400 nm as a basic water colour measure and; 465 and 665 nm, the ratio of which can be used to determine the E4:E6 ratio of the sample which is known to be a proxy (Thurman, 1985, pp 314–315) for the degree of humification of the sample, and is thus a basic measure of DOC composition.

All readings are taken with a clear plastic curvette (Kartel 4.5 ml Micro-Curvette), using the same curvette for each sample in order to minimise measurement errors. A blank (i.e. de-ionised water) sample is run at the start and subsequently every 12 samples in order to correct for drift on the machine.

2.3.2 – Determination of Soil Pore Water Anion Concentrations

Water samples were analysed for their anion concentrations using an ion chromatography method (Metrohm 761 Compact IC). This method required 5 ml of sample to be filtered into a plastic vial.

The vial was then placed into a metrohm auto-sampler (Metrohm 813 Compact Auto-sampler and Control Panel) and a sample queue was then constructed on the Metrohm IC Net 2.3 software.

The machine was set up for the following anions: fluoride, chloride, bromide, nitrate, phosphate and sulphate. The IC system used for this analysis was a suppressed system employing a chromatography column (Metrosep A supp 5) with a pulsation dampener using a 1.3 mmol/L Na_2CO_3 and 2.0 mmol/L $NaHCO_3$ solution as the baseline eluent, supressed with 50 mmol/L H_2SO_4 with de-ionised water as the diluent.

Once executed, all sample queues started with a calibration blank followed by a set of four standards from 1.25 ppm to 10 ppm of each anion being analysed (doubling in concentration each time) followed by another calibration blank. A set of 12 samples (i.e. two normal sized sites) followed these followed by a calibration blank. A set of standards was run every time a new queue is executed and/or every 100 samples.

If the machine had been sat idle and/or when the machine had been running continually for a long period of time, cleaning solutions, of 10x the concentration of the eluent solution, were run in order to clear any build-up of organic material in the Teflon and PEEK capillary tubing. Baseline testing runs (> 20 min duration) were undertaken while populating each sample queue to ensure the machine had equilibrated prior to beginning analysis.

2.3.3 – Dissolved Organic Carbon Analysis

Dissolved organic carbon (DOC) concentrations were determined by the colorimetric method of Bartlett and Ross, (1988). For this method a developing solution containing the following reagents is created: 0.1 M sodium pyrophosphate, 0.5 M sulphuric acid, 0.1 M potassium permanganate and 0.1 M manganese sulphate.

Two millilitres of sample (diluted with de-ionised water either; 0, 4 or 8x depending on colour), is added to one millilitre of developing solution in a test tube. Samples with more than 60 mg C l^{-1} of DOC require dilution as this test is only sensitive to this level. The developing reaction is then activated by the addition of one millilitre of 98% (concentrated) sulphuric acid. Once activated, the dark ruby red colour of the developing solution will lighten in the presence of oxidisable organic carbon. Any solution containing more than 60 mg C l^{-1} of DOC will lighten to be completely clear and indistinguishable from a calibration blank of de-ionised water. The samples are left to develop for 18 hours.

Once the developing time has elapsed each sample is analysed in a visible spectrum spectrophotometer (Camspec M202 Visible Spectrophotometer) at 495 nm wavelength. The samples are placed into the device in a transparent plastic cuvette. The device is calibrated using a de-ionised water blank, with a blank being run at the start and then every 12 samples. The same curvette is used for each sample and blank to avoid errors associated with slight differences in curvette wall transparency. The curvette is cleaned between samples with de-ionised water.

In order to determine the concentration of DOC in units of mg C l^{-1} a calibration curve is created using a set of standards of known concentrations of oxalic acid ($H_2C_2O_4$): 0 (i.e. deionised water), 7.5, 15, 30 and 60 mg C l^{-1}. Each standard is run in duplicate and using the same reagents as the samples. All calibration curves were required to have an R^2 of greater than 99% or else the developing solution was re-made and the samples re-analysed.

2.3.4 – Determination of Soil, Vegetation and Litter C and N Contents

The vegetation, litter and peat samples taken for C and N content measurement were kept refrigerated until analysis. Firstly, they were dried in an oven for 48 hours at 55°C so that any subsequent weights taken would represent dry weights. After drying all samples were ground to < 2 mm grain size in an agate pestle and mortar set. Samples were subsequently analysed for their carbon and nitrogen (CN) contents on a Costech ECS 4010 elemental combustion system set up for CN analysis, with chromium (III) oxide/silvered cobaltous-cobaltic oxide catalysts in reactor one and reduced, high purity copper wire in reactor two. Helium was used as the carrier gas. A porous polymer 3m GC column was used for the separation of the gases. A thermal conductivity detector (TCD) was used to measure the signal intensity of each sample. Calibration curves with a known standard were created using laboratory standard purity Acetanilide. The machine was checked for drift by running a known quantity of standard every 12 samples. All calibration curves had an $R^2 > 0.9999$.

2.3.5 – Methane Flux Measurement with Gas Chromotography

Once collected the methane gas samples were analysed within two weeks using the method described below. For each vial a 1 ml sample of gas is extracted using a gas tight syringe (SGE 1 ml glass syringe) and injected into a gas chromatography system (Carlo ERBA HRGC 5160, CE Systems, UK) through a silicone septa that was replaced every 25 samples. The injector and oven components of the system were run at constant temperatures of 250 and 350 ^{o}C respectively. The carrier gas used was helium and the column used was a pot fused silica capillary column (30m x 0.33 mm; Chrompak, UK). Methane was detected using a flame ignition detection (FID) system and quantified on the basis of chromatogram peak area calibrated to a range (1.25, 2.5, 5 and 10 ppm) of CH_4 standards, diluted from a calibration grade (BOC 10 ppm Methane Calibration Gas) gas standard. The flux rates of methane from the collars were then estimated by the approach given in section 2.4.2.

2.4 – Data Analyses

This study made use of two principal programs for manipulating and analysing datasets. Firstly, Microsoft Office Excel (2010 release) was employed to store, sort, categorise and produce simple graphs and tables of the datasets gathered. Secondly, Minitab (version 14) statistical software was employed to undertake complex statistical analysis and modelling and to produce more complex graphs and figures. All spatial projections and visualisations of the data gathered in this thesis were produced using ArcGIS software.

2.4.1 – Analysis of Variance (ANOVA) and Analysis of Covariance (ANCOVA)

The principal objective of ANOVA and ANCOVA techniques is to test whether the means of various experimental/observational conditions (known henceforward as factors) are significantly different for a given dependent variable (e.g. R_{eco}). ANOVA modelling calculates how much dataset variation can be attributed to differences between the means of the factors (known as interactions) and their respective factor levels (known as main effects) in a given dependent variable. From this a main effects plot can be constructed showing the means for each factor level versus the overall dataset mean. By examining factor level errors ANOVA determines what the probability is that the differences observed between means would occur by chance. The term ‘factor’ has a number of different meanings both within and outside statistics. As such, it is important to note that the term ‘factor’, in this thesis, is exclusively defined as a categorical variable (i.e. non-numeric) used in ANOVA/ANCOVA models. The approach to ANOVA and ANCOVA analysis chosen in this study is the general linear model (GLM) which postulates that all variation within a dataset can be accommodated by the following equation; data = model + error, where; model is the dataset variation attributable to the factors being studied and error is any dataset variation unaccounted for by the model, also known as the residual error (Rutherford, 2001, pp 3).

ANOVA assumes a normal distribution and thus dataset normality is tested prior to analysis with the Anderson-Darling test. If a dataset was not normally distributed to a level of $p \leq 0.05$ then dataset transformations (e.g. taking the natural log) were undertaken to see whether they improved normality. In addition, it is often found that dataset normality was adversely affected by a small number of extreme values (i.e. outliers) which may represent gross error or highly abnormal real samples. In these cases, where outliers were biasing dataset distributions these data were removed. The justification for this approach is that this study is interested in the typical effects of the factors it looks at and while very infrequent or non-repeating aberrant values may represent real events they are not representative of the general pattern of results and thus given their biasing effects it seems reasonable to discount them and indeed it seems likely that many of these points will represent large errors (relative to overall dataset variation). In cases where removal of outliers and dataset transformation still could not produce a normally distributed dataset, the dataset with the lowest Anderson-Darling normality statistic is chosen. This is because these datasets were the closest to being normal and their use, while not ideal, minimises potential error associated with the violation of the normality assumption.

A second important consideration when performing ANOVA/ANCOVA analyses is homogeneity of variances between factor levels (i.e. the error is evenly distributed between the factor levels). This assumption was tested using Levene’s test and a dataset failing this test was subject to the same outlier removal and transformation procedures as a dataset failing the normality test. Again, in the same way as for the normality testing, if all permutations of a dataset regardless of transformation or outlier removal failed the homogeneity of variances testing then the dataset which was closest to meeting this assumption, as quantified by Levene’s test statistic, was selected for analysis.

While datasets failing to meet the some or all of the assumptions of ANOVA are not ideal, it has been reported that interpretations of GLM-ANOVA/ANCOVA models remain “robust” with moderate amounts of assumption violation provided the factor level sample sizes are greater than five (Rutherford, 2001), which is the case for all analyses undertaken in this thesis.

ANCOVA is fundamentally the same as ANOVA; however, it involves an additional step not undertaken in ANOVA. The ANCOVA technique, will measure and remove the effects of a number of independent variables (e.g. air temperature) upon which the variable being studied (e.g. R_{eco}) is thought to depend, doing this prior to assessing for the main and interaction effects of the factors being studied. These variables, referred to in this thesis as covariates, are so named because the dependent variable in question is said to covary with them. This process is done using a multiple linear regression approach (see section 2.4.3) and is a useful technique to control for the effects of confounding variables that could not be controlled for as factors in the experimental design. By removing the effects of the significant covariates upon the dependent variable a residual dataset is created. The next step in the ANCOVA process is to carry out an ANOVA on the residual dataset. This method can now be thought of as a residual analysis.

Each experimental chapter contains a section detailing the experimental design used, but a general overview on the essential characteristics required from an experimental design for ANOVA/ANCOVA is given below. ANOVA/ANCOVA techniques are known as factorial statistical techniques as they account for the effects of factors on dependent variables. This study often sought to analyse for the effects of multiple factors on a dataset at the same time (e.g. vegetation type and month). In order to do this a factorial experimental design was employed for all experiments and observational studies in this thesis. A factorial experimental design requires that all the levels of one factor (e.g. vegetation type) are sampled within all the levels of the others factor(s) present (e.g. month). For the examples given above this would require that every vegetation type is sampled every month in order for the experimental design to be considered fully-factorial. When a design was fully-factorial the factors were said to be cross-classified with respect to each other. It should be noted, however, that there are limitations to the experiment design of some of the studies presented in this thesis that affect the way certain factors can be considered within the modelling ANOVA framework. Specific and thorough details of these limitations are provided in the experimental design sections of each of the experimental chapters of this thesis.

2.4.1.1 – Generalised Omega Squared (ω^2) Statistics

When producing a statistical model, like an ANOVA/ANCOVA model, the overall amount of variation the predictors jointly account for is given as the model's coefficient of determination or R^2 (see section 2.4.3). This value is useful to assess the overall appropriateness of the model but it does not give any information about the individual contribution of each factor, interaction or independent variable in the model as a whole. This information, however, is very useful when assessing which factors and/or covariates are the most important controls on a given parameter. As such, this study uses the generalised omega squared (ω^2) statistic to estimate effect sizes of factors and covariates in ANOVA/ANCOVA models.

The method and standard equations employed for calculating ω^2 are given in detail in Olejnik and Algina (2003). The choice of standard equation used to calculate an ω^2 statistic is dependent on the number of factors in the model and the number of between factor interactions being investigated. The statistic is calculated by finding the total amount of dataset variation accounted for by each given factor and subtracting from this the variation in the dataset ascribed to error. The next step is to divide the value obtained by the total amount of dataset variation. An example of a standard form equation, for a three factor (i.e. abc) model with no interactions, is given in equation 2.4.1.1.1. For factor a:

$$\boldsymbol{\omega_G}^{\mathbf{2}} = \frac{[(\boldsymbol{Seq\,SS_a - d_{fa} \times Adj\,MS_{error}})]}{[\boldsymbol{Seq\,SS_{total} + Adj\,MS_{error}}]} \qquad \textbf{Equation 2.4.1.1.1}$$

where: a is factor a, Seq SS_a is the sequential sum of squares for factor a, df_a is the degrees of freedom within factor a, Adj MS_{error} is the adjusted mean squared error of the model and Seq SS_{total} is the sequential sum of squares for the whole model.

2.4.1.2 – *Post Hoc* Testing

The output table of a GLM-ANOVA/ANCOVA analysis indicates the probability that the differences between factor level means found are due to random chance. This information is useful to determine whether significant (i.e. $p \leq 0.05$) differences exist within factors but it does not indicate where these differences lie between the individual factor levels. In order to acquire this information *post hoc* (i.e. post ANOVA) analysis is conducted on factors known to contain significant differences between factor levels.

In this thesis *post hoc* testing was performed using Tukey’s pairwise comparisons. This test compares, using matrices, all possible combinations of factor levels and calculates the probability that the differences found between the factor level means could be due to chance. This test has the same assumptions as the main ANOVA/ANCOVA test (i.e. data normality and homogeneity of variances) and thus the outlier removal and transformation processes undertaken on datasets violating these assumptions are relevant for this test also. This method is thought to be conservative (i.e. prone to type I errors) when comparing three means with unequal sample sizes (e.g. Keselman and Rogan, 1978). However, while this study does often have unequal sample sizes between factor levels, it has not been proven that Tukey’s test is conservative when looking at larger numbers of factor levels (Howell, 1992). As such, it should be noted that Tukey’s test is conservative for three, unequal level factors when interpreting the results of ANOVA/ANCOVA models but that this problem is less likely to affect factors with a greater number of factor levels.

2.4.2 – Gas Flux Calculations

As mentioned in section 2.2.2 the instantaneous CO_2 concentrations within the CPY-2 gas chamber were recorded at 4 s intervals, for 2 min, after the system equilibration time had passed. The data were recorded in .txt file format on the EGM-4 system. These files were downloaded from the IRGA to a PC using an RS-232 serial cable with ‘Transfer’ software supplied by PP-Systems. Once downloaded the files are converted to .xls format. From this equation 2.4.2.1 is used to convert the concentrations of gas into masses for each time interval sampled. From this a linear regression is performed, with respect to time, in order to calculate the flux of CO_2 in grams per unit surface area of the collar per unit time of flux measurement. These units were then spatially and temporally upscaled to give units of g CO_2 m^{-2} h^{-1}. On occasions where the system took longer than the allotted time to equilibrate the best fit part of the raw data file is taken to estimate the overall flux rate.

$$\boldsymbol{M_{gas} = [gas]\left(\frac{PV}{RT}\right)MR_{gas} \times 10^{6}} \qquad \textbf{Equation 2.4.2.1}$$

Where: M_{gas} is the mass of the gas being studied; [gas] is the concentration of the gas being studied in ppmv; P is the pressure within the chamber (taken to be equal to sea level air pressure in this research) in units of atm; V is the volume of the chamber in m^3; R is the universal gas constant in units of m^3 atm K^{-1} mol^{-1}, T is the chamber air temperature in K and MR_{gas} is the molecular weight of the gas in question.

This process has been automated in this thesis using a 'flux calculator' spreadsheet developed by another member of the research group (Rowson, 2009, upublished speadsheet). This spreadsheet takes the raw data from the .txt IRGA output files and calculates individual fluxes for each collar by linear regression. It uses an iterative process to maximise the R^2 of the fitted regression by removing data points (to a maximum of 25%) from the beginning of the record. Data are removed to minimise any potential initial disequilibirum effects that may affect the accuracy of the flux calculated. Prior to the creation of this tool, data were removed by visual inspection. This procedure is subjective and may vary between users and as such data removal by the spreadsheet method commends itself as a more objective method for calculating CO_2 flux rates.

The method given above was also used to estimate the flux of methane with masses of methane being calculated with equation 2.4.2.1 and then the gradient of the linear regression with time being temporally and spatially upscaled to give the desired units.

2.4.3 – Multiple Linear Regression (MLR) Analysis

Multiple linear regression (MLR) is the process by which a model is constructed to predict/desrcibed variation in variable y in terms of k numbers of predictors $x_1 … x_k$. assuming that y responds in a linear fashion to the x variables. The process has the general form given in equation 2.4.3.1 and the model constants and coefficients are estimated by a least squares method (i.e. minimising the sum of squares error of the model). This process, like ANOVA/ANCOVA assumes that the data are normally distributed and the same outlier removal and transformation processes as for ANOVA/ANCOVA were employed in this study to improve normality where datasets were non-normal.

$$\hat{y}_i = b_0 + b_1 x_{i,1} + \cdots + b_k x_{i,k} + \hat{e}_i \qquad \textbf{Equation 2.4.3.1}$$

where: yi is the predicted value of i^{th} y data point, b_0 is the regression constant (equivalent to the intercept in the linear equation), b_k is the regression coefficient for the k^{th} x dataset, $x_{i,k}$ is the i^{th} value of the k^{th} x dataset, ei is the residual error term, estimated by equation 2.4.3.2 and k is the total number of significant predictors (i.e. x datasets).

$$\hat{e}_i = y_i - \hat{y}_i \qquad \textbf{Equation 2.4.3.2}$$

where: ei is the estimated residual error term, y_i is the i^{th} observed y data point and yi is the i^{th} y data point predicted by the regression.

For well-fitting models the size of the residual error term should approach zero. In addition, the distribution of the residual y dataset can yield important information about the adequacy of the MLR model. For example, if the residuals of y plotted against some other dataset, say x_z, are randomly distributed then it is likely the residuals represent only random (i.e. non-systematic) error. However, if the residuals of y are distributed in a systematic way about x_z, (e.g. linear, logarithmic, trigonometric, bi-modal distributions) then it is likely that some of the residual variation can be attributed to another, as yet, unmodelled variable, unknown bias or non-random (i.e. systematic) error.

For all statistical analyses, including MLR and ANOVA, the goodness of fit of the model is quantified using the squared coefficient of correlation, known as the coefficient of determination (R^2). This parameter is a measure of the proportion of dataset variability in y that is accounted for the predictors $x_1 \ldots x_k$ and is a crude measure of how well future outcomes would be predicted by a given MLR model. R^2 values are calculated between 0 and 1, where 0 denotes no correlation at all and 1 denotes perfect correlation. This value is often multiplied by 100 in this thesis to express it as a percentage of dataset variation.

When fitting a model to the response variable Minitab 14 employs a least squares approach to minimising error for single predictor models. In MLR models, where the number of predictors is greater than one, a partial least squares approach is taken. The regression method employed is backwards, i.e. all of the possible predictors are included in the initial model. Predictors that are insignificant are removed from the model and an iterative process takes place until all that remains in the model are significant predictors. This method was chosen to avoid bias as it makes no assumptions about the final model composition and treats all predictors equally. Where appropriate, simple single predictor regressions have been carried out in order to better characterise the relationships between key variables. The models reported in this thesis are the final model iterations and as such if a given predictor is not in a model then a significant relationship with the response variable was not found. Vice versa any predictors given in a model in any part of this thesis will be significantly related to the response variable.

2.4.3.1 –Partial Correlation Coefficients

As mentioned in section 2.4.1.1, when producing a statistical model, it is often interesting to know what the effect size (i.e. the individual contribution) of a given factor or variable is to the overall dataset variability. For ANOVA/ANCOVA generalised omega squared (ω^2) statistics are computed for this purpose, however, this approach is not valid for MLR models and instead squared partial correlation coefficients are determined.

A squared semi-partial correlation coefficient is calculated by finding the R^2 of a linear regression model between the predictor in question (x_k) and the residual y dataset after the effects of all the other significant predictors in the main MLR model have been removed. This approach yields a value that estimates the proportion of dataset variation in y accounted for by dataset x_k when the effects of all other x datasets (i.e. significant predictors) are held constant. As this value is a special form of the coefficient of determination it is calculated as a value between 0 and 1 and is quoted in this thesis as a percentage.

It is important to note that semi-partial regression coefficients (and generalised omega squared statistics) are completely unrelated to statistical significance. Semi-partial regression coefficients are a measure of the relative importance of predictors within an MLR model. As such, they do not give any information regarding how probable it is that the relationship presented is due to chance. As stated above all of the statistical analyses employed in this thesis are presented with a p-value, determined by Minitab, and no model/predictor is shown unless it has a p value of less than or equal to 0.05. Moreover, it is possible to identify a statistically significant relationship between two variables that has a small semi-partial regression coefficient/ coefficient of determination/ generalised omega squared statistic. This should be borne in mind when inspecting the results given later in this thesis.

3 – The Role of Altitude

3.1 – Introduction

Understanding, characterising and accurately modelling the global carbon cycle is an increasingly important area of scientific endeavour. The framework of science regarding contemporary climate change and its forcings is expanding rapidly. Furthermore the growing consensus identifying anthropogenic carbon emissions as the principle driver of such changes (IPCC, 2007) makes studies of carbon cycling all the more timely and relevant.

Since the last deglaciation soils globally have acted as large carbon sinks with an estimated 770 Gt C sequestered into all soils from the atmosphere over this period (Faure et al., 1996). Of all soil types worldwide, peats hold the most carbon both in terms of concentration and mass. Peatlands are global in extent, occurring at all latitudes from equatorial rainforests to sub-Arctic/Antarctic bogs and mires. Joosten, (2009) estimated that in 1990 about 2.54% of the earth's surface was defined as peatland, accounting for around 453 Gt C stored therein. Within that study the United Kingdom (UK) was estimated to hold 1.75 Gt C in its peatlands which is thought to account for 14.8% of the surface area of Western Europe's soils with greater than 25% soil organic carbon concentrations (Montanarella et al., 2006).

As discussed in chapters 1 and 2, the post glacial climate and geomorphology of the UK provided an ideal environment for the formation of ombrotrophic blanket peatlands on top of the impermeable, surficial glacial strata. These peatlands account for 86.8% of the peatlands on the island of Britain (Lindsay, 1985). Aside from being latitudinally (i.e. hydro-climatically) controlled and, in contrast to other peatland types (e.g. fens), blanket peat bogs are draped across the landscape and thus span fairly large variations in altitude (i.e. span large vertical distances relative to sea level) within relatively constrained geographical areas. Moreover, they occur on comparatively steep inclines of up to 18° (Taylor and Tucker, 1968). This is in contrast to the relative flatness of lowland fen peatlands, the next most common UK peatland type (Charman, 2002, pp 80).

Blanket peat formation is controlled by a number of variables. Lindsay et al., (1988) defined the limiting conditions for ombrotrophic mire (i.e. blanket peat) formation in the UK as: an annual precipitation above 1,000mm, >160 rain days per annum, warmest month mean temperature <15°C and limited seasonal variability. UK blanket peat occurs in the uplands; however, the average basal elevation of first blanket peat occurrence decreases as latitude increases, such that the average basal occurrence in the South Pennines is ~500m above sea level (asl) but 0 m asl in the Shetland Isles (Evans and Warburton, 2007). This altitude effect is due to differing regional water balances in the UK, with roughly equal amounts of rainfall but differing mean temperatures. Given the fact that UK peatlands are dominated by blanket bogs, they will be subject to variability in altitude.

Altitude is thought to play a crucial role in controlling the rate of erosion in actively eroding blanket peat bogs in the South Pennines. Bower (1961) demonstrated that the degree of dendritic style gully erosion increases with increasing elevation, reporting generally increased amounts of erosion on both the flat lying and sloping faces as elevation (i.e. altitude) increases. Evans et al. (2006) established that in actively eroding blanket peat bogs fluvial fluxes of particulate organic carbon (POC) are the largest single carbon flux from the system. Given that erosion is concentrated at higher elevations, it can be seen that altitude has a major impact on carbon flux in the uplands.

Environmental lapse rates, with increasing rainfall and decreasing temperature, exist between the uplands and lowlands of the U.K. A lapse rate is simply the rate of change in a given environmental variable (i.e. temperature, rainfall etc.) with changing altitude. These lapse rates have been shown to vary both spatially and seasonally (Burt and Holden, 2010). As rainfall, air and soil temperature, and soil moisture variations are known to control CO_2 flux from soils (Lloyd and Taylor, 1994; Riveros-Iregui et al., 2007; Sottocornola, 2010; Zhao et al., 2006), carbon budget models for peatlands have begun to take these lapse rate effects into account (e.g. Worrall et al., 2009a).

Furthermore Gerdol et al. (2008), established that summer temperature was more effective at controlling CO_2 exchange than experimental fertilisation in an Alpine bog. In addition to temperature, it has been shown that increasing nitrogen deposition on mesotrophic bogs caused reduced CO_2 fluxes due to increasing acidification (Aerts and de Caluwe, 1999). As nearly all nitrogen inputs to ombrotrophic bogs come from rainfall, variations in rainfall amounts with changing altitude have the potential to alter the nitrogen deposition rate between differing elevations, which may in turn affect CO_2 flux. Rainfall totals have been changing in recent decades with increases in the amount of upland winter rain and decreases in the amount of upland summer rains (Burt and Ferranti, 2012).

Thus it is expected that altitude would have an effect upon carbon fluxes and consequently the carbon budgets of blanket peatlands due to environmental lapse rates effects. However, it is currently unknown whether any additional altitudinal effects exist besides those due to the environmental lapse rates already accounted for. Put another way, is there a residual affect attributable to altitude whose magnitude is not explained by the environmental variables that exhibit lapse rate effects or for which information is lacking on possible lapse rates?

Elevation data is easily obtainable, in the form of digital elevation models, for carbon budget modelling purposes. As such the addition of altitude as a model parameter may, should an altitudinal effect exist, improve the accuracy of landscape carbon budget models without greatly increasing their input requirements. Therefore, this study aims to determine whether altitude (when used as a covariate) has a significant relationship to CO_2 flux on upland blanket peat. This analysis is to be carried out on two different datasets, details given below:

(i) A longitudinal dataset of CO_2 flux on various sites of differing vegetation types, which span a range of altitudes, spread across the Peak District and South Pennies of Central England.

(ii) A dataset gathered for one seasonal cycle along an altitude transect, on a single hillslope, in one vegetation type, which has been unmanaged (i.e. no burning) for more than five years, within the Goyt Valley area in the Southern Peak District of Central England.

The hypotheses being that:

H_0 – no statistically significant relationship between CO_2 flux (i.e. R_{eco}/NEE) and altitude is apparent.

H_1 – a statistically significant relationship between CO_2 flux (i.e. R_{eco}/NEE) and altitude is apparent.

3.2 – Experimental Design

Data were gathered for this study using the methods outlined in chapter 2. The following variables were measured: CO_2 flux (R_{eco}, NEE and P_g); air temperature; PAR; water table depth; C:N ratios for vegetation, litter and soil; and soil pore water DOC concentration. As stated above, two analyses were carried on different datasets to determine the effect of altitude on the carbon fluxes from upland blanket peat.

Experiment I sought to test whether any effect of altitude is apparent in a large dataset of CO_2 exchange, gathered to study the effects upland restoration and vegetation on CO_2 exchange and water quality, from sites widely distributed around the Peak District and the South Pennines (table 3.2.1). This dataset has the benefit of being long (over three years for some sites), regular (all sites sampled monthly during their period of operation), sampling a wide range of altitude (251 m range, between 617 and 366 m asl) and included a broad range of upland vegetation types (*C. vulgaris*, *Eriophorum* spp., *Sphagnum* spp., non-*Sphagnum* Mosses i.e. *Polytrichum* spp*.*, *Hypnum* spp. etc., and bare peat). Although not all sites were established at the same time all sites within this experiment were monitored for a minimum of twelve months. The non-*Sphagnum* moss dataset was compiled from data from a number of moss genera (primarily *Hypnum* spp. with some *Polytrichum* spp.) which on their own would not have constituted large enough datasets for analysis, but together are acceptable. While not of the same genus the moss types in this group are non-peat forming and the comparison with the peat forming *Sphagnum* spp. group is considered to be useful in this respect.

Experiment II was designed to assess whether any effect of altitude was evident on an individual hillslope scale. There was a trade-off in selecting a hillslope for consideration in this study as whilst a large span of altitude was desired it was also essential that there was no variation in vegetation or land management down the hillslope. As such the hillslope which best matched these conditions has a relatively small altitudinal range (69 m) compared to the altitudinal range of some of the vegetation groups considered as part of experiment I (e.g. 251 m for bare peat); however, it was comparable to some of the other datasets in experiment I (e.g. 72 m for *C. vulgaris*). Moreover, the hillslope selected was located in the Goyt Valley of the southern Peak District, England, one of the most southerly occurrences of blanket peat in England. Its altitudinal range spanned between 447 and 378 m asl (figure 3.2.1) and is well below the average 500 m basal extent of peatland occurrence typical for Peak District blanket peats (Evans and Warburton 2007). As such the site is considered to be climatically marginal, with respect to other Peak District blanket peat, and should therefore be more sensitive to environmental variations than blanket peats in more climatically favourable areas.

Table 3.2.1 – Sites used in the Altitude Study by Vegetation Type

Vegetation	Site	Collar(s)	Locality	Altitude (m asl)	Region
Bare	BVD	1	Bleaklow Plateau	521	Peak District
	JPG	1		568	
	Pen	2		507	
	TE	5		617	
	TN	6		608	
	TS	6		614	
	Moss	1	Goyt Valley	449	
	S2:b	1	Green Withens	366	South Pennines
	S2:c	1		368	
	S2:d	1		374	
	BA:b	1	Keighley Moor	411	
	BB:d	1		413	
Eriophorum spp.	BVD	4	Bleaklow Plateau	521	Peak District
	Ori	6		613	
	Pen	4		507	
	Ben	1	Goyt Valley	430	
	GS1	1		451	
	Kra	2		431	
	Moss	2		449	
	Nep	4		431	
	Pat	1		448	
	Pos	3		430	
	BB:a	1	Keighley Moor	425	South Pennines
	BB:b	1		414	
	SB	1		391	
Calluna vulgaris	WM	2	Bleaklow Plateau	468	Peak District
	WR	5		468	
	Ben	2	Goyt Valley	430	
	BN	2		432	
	BS	3		442	
	Kra	1		431	
	Nep	1		431	
	OB	5		430	
	Prom	4		456	
	BA:a	3	Keighley Moor	411	South Pennines
	BA:c	2		406	
	BA:d	2		396	
	BB:a	2		425	
	BB:b	2		414	
	BB:c	2		413	
	BB:d	1		413	
NS - Moss	BN	1	Goyt Valley	432	Peak District
	GS1	5		451	
	GS3	1		449	
	Kra	3		431	
	LA	2		412	
	LB	3		378	
	Moss	2		449	
	Pat	1		448	
	UB	1		438	
Sphagnum spp.	BVD	3	Bleaklow Plateau	521	Peak District
	Dory	3	Goyt Valley	441	
	Nemo	3		436	
	Nep	1		435	
	BA:c	1	Keighley Moor	406	South Pennines
	BB:c	1		413	
	SA	3		404	
	SB	2		391	

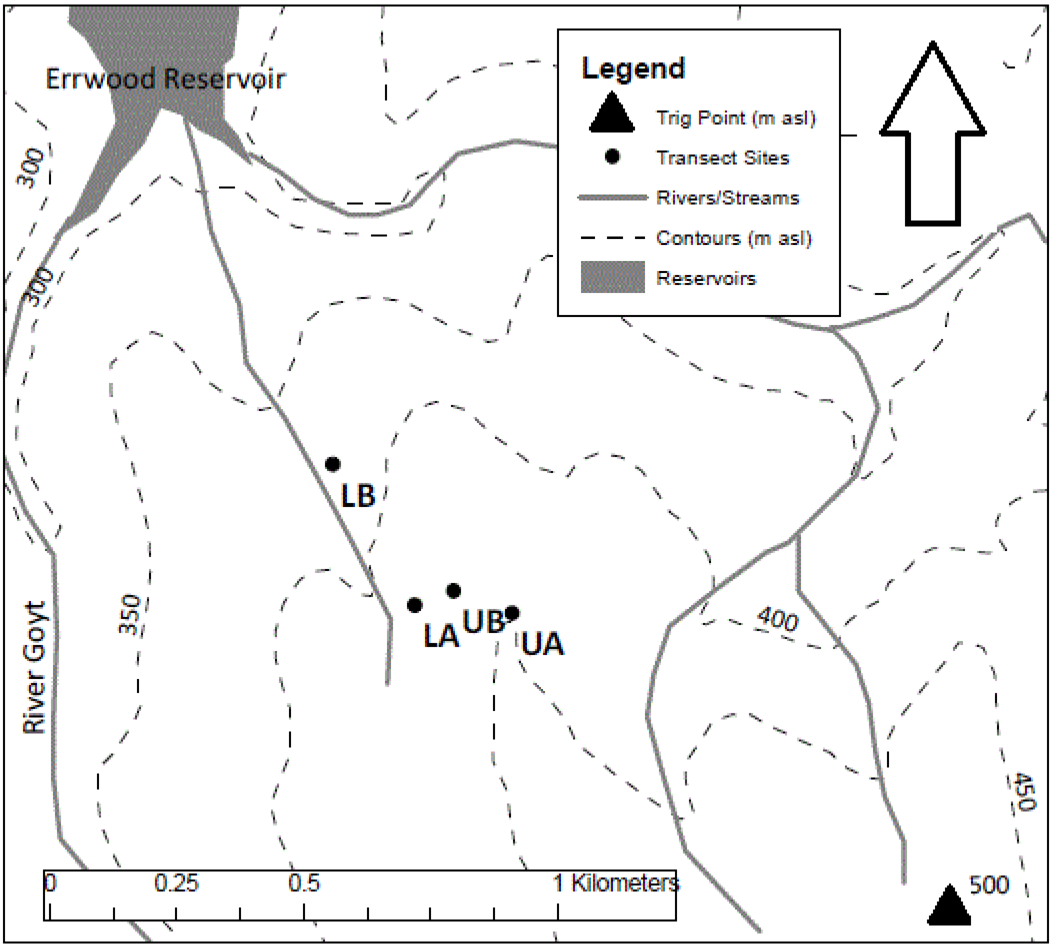


Figure 3.2.1 –Locations of the sites used for the altitude transect in experiment II.

Data were analysed by two methods (i) multiple linear regression (MLR) analysis with squared partial correlation coefficients calculated as a measure of the effect size of each variable in the model and (ii) ANOVA/ANCOVA with ω^2 statistics. All statistical analyses were carried out on Minitab statistical software (version 14) and the level of statistical significance was defined as $p \leq 0.05$ for all tests.

In order to find the best fit MLR/ANOVA models for CO_2 flux, both the R_{eco} and NEE response variables and the explanatory variables were considered both untransformed and natural log transformed. However, in most cases the untransformed data provided slightly better MLR model fits, as attested by the value of R^2. Thus, all results reported in this chapter are based on the untransformed response variable. As all results reported are based on untransformed datasets and predictive variables, an inter-group comparison of the regression coefficients of altitude versus carbon flux is possible. Covariates considered in each MLR/ANCOVA model, aside from altitude, are: surface slope (^{o} from horizontal), air temperature (K), *C. vulgaris* height (where appropriate) (mm), water table depth (mm), PAR (µmol m^{-2} s^{-1}) and P_g (where appropriate) (gCO2 m^{-2} h^{-1}).

ANOVA makes use of a number of different factors to attempt to account for as much confounding dataset variation as possible. In experiment I factors to be employed include: vegetation type, month, year, locality, region, orientation (aspect data split into eight categories i.e. N, NE, E etc.) and peatland morphology (see table 2.1.5). In order to minimise the potentially confounding effects of vegetation type, variation with altitude the dataset in experiment I was analysed both as an amalgam and as individual vegetation specific datasets. Looking at the site description tables (2.1.5 and 3.3.1.1), it can be seen that the dataset of each vegetation type is subject to differing factors and different factor levels than the others. For example non-*Sphagnum* moss is found only on one locality (Goyt Valley) whereas *C. vulgaris* is found on three, with these localities being nested within the two areas. As such the *C. vulgaris* dataset will likely be subject to more micrometeorological variation (due to the spatial separation of its plots) than the non-*Sphagnum* moss dataset. In order to ensure that variation attributable to these micrometeorological changes is not incorrectly attributed to altitudinal variation, the ANOVA/ANCOVAs will incorporate appropriate combinations of factors to the dataset’s particular experimental layout. The coding of these models will be reported in the tables presented. The ANOVA/ANCOVA models will be run iteratively with all appropriate factors considered at first, with insignificant factors being successively removed until a final, entirely significant, model is presented. Only the final model is presented in this chapter, so if a particular factor is not present in a model, it was that it is insignificant with respect to the particular response variable considered, not that it was not included in the first place. This final point is important to bear in mind when considering the results reported throughout this chapter and the rest of this thesis.

There are three primary types of factors considered in the models in this chapter: fixed factors, nested factors and random factors. Fixed factors are fully cross-classified with respect to each other, for example month and region. Nested factors are also cross classified, but due to the hierarchal layout of the experimental design, the factor levels of some factors, like locality, are nested within others, in this case region. In order to try to remove variation introduced by spatial separation of plots within the all data analysis, vegetation is to be considered as a nested factor within locality and sites. The principal limitation to this approach is that vegetation type is neither fully cross-classified with locality and area, nor is it fully nested within them (i.e. some vegetation types repeat between factor levels). By employing a nested design, the model will consider the same vegetation in different localities and areas to be different (whereas in reality it may not be), and as such will not compute an overall main effect for a given vegetation type. This introduces the risk of falsely attributing variation to locality and area which may in fact be better explained by differences in vegetation between these locations. If a nested factor is significant in a model but the fixed factor it is nested within is insignificant, the nested factor will then be considered as a fixed factor as there are no significant differences between the factor levels of the factor it is nested within. Therefore, locality may appear in results tables as a nested factor within region or where region is insignificant as a fixed factor alone. Random factors are factors that have incompletely sampled factor levels. For example, orientation is treated as a random factor as no datasets, with the exception of all data, sample all eight factor levels. This is also true for year, as the plots may have differing time series (table 2.1.5). As such, both of these factors are considered as random factors.

3.3 – Results

Bivariate plots and linear regressions of R_{eco}/NEE versus air temperature, water table depth and P_g/PAR are presented in figure 3.3.1. For R_{eco} it can be seen that strong correlations exist between R_{eco} and air temperature and P_g. A much weaker, but still significant, relationship is identified for water table depth. Air temperature was tested both untransformed and natural log transformed. It was found that the untransformed model was the better fitting. These bivariate regressions do not take into account the effects of any other significant covariates or factors and as such they should be thought as a simple first pass at the data. For NEE only a weak correlation is identified with PAR. However, once again this analysis does not control for the effects of any other significant factors or covariates and, moreover, NEE is a vector dataset (i.e. has both magnitude and direction) varying around zero which makes finding linear bivariate relationships, without taking other sources of variation into account, problematic.

Consideration also needs to be given to the apparent relationships between the response variables and altitude. These relationships are shown in figures 3.3.2 and 3.3.3 for R_{eco} and NEE respectively. For R_{eco} (figure 3.3.2) the bare peat, *Sphagnum* spp. and all data datasets showed a significant relationship with altitude. For NEE (figure 3.3.3); however, no significant relationships are identified by the bivariate regressions performed. That said, all of the insignificant trends identified are in the same direction with NEE becoming more negative with increasing altitude (i.e. respiration decreases with increasing altitude and/or photosynthesis increases with increasing altitude). This seems to agree with the R_{eco} data which showed that all significant trends and four out of the six trends overall had a negative sign, i.e. respiration decreases with increasing altitude.

Finally, as mentioned in the introduction to this chapter (section 3.1), environmental lapse rate effects may induce some of the altitudinal effects found (if any). As such, figure 3.3.4 shows the bivariate relationship between air temperature and water table depth versus altitude. From this figure it can be seen that, as would be anticipated, air temperature is strongly correlated with altitude, showing a decreasing trend with increasing altitude. This trend implies that temperature varies by ±1 K with every ±72.46 m change in altitude. This is equivalent to 1.38 K/100 m change in altitude, which is nearly twice as large as the 1991-2006 North Pennine (Moor House to Durham) annual average lapse rate of 0.77 K/100 m reported by Holden and Rose (2011). This discrepancy may be explained by the fact that only low-resolution, monthly, day time data were used to estimate the lapse rate in this study whereas a high resolution, diurnal dataset was used to create the Holden and Rose (2011) estimate. Water table depth does not show a significant relationship with altitude in this analysis.

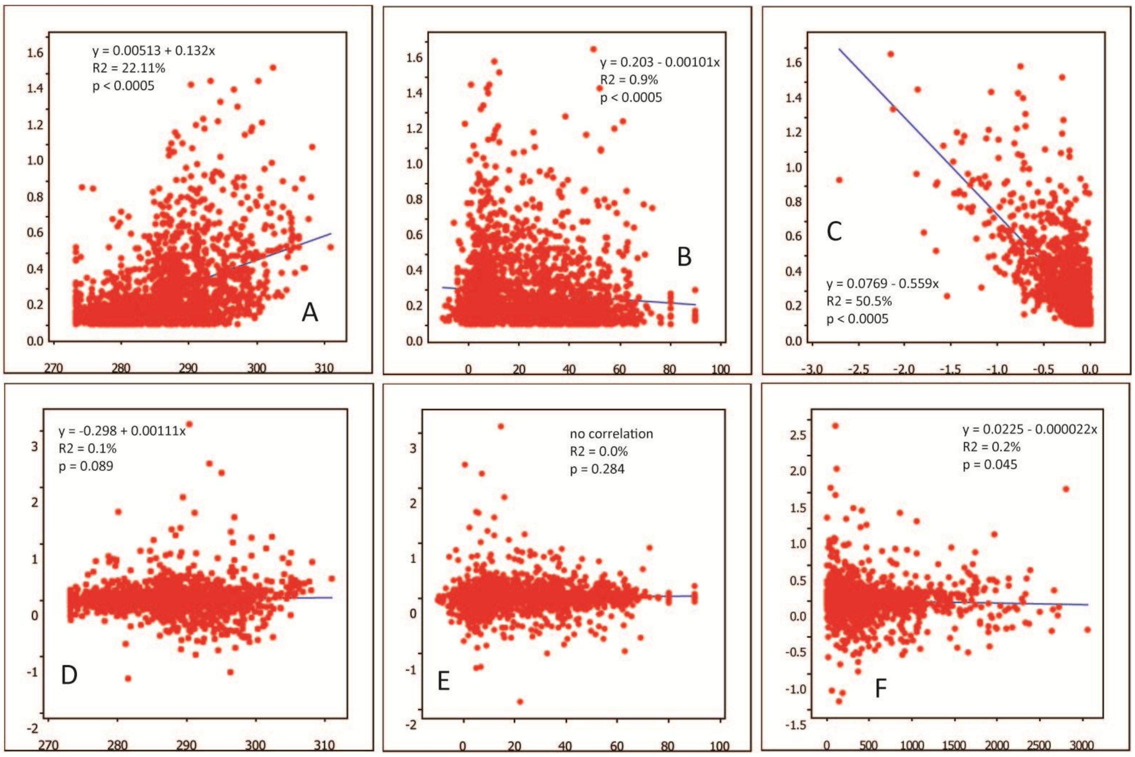


Figure 3.3.1 **–** Bivariate plots of; R_{eco} (g CO_2 m^{-2} h^{-1}) versus air temperature (K) (Panel A), water table depth (cm) (Panel B) and P_g (g CO_2 m^{-2} h^{-1}) (Panel C); and NEE (g CO_2 m^{-2} h^{-1}) versus air temperature (K) (Panel D), water table depth (cm) (Panel E) and PAR (µmol m^{-2} s^{-1}) (Panel F).

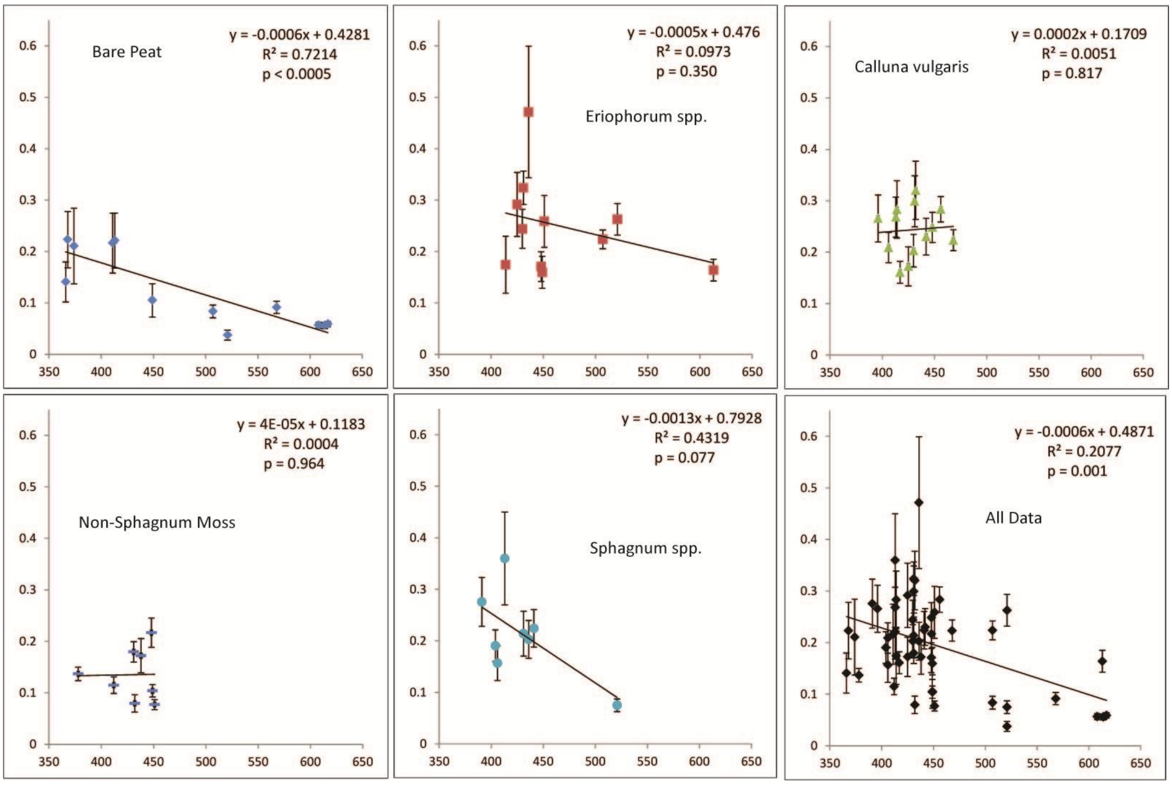


Figure 3.3.2 **–** Bivariate plots showing the relationship between mean R_{eco}($g\ CO_2\ m^{-2}\ h^{-1}$) at each altitude (m asl) sampled for: bare peat, *Eriophorum* spp., *Calluna vulgaris*, non-*Sphagnum* moss, *Sphagnum* spp. and all experiment I & II data. Error bars represent one standard error of the mean.

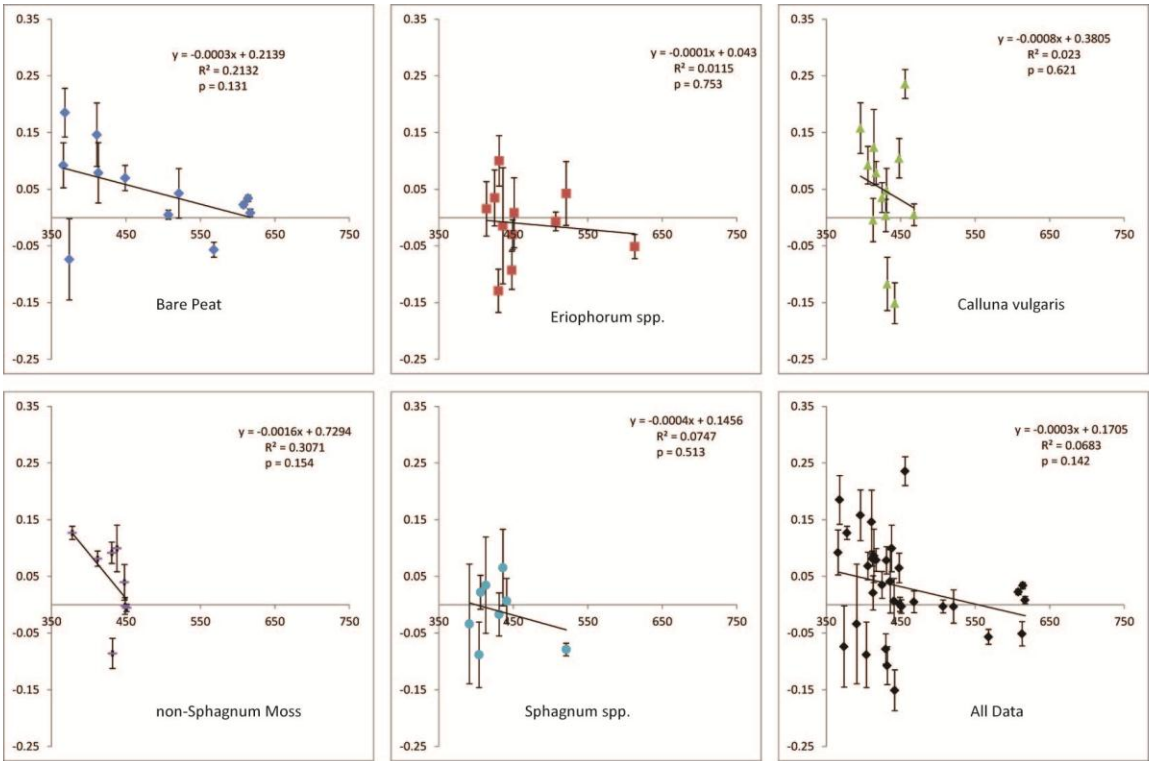


Figure 3.3.3 **-** Bivariate plots showing the relationship between mean NEE (g CO_2 m^{-2} h^{-1}) at each altitude (m asl) sampled for: bare peat, Eriophorum spp., Calluna vulgaris, non-Sphagnum moss, Sphagnum spp. and all experiment I & II data. Error bars represent one standard error of the mean.

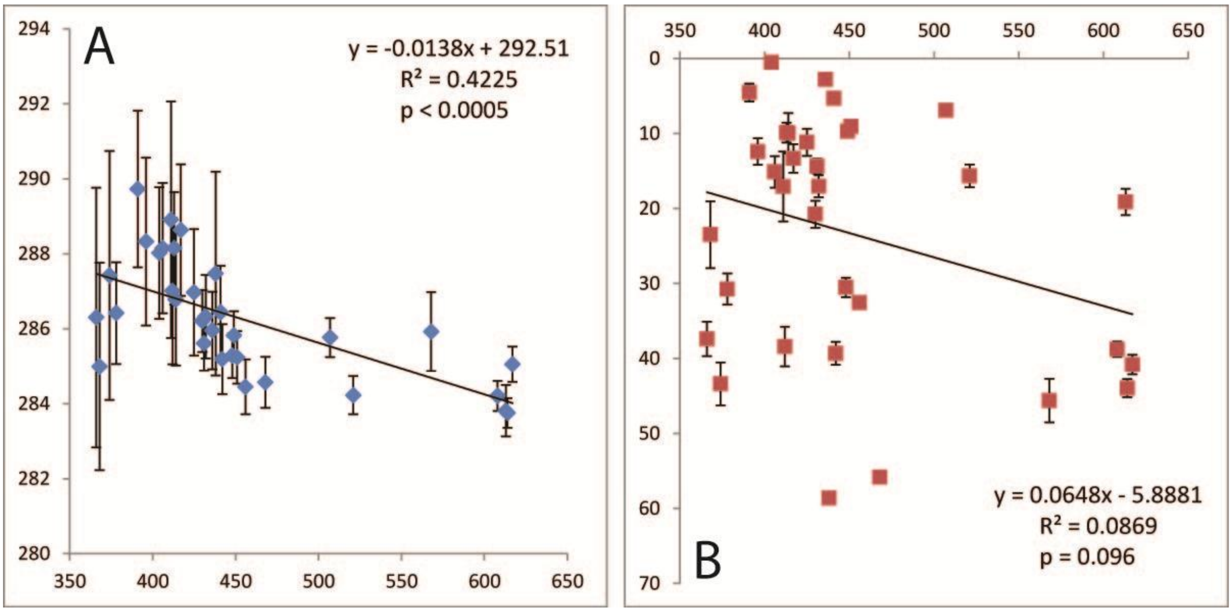


Figure 3.3.4 **–** Bivariate plots showing the relationship between altitude (m asl) and air temperature (K) (Panel A) and water table depth (cm) (Panel B). The error bars denote one standard error of the mean.

The amount of data removed prior to analysis of the datasets is below given, by dataset, in table 3.3.1.

Table 3.3.1 – Data removed by quality control measures

	Data Collected	Data Used	% Removed
WTD	2633	2487	5.55
PAR	2473	2292	7.32
AT	2561	2371	7.42
R_{eco}	2628	2237	14.88
NEE	2764	2512	9.12
P_g	2226	1938	12.94

3.3.1 – MLR Experiment I

Values of the average measured CO_2 fluxes (based on all monthly readings taken), altitudinal range and key environmental variables measured for each vegetation type are given in table 3.3.1.1. These results show that while CO_2 fluxes differ considerably between vegetation types while the environmental variables they were recorded under were similar.

Table 3.3.1.1 – Mean Dataset Values for Each Data Set and Experiment

		NEE	± Error	**R_{eco}**	± Error	**P_g**	± Error	**Alt Range**	**Air Temp**	**PAR**	**WTD**
Experiment	**Vegetation**			(gCO2 m^{-2} h^{-1})				(m)	(K)	(µmol m^{-2} s^{-1})	(mm)
I	All Data	0.021	0.005	0.176	0.004	-0.196	0.006	251	285.36	357.97	240.27
	Bare Peat	0.023	0.014	0.070	0.004	-0.071	0.004	251	284.59	342.53	363.58
	Eriophorum spp	-0.002	0.014	0.243	0.013	-0.302	0.016	199	285.46	328.46	125.17
	Calluna vulgaris	0.035	0.006	0.231	0.245	-0.247	0.013	72	285.28	378.86	302.72
	Non-*Sphagnum* Moss	0.035	0.006	0.116	0.124	-0.102	0.007	73	285.86	344.05	159.46
	Sphagnum spp	-0.021	0.019	0.177	0.188	-0.241	0.018	130	286.47	426.72	48.80
II	*Calluna vulgaris*	0.107	0.009	0.163	0.0104	-0.081	0.009	69	286.29	255.60	317.30

Multiple linear regression analysis of the Experiment I datasets identified a statistically significant relationship between altitude versus R_{eco} and NEE in the following datasets: all data, bare peat, *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* spp. A relationship was also identified in the R_{eco} dataset of *C. vulgaris*, but this effect was explained by the addition of *C. vulgaris* height (within the gas collar) into the MLR model. During the analysis when a significant relationship was identified between R_{eco} or NEE and altitude, the addition of air temperature into the model was not able to account for the full magnitude of the effect.

The relationship found between R_{eco} and altitude for *Sphagnum* spp. was the most sensitive to changes in altitude with a partial regression coefficient of -0.00097 ± 0.00019 $\Delta F\ m^{-1}$ asl ($p < 0.0001$, where F = CO_2 flux (R_{eco} or NEE) in $gCO_2\ m^{-2}\ h^{-1}$) with the least sensitive, but still significant, being bare peat. at -0.00031 ± 0.00005 $\Delta F\ m^{-1}$ asl ($p = 0.0011$). For the all data analysis the sensitivity was found to be -0.00039 ± 0.00005 $\Delta F\ m^{-1}$ asl ($p < 0.0001$). In all the cases where a significant relationship was found with altitude R_{eco} is predicted to get smaller with increasing altitude (i.e. less CO_2 is respired) (figure 3.3.1.1 and table 3.3.1.2) this agrees with the pattern seen in the bivariate regressions earlier in this section. In each case it is the multiple regression coefficient that is being reported (i.e. the effect of altitude when the effects of all other measured covariates have been held constant).

In the same pattern as R_{eco} the rate of NEE above *Sphagnum* spp. was the most sensitive to changes in altitude with a regression coefficient of -0.001032 ± 0.00019 $\Delta F\ m^{-1}$ asl ($p <0.0001$) and the least sensitive being bare peat (-0.00032 ± 0.00005 $\Delta F\ m^{-1}$ asl) ($p \leq 0.003$, 0.003 and 0.0001 respectively). In each case NEE is predicted to get more negative with increasing altitude (i.e. more CO_2 is sequestered) (figure 3.3.1.1 and table 3.3.1.2).

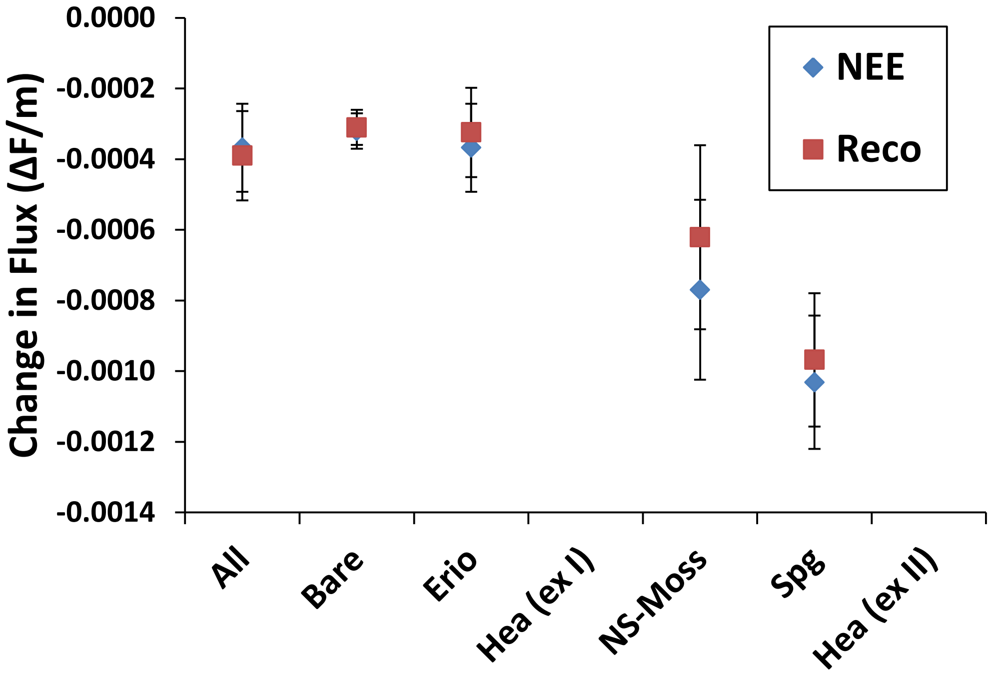


Figure 3.3.1.1 **–** All – all data, Bare – bare peat, Erio – *Eriophorum* spp., Hea (Ex I/II) – *C. vulgaris* (experiments I/II), NS-Moss – Non-*Sphagnum* Moss and Spg – *Sphagnum* spp. This chart shows vegetation/ground cover group carbon flux (F – gCO_2 m^{-2} h^{-1}) sensitivity to changes in altitude, where a statistically significant relationship was established by multiple linear regression analysis. Error bars represent one standard error from the mean.

Table 3.3.1.2 – MLR Results for CO$_2$ Flux by Experiment and Vegetation Type

		NEE					R_{eco}				
Vegetation	**Variable**	**Coefficient**	**± Error**	**P**	**% Variance Explained**	**n**	**Coefficient**	**± Error**	**P**	**% Variance Explained**	**n**
Experiment I - All Data	C	-2.46150	0.17220	<0.0001		1689	-1.69350	0.14400	<0.0001		1672
	P_g	0.54124	0.01421	<0.0001	46.30%		-0.46683	0.01415	<0.0001	39.40%	
	Air Temperature	0.00970	0.00060	<0.0001	13.10%		0.00692	0.00050	<0.0001	10.40%	
	PAR	-0.00006	0.00001	<0.0001	2.60%						
	Altitude	**-0.00041**	**0.00004**	**<0.0001**	**4.60%**		**-0.00039**	**0.00005**	**<0.0001**	**4.20%**	
				R^2	46.90%				**R^2**	57.30%	
Experiment I - Bare Peat	Constant	-0.9372	0.1548	<0.0001		500	-0.87460	0.15350	<0.0001		468
	P_g	0.47504	0.03802	<0.0001	23.90%		-0.51397	0.03868	<0.0001	27.40%	
	Air Temperature	0.0041	0.0005	<0.0001	10.60%		0.00380	0.00055	<0.0001	9.20%	
	Altitude	**-0.00032**	**0.00005**	**<0.0001**	**7.40%**		**-0.00031**	**0.00005**	**<0.0001**	**7.70%**	
				R^2	29.00%				**R^2**	44.30%	
Experiment I - *Eriophorum* spp.	Constant	-3.38530	0.42080	<0.0001		428	-2.21500	0.35560	<0.0001		434
	Air Temperature	0.01302	0.00148	<0.0001	15.50%		0.00870	0.00122	<0.0001	10.60%	
	PAR	-0.00011	0.00002	<0.0001	4.90%						
	P_g	0.58271	0.02840	<0.0001	49.40%		-0.48320	0.02735	<0.0001	37.40%	
	Altitude	**-0.00037**	**0.00012**	**0.0030**	**2.00%**		**-0.00032**	**0.00013**	**0.0110**	**1.50%**	
				R^2	51.20%				**R^2**	56.60%	
Exeriment I - *Calluna vulgaris*	Constant	-3.91110	0.40910	<0.0001		399	-3.36810	0.47710	<0.0001		435
	Air Temperature	0.01419	0.00147	<0.0001	19.30%		0.01049	0.00119	<0.0001	16.80%	
	PAR	-0.00009	0.00002	<0.0001	5.00%						
	Water Table Depth	-0.00105	0.00042	0.0120	1.60%						
	P_g	0.55803	0.02946	<0.0001	47.40%		-0.45858	0.03034	<0.0001	35.00%	
	Calluna Height	0.00487	0.00074	<0.0001	9.80%		0.00499	0.00076	<0.0001	10.90%	
				R^2	57.40%				**R^2**	56.80%	
Experiment I - Non-*Sphagnum* Moss	Constant	-1.22180	0.29120	<0.0001		144	-0.85380	0.26130	0.0010		145
	Air Temperature	0.00563	0.00089	<0.0001	22.60%		0.00407	0.00080	<0.0001	15.60%	
	PAR	-0.00004	0.00001	<0.0001	3.90%						
	Water Table Depth	0.00126	0.00054	0.0200	3.80%		0.00178	0.00055	0.0020	6.60%	
	P_g	0.56769	0.05007	<0.0001	47.70%		-0.41387	0.05232	<0.0001	30.50%	
	Altitude	**-0.00077**	**0.00025**	**0.0030**	**6.20%**		**-0.00062**	**0.00026**	**0.0180**	**3.90%**	
				R^2	61.30%				**R^2**	54.80%	
Experiment I - *Sphagnum* spp.	Constant	-1.7944	0.4554	<0.0001		175	-0.87230	0.37450	0.0210		169
	Air Temperature	0.008088	0.01615	<0.0001	12.90%		0.00470	0.00129	<0.0001	7.30%	
	PAR	-4.111E-05	2E-05	0.0410	2.40%						
	Water Table Depth	0.006157	0.001545	<0.0001	8.60%		0.00613	0.00149	<0.0001	9.30%	
	P_g	0.59943	0.04235	<0.0001	50.50%		-0.43817	0.04165	<0.0001	40.10%	
	Altitude	**-0.0010318**	**0.000189**	**<0.0001**	**15.00%**		**-0.00097**	**0.00019**	**<0.0001**	**13.80%**	
				R^2	57.50%				**R^2**	73.10%	
Experiment II - *Calluna vulgaris* Transect	Constant	-2.28910	0.32180	<0.0001		84	-2.22490	0.31390	<0.0001		84
	Air Temperature	0.00844	0.00113	<0.0001	40.70%		0.00823	0.00110	<0.0001	40.90%	
	P_g	0.43240	0.13680	0.0020	11.00%		-0.52650	0.12910	<0.0001	16.90%	
				R^2	42.00%				**R^2**	62.50%	

3.3.2 – MLR Experiment II

The average CO_2 flux and environmental data across all sites in experiment II is given in table 3.3.1.1. These data indicate that the average environmental conditions under which the dataset in experiment II was recorded are comparable to those in present in experiment I, except for PAR, which is slightly lower. As the *C. vulgaris* in experiment II was degenerate, and therefore the much taller than the; young *C. vulgaris*, bryophytes and graminoids in experiment I, the chamber was likely subject to more shading by the taller canopy. This is likely to have reduced the amount of PAR getting to the detector thus causing the lower average PAR seen in table 3.3.1.1. Details of the average CO_2 fluxes and C/N ratios from each site along the altitude transect are given in table 3.3.2.1.

Multiple linear regression of the transect data showed no significant relationship between R_{eco} and NEE versus altitude (table 3.3.1.2). Addition of the C/N data into the MLR models found no significant relationships with any CO_2 flux. The addition of *C. vulgaris* height into to the model also provided no significant relationships to any carbon flux measured. This is not surprising given the fact all *C. vulgaris* was degenerate and thus there was little variation in height between sites. Within the C/N ratio dataset the C/N values for *C. vulgaris* are greater (mean = 37.2) than the litter/*Hypnum* spp. values (mean for litter and *Hypnum* spp. respectively = 34.1 and 32.3) which are greater than the peat soil values (mean = 23.4).

Table 3.3.2.1 – Mean Dataset Values for Each Site in Experiment II

	R_{eco}	± Error	**P_g**	± Error	**NEE**	± Error	**Altitude**	**Peat C/N**	**Litter C/N**	***Hypnum* spp. C/N**	***C. Vulgaris* C/N**
Site			(gCO2 m^{-2} h^{-1})				(m asl)				
UA	0.1918	0.0252	-0.1006	0.0246	0.1083	0.0190	447	28.39	37.82	30.42	39.26
UB	0.2172	0.0274	-0.1042	0.0169	0.1081	0.0258	438	20.50	36.18	28.26	36.36
LA	0.1135	0.0123	-0.0614	0.0116	0.0861	0.0110	412	23.27	31.50	37.60	36.23
LB	0.1408	0.0130	-0.0424	0.0078	0.1268	0.0117	378	21.60	30.69	33.10	36.97

3.3.3 – ANOVA Experiment I

The results of the ANOVA aspect of this chapter for R_{eco} are summarised in table 3.3.3.1. This table is split into three distinct sections based on the structure of the ANOVA model run. The upper part of the table shows the results for the model that included all potential factors but only altitude as a potential covariate; the middle section shows the model that included all potential factors and all potential covariates excluding P_g and the bottom section includes all potential factors and covariates (i.e. including P_g). The section excluding P_g as a potential covariate was run in order to see the direct effects of the environmental covariates (like air temperature) on R_{eco} without any potential masking by the colinearities between P_g and environmental covariates. Moreover, given the potential for self-correlation between the P_g and R_{eco} datasets, having models with and without P_g presents the results with and without the assumption that the P_g-R_{eco} relationship is real.

The upper section of table 3.3.3.1 shows that a relationship with altitude is only apparent in the bare peat and all data datasets. The estimated sensitivities of the all data dataset (-0.00056 ± 0.00009 $\Delta F\ m^{-1}$ asl, $p < 0.0001$) to altitude is within errors of its sensitivity in the MLR analyses (figure 3.3.3.1). This is also the case for the bare peat (-0.00032 ± 0.00009 $\Delta F\ m^{-1}$ asl, $p = 0.018$) dataset. The importance of altitude in the bare peat model increased from 4.2% in the MLR to 8.2% in the ANOVA model. The importance of bare peat stayed similar with values of 13.40% and 13.03% for MLR and ANOVA respectively. However, without taking into account the effects of covariates in the ANOVA model, it is apparent that the altitudinal correlations found in the MLR analyses for non-*Sphagnum* moss and *Sphagnum* spp. are not evident in the ANOVA results.

The middle section of table 3.3.3.1 shows that once again both all data and bare peat show altitudinal correlations with sensitivities of -0.00052 ± 0.00008 ($p < 0.0001$) and -0.00019 ± 0.0001 ($p = 0.05$) $\Delta F\ m^{-1}$ asl respectively, which are within errors of the original ANOVA for both datasets, and within errors of the MLR results for the all data dataset also (figure 3.3.3.1). The importance of the all data relationship increases slightly to 9.07%, while staying roughly similar (13.48%) in the bare peat dataset relative to the upper section of table 3.3.3.1 results. Moreover, with the inclusion of environmental covariates, excluding P_g, an altitudinal correlation has been found in the *Sphagnum* spp. dataset once again, with a sensitivity (-0.0014 ± 0.0002 ΔF m^{-1} asl, $p < 0.0001$) within errors of that found in the MLR analysis (figure 3.3.3.1). The importance of the correlation with altitude found in the *Sphagnum* spp. dataset is slightly less than in the MLR analysis with values of 13.08% and 10.59% for MLR and ANCOVA (excl. P_g) respectively.

In the lower section of table 3.3.3.1, it is evident that a significant relationship with altitude has been determined in the all data and *Sphagnum* spp. datasets. Moreover, the sensitivities of these relationships -0.00033 ± 0.00008 and -0.00086 ± 0.00018 ΔF m^{-1} asl for all data and *Sphagnum* spp. respectively is within errors of the MLR and ANOVA/ANCOVA results (figure 3.3.3.1). The introduction of P_g as a covariate alongside locality as a fixed factor appeared to cause the altitudinal relationship previously identified in the bare peat dataset in all previous analyses to become insignificant. Conversely, the inclusion of P_g appeared to allow for the identification of a significant relationship in the *Eriophorum* spp. and non-*Sphagnum* moss datasets with sensitivities of -0.0003 ± 0.00012 and -0.00091 ± 0.00031 ΔF m^{-1} asl respectively. These sensitivities are within errors of those estimated in the MLR analysis (figure 3.3.3.1). The importance of these relationships in the models were 1.63% and 3.20% for *Eriophorum* spp. and non-*Sphagnum* moss respectively which are close to the values reported in the MLR analysis.

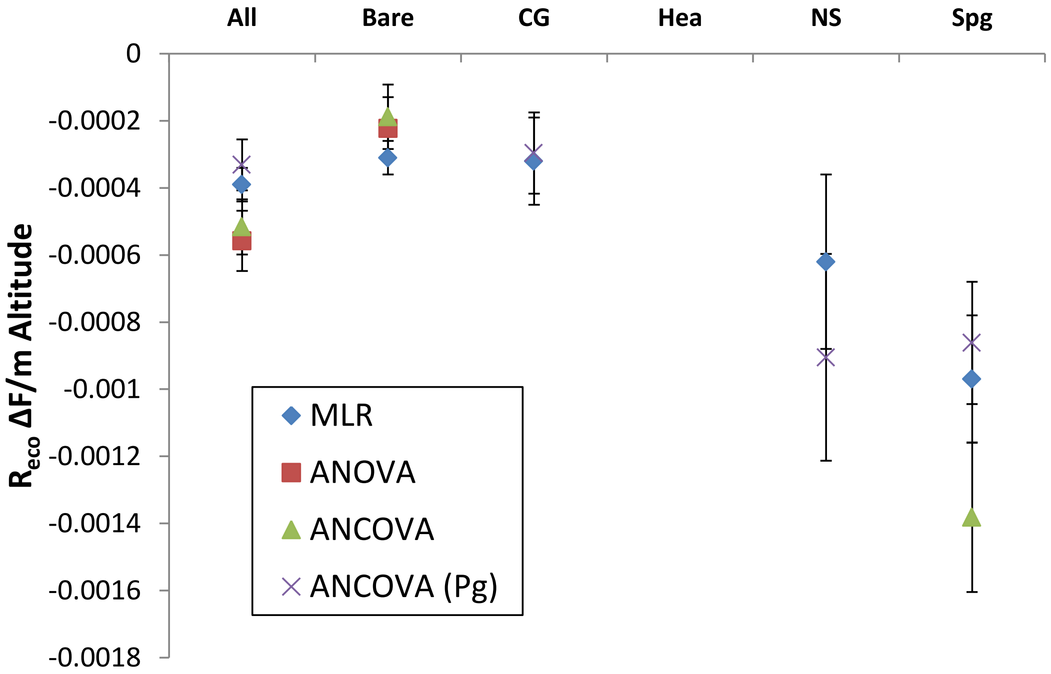


Figure 3.3.3.1 **–** The variation in sensitivity of R_{eco} to altitude by dataset and statistical approach employed. F = g CO_2 m^{-1} h^{-1}. Error bars denote one standard error.

Table 3.3.3.1 – R_{eco} ANOVA/ANCOVA Results

R_{eco} (ANOVA + Altitude)

Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**38.02**	**< 0.0001**	**8.20**	**-0.00056**	**0.00009**	40.55	2237
	FF	Vegetation	4	54.18	< 0.0001	6.61				
	FF	Month	11	75.53	< 0.0001	23.51				
	RF	Year	4	6.39	< 0.0001	0.55				
	RF	Orientation	7	5.97	< 0.0001	0.94				
Bare	Cov	**Altitude**	**1**	**5.61**	**0.018**	**13.03**	**-0.00022**	**0.00009**	25.18	647
	FF	Locality	3	8.27	< 0.0001	2.61				
	FF	Month	11	6.94	< 0.0001	7.74				
CG	FF	Month	11	31.26	< 0.0001	36.61			40.88	554
	RF	Year	4	6.87	< 0.0001	2.58				
Hea	FF	Month	11	34.29	< 0.0001	40.21			40.21	477
NS-Moss	FF	Month	11	11.82	< 0.0001	27.22			42.44	265
	RF	Year	2	4.91	0.008	2.24				
	RF	Orientation	3	14.21	< 0.0001	9.18				
Sphag	FF	Locality	2	26.35	< 0.0001	10.10			58.52	198
	FF	Month	11	19.33	< 0.0001	45.36				

R_{eco} (Full ANCOVA excl. Pg)

Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**39.65**	**< 0.0001**	**9.07**	**-0.00052**	**0.00008**	44.39	2035
	Cov	Slope	1	9.06	0.003	0.11	-0.0049	0.00163		
	Cov	Air Temperature	1	119.94	< 0.0001	19.91	0.007827	0.00072		
	FF	Vegetation	4	44.38	< 0.0001	7.96				
	FF	Month	11	19.95	< 0.0001	5.94				
	RF	Orientation	7	4.58	< 0.0001	0.69				
Bare	Cov	**Altitude**	**1**	**3.85**	**0.05**	**13.48**	**-0.00019**	**0.00010**	28.88	624
	Cov	Air Temperature	1	27.14	< 0.0001	8.50	0.003722	0.00072		
	FF	Locality	3	8.96	< 0.0001	2.71				
	FF	Month	11	2.76	0.002	2.27				
CG	Cov	Air Temperature	1	22.12	< 0.0001	30.83	0.008756	0.00186	44.71	495
	FF	Month	11	9.94	< 0.0001	10.26				
	RF	Year	4	4.74	0.001	1.73				
Hea	Cov	Air Temperature	1	14.25	< 0.0001	29.79	0.006952	0.00184	43.84	525
	Cov	*Calluna* Height	1	7.51	0.006	1.00	0.001859	0.00068		
	FF	Month	11	10.59	< 0.0001	11.58				
NS-Moss	Cov	WTD	1	17.13	< 0.0001	6.78	0.001773	0.00043	42.36	177
	Cov	Air Temperature	1	11.87	0.001	26.36	0.004666	0.00135		
	FF	Month	11	2.16	0.019	4.49				
Sphag	Cov	**Altitude**	**1**	**38.54**	**< 0.0001**	**10.59**	**-0.00138**	**0.000223**	44.67	483
	Cov	WTD	1	5.33	0.022	17.28	0.004516	0.001955		
	Cov	AbsAT	1	22.7	< 0.0001	27.50	0.008996	0.001888		
	FF	Month	11	3.65	< 0.0001	6.11				

R_{eco} (Full ANCOVA incl. Pg)

Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**19.22**	**< 0.0001**	**8.50**	**-0.00033**	**0.00008**	63.66	1672
	Cov	Slope	1	8.3	0.04	0.04	-0.00429	0.00149		
	Cov	Air Temperature	1	29.32	< 0.0001	20.70	0.003705	0.000662		
	Cov	Pg	1	835.75	< 0.0001	27.83	-0.42083	0.01458		
	FF	Vegetation	4	16.37	< 0.0001	1.93				
	FF	Month	11	11.96	< 0.0001	2.82				
	RF	Orientation	7	8.82	< 0.0001	1.21				
Bare	Cov	Air Temperature	1	48.04	< 0.0001	13.30	0.003711	0.000535	47.18	468
	Cov	Pg	1	184.53	< 0.0001	26.08	-0.51232	0.03771		
	FF	Locality	3	21.96	< 0.0001	7.18				
CG	Cov	**Altitude**	**1**	**6.02**	**0.015**	**1.63**	**-0.0003**	**0.00012**	61.82	434
	Cov	Air Temperature	1	8.24	0.004	28.77	0.004555	0.00159		
	Cov	Pg	1	200.57	< 0.0001	25.83	-0.39034	0.02756		
	FF	Month	11	5.25	< 0.0001	4.25				
Hea	Cov	Pg	1	244.24	< 0.0001	41.27	-0.43241	0.02767	62.09	476
	Cov	Calluna Height	1	44.65	< 0.0001	5.95	0.004238	0.000634		
	FF	Month	11	16.24	< 0.0001	13.74				
NS-Moss	Cov	**Altitude**	**1**	**8.64**	**0.004**	**3.20**	**-0.00091**	**0.000308**	50.59	193
	Cov	WTD	1	6.63	0.011	4.49	0.001624	0.000631		
	Cov	Pg	1	59.37	< 0.0001	24.90	-0.45456	0.05899		
	FF	Month	11	5.59	< 0.0001	13.99				
Sphag	Cov	**Altitude**	**1**	**22.57**	**< 0.0001**	**10.38**	**-0.00086**	**0.000182**	73.34	178
	Cov	WTD	1	7.26	0.008	8.05	0.00351	0.001303		
	Cov	Pg	1	107.67	< 0.0001	48.08	-0.4561	0.04396		
	FF	Month	11	3.46	< 0.0001	4.43				

Codings: Cov = Covariate, FF = Fixed Factor, RF = Random Factor, NF = Nested Factor
RC = regression coefficient

In the same fashion as the R_{eco} results, the results of the NEE analysis are reported in a three section table (table 3.3.3.2) where the sections correspond to the same statistical approaches as in table 3.3.3.1. It should be noted that for NEE the importance of altitude in the MLR and ANOVA analyses was less (range 0.01-18.40%, median 1.97%) than the R_{eco} datasets (range 1.50-13.80%, median 8.20%).

In the upper section of table 3.3.3.2 (the ANOVA plus altitude analysis) four out of the six datasets; all data, bare peat, *C. vulgaris* and non-*Sphagnum* moss showed significant relationships with altitude. For the all data dataset the sensitivity of NEE to altitude (-0.000821 ΔF m^{-1} asl, $p = 0.002$) appears to be significantly more negative (i.e. non-overlapping error bars - figure 3.3.3.2) than the estimate from the MLR analysis. For bare peat the sign of the correlation (0.001822 ± 0.00041 ΔF m^{-1} asl, $p < 0.0001$) changes (i.e. NEE becomes more positive with increasing altitude) relative to the MLR analysis. Furthermore the error bars between both estimates are non-overlapping (figure 3.3.3.2). A significant relationship (0.006149 ± 0.0012 ΔF m^{-1} asl, $p < 0.0001$) between NEE and altitude in the *C. vulgaris* dataset was apparent. The relationship identified had a positive sign (i.e. NEE becomes more positive with increasing altitude). The relationship identified for non-*Sphagnum* moss (-0.001594 ± 0.00029 ΔF m^{-1} asl, $p < 0.0001$) was significantly more negative than the MLR estimate (figure 3.3.3.2). The importance of altitude in this section of table 3.3.3.2 was lower than the equivalent MLR model for each dataset with the exception of non-*Sphagnum* moss where it remained similar.

The results shown in the middle of table 3.3.3.2 (i.e. ANCOVA excluding P_g) indicate that an altitudinal correlation was identified in the same datasets as the upper part of the table. For the all data dataset the estimate of altitude sensitivity (-0.001015 ± 0.000266 ΔF m^{-1} asl, $p < 0.0001$) was within errors of the ANOVA result (figure 3.3.3.2). For bare peat (-0.0257 ± 0.005 ΔF m^{-1} asl, $p < 0.0001$) the sign has changed (i.e. NEE becomes more negative with increasing altitude) relative to the ANOVA analysis. For *C. vulgaris* the sensitivity of NEE to altitude (0.0065 ± 0.0013 ΔF m^{-1} asl, p <

0.0001) is within errors of the ANOVA estimate. For non-*Sphagnum* moss also the sensitivity of NEE to altitude (-0.0017 ± 0.0003 ΔF m^{-1} asl, $p < 0.0001$) estimated by ANCOVA excluding P_g is within errors of the ANOVA estimate. In general the importance of altitude in the results in the middle section of table 3.3.3.2 does not differ much from those estimated in the upper section of the table.

The results in the lower section of table 3.3.3.2 showed that the all data and non-*Sphagnum* moss datasets had significant correlations with altitude. The sensitivity of the all data dataset to altitude (-0.000294 ± 0.00008 ΔF m^{-1} asl, $p < 0.0001$) which was within errors of all other MLR and ANOVA models constructed for that dataset. For non-*Sphagnum* moss the sensitivity of NEE to altitude (-0.00091 ± 0.00008 ΔF m^{-1} asl, $p = 0.001$) as determined by the ANCOVA including P_g was within errors of the estimate from the MLR model only. The use of ANCOVA with P_g also found a relationship between NEE and altitude within the *Eriophorum* spp. dataset with a sensitivity of -0.00035 ± 0.00012 ΔF m^{-1} asl, $p = 0.004$. The importance of the relationship between NEE and altitude in the all data and *Eriophorum* spp. datasets was very low (< 1%) in this section of the table, and was much lower than the values determined in the MLR analyses. This was not true for non-*Sphagnum* moss where the importance of altitude increased in this section of the table relative to all other MLR or ANOVA results.

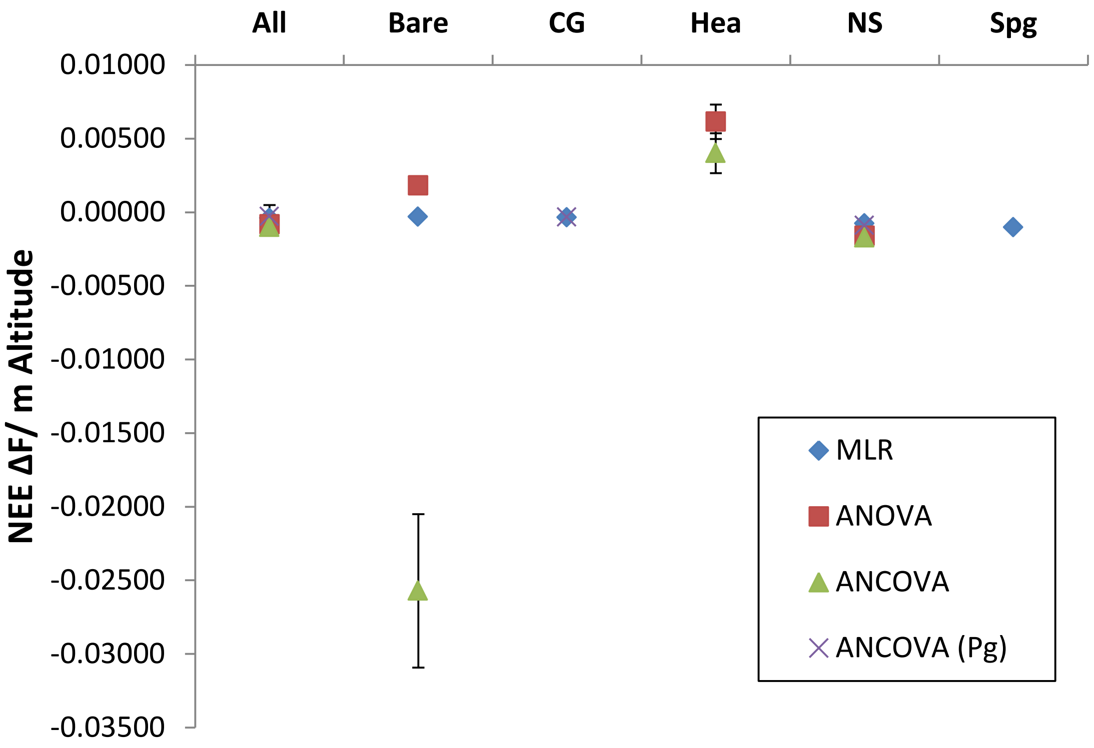


Figure 3.3.3.2 **–** The variation in sensitivity of NEE to altitude by dataset and statistical approach employed. F = g CO_2 m^{-2} h^{-1}. Error bars denote one standard error. Note that due to the large difference in sensitivity of NEE to altitude between datasets and methods some of the error bars are too small relative to the y-axis to be visible, in these cases please refer to table 3.3.3.2 below for the precise values displayed on this graph.

Table 3.3.3.2 - NEE ANOVA/ANCOVA Results

				NEE (ANOVA + Altitude)						
Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**9.2**	**0.002**	**0.19**	**-0.000821**	**0.000271**	5.4	2512
	NF	Vegetation(Locality)	10	3.49	< 0.0001	0.99				
	FF	Locality	3	2.73	0.043	0.01				
	FF	Month	11	3.29	< 0.0001	1.03				
	RF	Orientation	7	7.73	< 0.0001	1.59				
	RF	Morphology	2	4.83	0.008	0.29				
Bare	Cov	**Altitude**	**1**	**20.07**	**< 0.0001**	**1.81**	**0.001822**	**0.000407**	13.4	800
	NF	Locality(Region)	2	5.45	0.004	1.08				
	FF	Region	1	33.59	< 0.0001	1.23				
	FF	Month	11	2.8	0.001	2.23				
	RF	Year	4	3.88	0.004	1.05				
	RF	Orientation	5	6.93	< 0.0001	3.31				
CG					n/a					
Hea	Cov	**Altitude**	**1**	**27.34**	**< 0.0001**	**0.14**	**0.006149**	**0.001176**	17.08	599
	NF	Locality(Region)	1	50.18	< 0.0001	0.22				
	FF	Region	1	51.88	< 0.0001	4.51				
	FF	Month	11	4.82	< 0.0001	4.86				
	RF	Year	3	13.12	< 0.0001	5.18				
NS-Moss	Cov	**Altitude**	**1**	**30.71**	**< 0.0001**	**14.50**	**-0.001594**	**0.000288**	39.99	302
	FF	Month	11	6.44	< 0.0001	13.91				
	RF	Orientation	3	14.3	< 0.0001	8.36				
Sphag					n/a					

				NEE (Full ANCOVA excl. Pg)						
Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**14.57**	**< 0.0001**	**0.11**	**-0.001015**	**0.000266**	10.43	2178
	Cov	ln PAR	1	42.29	< 0.0001	0.72	-0.03207	0.004932		
	Cov	Air Temperature	1	5.01	0.025	0.88	0.002411	0.001077		
	FF	Vegetation	10	5.41	0.001	1.64				
	FF	Month	11	4.62	< 0.0001	1.81				
	RF	Orientation	7	13.44	< 0.0001	2.92				
	RF	Morphology	2	9.66	< 0.0001	0.72				
Bare	Cov	**Altitude**	**1**	**24.29**	**< 0.0001**	**1.94**	**-0.025716**	**0.005218**	14.68	775
	Cov	Slope	1	28.21	< 0.0001	0.79	-0.17107	0.03221		
	Cov	Air Temperature	1	26.32	< 0.0001	2.40	0.0026	0.000507		
	NF	Locality(Region)	2	12.55	< 0.0001	1.40				
	FF	Region	1	23.53	< 0.0001	0.65				
	RF	Orientation	5	12.2	< 0.0001	6.26				
CG	Cov	ln PAR	1	13.73	< 0.0001	2.23	-0.05051	0.01363	6.37	492
	FF	Month	11	1.83	0.046	1.78				
Hea	Cov	**Altitude**	**1**	**8.82**	**0.003**	**0.13**	**0.004014**	**0.001352**	28.81	525
	Cov	ln PAR	1	20.48	< 0.0001	1.26	-0.043436	0.009599		
	Cov	Calluna Height	1	30.88	< 0.0001	9.43	0.005318	0.000957		
	NF	Locality(Region)	1	35.01	< 0.0001	0.04				
	FF	Region	1	35.17	< 0.0001	2.59				
	FF	Month	11	7.03	< 0.0001	7.21				
	RF	Year	3	14.72	< 0.0001	5.79				
NS-Moss	Cov	**Altitude**	**1**	**32.29**	**< 0.0001**	**15.85**	**-0.001733**	**0.000305**	41.22	267
	Cov	WTD	1	4.27	0.04	0.50	0.001373	0.000665		
	FF	Month	11	5.27	< 0.0001	12.74				
	RF	Orientation	3	12.76	< 0.0001	8.28				
Sphag					n/a					

				NEE (Full ANCOVA incl. Pg)						
Dataset	Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
All Data	Cov	**Altitude**	**1**	**13.7**	**< 0.0001**	**0.01**	**-0.000294**	**0.000079**	54.78	1676
	Cov	ln PAR	1	30.14	< 0.0001	0.94	-0.019084	0.003476		
	Cov	Air Temperature	1	61.35	< 0.0001	0.62	0.005858	0.000748		
	Cov	Pg	1	1505.81	< 0.0001	45.45	0.57273	0.01476		
	FF	Vegetation	4	10.96	< 0.0001	2.28				
	FF	Month	11	10.16	< 0.0001	2.96				
	RF	Orientation	7	9.69	< 0.0001	1.35				
	RF	Morphology	2	8.15	< 0.0001	0.39				
Bare	Cov	Pg	1	244.24	< 0.0001	41.27	-0.43241	0.02767	62.09	476
	Cov	Calluna Height	1	44.65	< 0.0001	5.95	0.004238	0.000634		
	FF	Month	11	16.24	< 0.0001	13.74				
CG	Cov	**Altitude**	**1**	**8.58**	**0.004**	**0.83**	**-0.000354**	**0.000121**	56.1	428
	Cov	Air Temperature	1	16.75	< 0.0001	0.83	0.007783	0.001902		
	Cov	PAR	1	11.15	0.001	0.63	-0.000086	0.000026		
	Cov	Pg	1	460.27	< 0.0001	48.42	0.62019	0.02891		
	FF	Month	11	4.19	< 0.0001	3.73				
Hea	Cov	Air Temperature	1	14.77	< 0.0001	0.08	0.008246	0.002145	63.34	399
	Cov	PAR	1	12.44	< 0.0001	1.93	-0.000075	0.000021		
	Cov	WTD	1	17.38	< 0.0001	0.52	-0.002164	0.000519		
	Cov	Pg	1	360.2	< 0.0001	49.82	0.57721	0.03041		
	Cov	Calluna Height	1	35.13	< 0.0001	4.54	0.004248	0.000717		
	FF	Month	11	4.77	< 0.0001	3.80				
	RF	Year	3	3.59	0.014	0.75				
NS-Moss	Cov	**Altitude**	**1**	**11.68**	**0.001**	**18.40**	**-0.000908**	**0.000266**	67.23	151
	Cov	Air Temperature	1	4.31	0.04	0.79	0.002655	0.001279		
	Cov	WTD	1	5.73	0.018	1.63	0.001623	0.000678		
	Cov	Pg	1	97.99	< 0.0001	34.95	0.51791	0.05232		
	FF	Month	11	2.36	0.011	3.93				
	RF	Orientation	2	7.47	0.001	3.18				
Sphag	Cov	Air Temperature	1	16.2	< 0.0001	0.07	0.009016	0.00224	58.64	399
	Cov	WTD	1	7.56	0.006	0.32	-0.001184	0.000431		
	Cov	PAR	1	18.18	< 0.0001	2.11	-0.000094	0.000022		
	Cov	Pg	1	444.82	< 0.0001	49.80	0.64141	0.03041		
	FF	Month	11	4.92	< 0.0001	4.66				

Codings: Cov = Covariate, FF = Fixed Factor, RF = Random Factor, NF = Nested Factor
RC = regression coefficient

3.3.4 – ANOVA Experiment II

The results of the ANOVA outputs for both the R_{eco} and NEE datasets for the experiment II datasets are summarised in table 3.3.4.1. In the same fashion as the ANOVA results for experiment I (section 3.3.3) the results are split into three sections for each dataset. These sections are equivalent to the three sections in tables 3.3.3.1 and 3.3.3.2, with an ANOVA plus only altitude, ANCOVA excluding P_g and ANCOVA including P_g.

For both R_{eco} and NEE no relationship with altitude was identified in any statistical approach taken. This agrees with the results of the MLR models. Moreover, for the NEE dataset no significant covariates were found, with the factor ‘month’ alone explaining 45.86% of dataset variation. For R_{eco}, month and vegetation type were significant in the ANOVA models, with the only significant covariate found being P_g. Vegetation type was used as a random factor in this analysis as while the transect was installed in ground covered by degenerate *C. vulgaris* not all collars actually contain this species and therefore it was felt that it would be prudent to include vegetation to account for this limitation. The transect of four sites used in experiment II was specifically designed to minimise the effects of potential confounding factors like land management, large differences in vegetation type etc. and thus it is unsurprising that relatively few, when compared to experiment I, factors and covariates have been shown to have a significant effect on the CO_2 fluxes studied.

Table 3.3.4.1 – ANOVA Results for Experiment II R_{eco} and NEE

R_{eco} (ANOVA + Altitude)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
FF	Month	11	12.48	< 0.0001	48.28238			57.53%	129
RF	Vegetation	2	6.78	0.002	4.256197				
R_{eco} (ANCOVA excl. Pg)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
No significant covariates									
R_{eco} (ANCOVA incl. Pg)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
Cov	Pg	1	28.72	< 0.0001	30.94979	-0.5399	0.1007	73.30%	93
FF	Month	11	10.42	< 0.0001	35.81197				
RF	Vegetation	2	3.27	0.043	1.548168				
NEE (ANOVA + Altitude)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
FF	Month	11	9.55	< 0.0001	45.86%			45.86%	136
NEE (ANCOVA excl. Pg)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
No significant covariates									
R_{eco} (ANCOVA incl. Pg)									
Coding	Source	DF	F	P	ω^2	RC	RC Error	R^2	n
No significant covariates									

Codings: Cov = Covariate, FF = Fixed Factor and RF = Random Factor

3.4 – Discussion

3.4.1 – General Discussion

The lack of a significant relationship with altitude for *C. vulgaris* in experiment I is likely explained by the fact that the *C. vulgaris* height in experiment I changed, in a non-linear fashion, with altitude. However, this relates to management (cutting and burning), which is clearly visible as rectangular patches of differing stand height *C. vulgaris* covering the landscape, and not environmental factors. This means that the *C. vulgaris* dataset is biased by land management and is therefore incapable of demonstrating a meaningful altitudinal effect. The lack of an unbiased dataset for *C. vulgaris* in experiment I underlines the importance of experiment II in the context of this study.

Variance within the R_{eco} dataset was generally the most well explained, in all of the statistical approaches taken, (range = 48.16, median = 47.18) when compared to NEE (range = 61.83, median = 45.45). Models where P_g was significant across all approaches taken had an increased median R^2 of 57.30% (range = 29.04) compared to a median R^2 of 42.40% (range = 33.34) in models without P_g. In R_{eco} models where P_g was significant P_g was always the most important predictor of dataset variance, with a median value of 35.00% (range = 24.37), with the exception of *C. vulgaris* in the MLR analysis and *Eriophorum* spp. in the ANCOVA analysis, where air temperature was more important. This general pattern of results agrees with the findings of Larsen et al. (2007) who used P_g to improve the fit of an Arrhenius type temperature based model of ecosystem respiration. It is argued by Larsen et al. (2007) that consideration of only environmental drivers of R_{eco} (i.e. air temperature, water table depth etc.) can be misleading as factors such as “phenology, photosynthesis, substrate supply or soil water content” can co-vary with temperature. This gives rise to misleadingly simplistic models of R_{eco} as the effects of temperature are, in fact, masking other drivers of CO_2 flux, like photosynthesis. Furthermore the addition of P_g into empirical and statistical models of CO_2 flux has the power to take into account variance in the CO_2 dataset due to factors like phenology and spatial factors which are not necessarily controlled for in the experimental design. Indeed, Migliavacca et al. (2011) argue that semi-empirical models of R_{eco} across FLUXNET sites using only climatic drivers failed to describe some of the temporal variability in the dataset and that this variability was accounted for by the inclusion of the “dependency on gross primary production”.

There is always the potential for self-correlation within P_g datasets estimated by the residual between NEE and R_{eco}, as is the case in this study, Larsen et al. (2007), Migliavacca et al. (2011) and Clay et al. (2012). However, Lasslop et al. (2010) show that, (see also chapter 2), the issue of self-correlation arises through the measurement error term of R_{eco} being a shared component between both the R_{eco} and P_g datasets. However, as measurement errors are systematic (i.e. constant) they will not contribute to temporal variability within the dataset and as such will only be reflected in the constant term of the linear equation rather than the gradient. Therefore, it is hereby assumed that the R_{eco}-P_g relationships identified within this chapter and the following chapters of this thesis represent real associations rather than spurious correlations. This is in accordance with the suggestion of Prairie and Bird (1989) who argue that relationships between variables with shared components are meaningful if they (1) can be logically expected to exist, (2) satisfy the assumptions of the analysis in question and (3) they do not share a large error term. While the R_{eco} and P_g datasets do share a measurement error term, it is ambiguous as to whether this is large (as "large" is not defined by Prairie and Bird, 1989) and nevertheless this is not thought to be a fatal limitation as, described above, the shared error term should be systematic and thus not expected to contribute to temporal variability within the dataset.

An important caveat on the assumption that correlations of R_{eco}/NEE to P_g are 'real' is that while measurement error is likely to be systematic (and therefore constant) there is still the potential for random error in the R_{eco}/NEE dataset to correlate to itself and thus induce a component of self-correlation. However, the magnitude of random errors within the datasets gathered should be minimized by the standard procedures used to gather the data, and will have been reduced further still by the quality control measures undertaken on the data (i.e. removal of outliers and logically inconsistent data points). In the absence of appropriately controlled, independent measures of the fluxes it is not possible to accurately characterise the magnitude of random error within this dataset. Therefore the assumption that the R_{eco}/NEE to P_g relationships are entirely real requires the caveat with the statement that this assumes minimal random errors. As such, the relationship is interpreted to be of interest and reflective of the real relationship, but with the limitation that some component of the correlation may be due to self-correlation of random error. That said, to not include P_g as a predictor will be of detriment to the modelling results as the importance of temperature and thus the temperature sensitivity of the fluxes will be overstated (i.e. Larsen et al. 2007, Lasslop et al. 2011). Furthermore, the relationship between P_g and R_{eco}/NEE is recognised in many biomes (e.g. Raich and Schlesinger, 1992) including northern peatlands (e.g. Moore, 1986) and on diurnal (e.g. Tang et al. 2005) to annual (e.g. Hogberg et al. 2001; Yuan et al. 2011) timescales.

Thus, to ignore such a prevalent and important relationship would seem to be contrary to the current consensus regarding the controls on terrestrial CO_2 fluxes.

Another reason to suppose that regression between R_{eco}/NEE versus P_g represents a 'real' relationship comes from the comparison between the importance (i.e. % of dataset variation explained) of P_g in models of R_{eco} and NEE. For R_{eco} the median value of importance is 30.50% (range = 31.18) versus a value of 46.85% (range = 39.50) for NEE. The fact that P_g is frequently more important in models of NEE than R_{eco} is to be expected as NEE is the balance between R_{eco} and P_g and it is well established that each component (i.e. gross) flux globally represents about half of the magnitude of the net flux (e.g. Grace, 2004). Moreover, the importance of R_{eco} found in the results of this chapter are comparable to other estimates, with Larsen et al. (2007) suggesting that 24% of R_{eco} is explained by P_g annually on a *C. vulgaris* dominated temperate heath, and Vickers et al. (2009) estimating that the 'real' magnitude of R_{eco} variance explained by P_g (i.e. when self-correlation is taken into account) on an annual basis is between 18-44% depending on the methodological setup employed. Moreover, in the case of Vickers et al. (2009), the method used to estimate the size of self-correlation was shown by Lasslop et al. (2010) to be prone to overstating the size of the effect due to it maximising the size of the shared error term in R_{eco} to P_g regressions, thus giving unrealistically high estimates of self-correlation. Despite this large limitation to the Vickers et al. (2009), it was still found that the magnitude of 'real' correlation between R_{eco} and P_g was significantly greater than zero on all occasions, i.e. even when using a method known to be ultra-conservative, there remains a significant relationship between the variables.

Aside from P_g, air temperature was shown to be a frequently found, significant predictor of both R_{eco} and NEE fluxes. For R_{eco}, across all statistical approaches taken, air temperature had a median importance of 18.36% (range = 33.60). There was a large increase in the median importance of air temperature in R_{eco} models between MLR and ANCOVA methods with air temperature in MLR models having a median importance of 10.06% (range = 33.6) and air temperature in ANCOVA models having a median importance of 26.63% (range = 22.33), which is comparable to the R^2 of the bivariate regression between all R_{eco} and air temperature data (R^2 = 22.11%) in figure 3.3.1. It is unsurprising that a relationship between R_{eco}/NEE and air temperature was apparent, as temperature is known to be an important driver of R_{eco} and NEE fluxes (e.g. Lloyd and Taylor, 1994; Davis, 1983). For NEE datasets, however, air temperature was less important overall (relative to R_{eco} datasets) with a median value of 6.50% (range = 40.63). Moreover, the importance of air temperature decreased greatly between MLR and ANCOVA approaches with air temperature in MLR models having a median importance of 15.50% (range = 30.10) and air temperature in ANCOVA models having a median importance of 0.79% (range 2.33), suggesting colinearities between air temperature and the covariate P_g and the factor month are accounting for much of this variation. The median importance of air temperature in the ANCOVA models again compares well the R^2 of the bivariate regression between all NEE and air temperature data (R^2 = 0.1%) in figure 3.3.1. It should be noted, however, that the bivariate regression between NEE and air temperature was insignificant.

Lapse rates with altitude in the environmental variables, such as air temperature (e.g. Burt and Holden, 2010; Holden and Rose, 2011) may be expected to induce an altitudinal effect in the dataset. However, taking these variables into account as covariates in MLR or ANCOVA approaches were not able to explain the altitudinal effects observed (i.e. the altitude effect does not appear to be colinear with air temperature or water table depth). Moreover, using the lapse rate in air temperature estimated earlier in this chapter (1.38 K/ 100 m) and the 1991-2006 average annual North Pennines lapse rate (0.77 K/ 100 m) reported in Holden and Rose (2011) estimates of the expected size of the lapse rate effect on R_{eco} have been produced (table 3.4.1.1). The temperature sensitivities employed in these calculations were taken from the ANCOVA results (excluding P_g) to avoid any potential masking of temperature sensitivity by colinearities between P_g and air temperature. It can be seen, even when using the larger estimate of the air temperature lapse rate, that the predicted sensitivity to altitude due to lapse rate is always much smaller (< 40%) than the observed sensitivities. Thus, lapse rate in air temperature cannot be used to explain the magnitude of the altitudinal effects observed in this chapter. It should be emphasised that the calculated sensitivities to altitude for both R_{eco} and NEE in the MLR and ANCOVA approaches take environmental variables (where significant) into account. Thus, any air temperature lapse rate effect will have been normalised for and thus will not be reflected in the magnitude of the observed sensitivity to altitude. As such, while the size of the potential lapse rate effect given in table 3.4.1.1 is compared to the observed effect, this predicted effect is not actually present in the observed effect as this 'lapse rate' variation has already been accounted for by the covariates. The comparison is to demonstrate that even when any potential lapse rate effects are accounted for the magnitude of the relationship observed is still much larger than would the potential lapse rate effect.

Table 3.4.1.1 – Predicted R_{eco} Sensitivities to Altitude by Dataset due to Air Temperature Lapse Rate

	Predicted Effect (ΔF/m asl)		% Median Altitude Effect	
Dataset	Thesis	Holden and Rose (2011)	Thesis	Holden and Rose (2011)
All Data	-0.000108	-0.000060	23.66	13.20
Bare	-0.000051	-0.000028	23.21	12.95
CG	-0.000120	-0.000067	38.73	21.61
Hea	-0.000095	-0.000053	-	-
NS-Moss	-0.000065	-0.000036	8.48	4.73
Sphag	-0.000124	-0.000069	13.57	7.57

Water table depth was identified as a consistent significant predictor of R_{eco}/NEE in all MLR and ANCOVA analyses for the bryophyte datasets, non-*Sphagnum* moss and *Sphagnum* spp. A significant relationship was identified between NEE and water table depth in the experiment I *C. vulgaris* dataset in the MLR analysis, which subsequently seemed to be explained by the significant factors and covariates used in the ANCOVA models. The importance of water table depth was greater in R_{eco} models (median importance = 7.42, range = 12.79) than NEE models (median importance = 1.62, range = 8.28). The knowledge that carbon fluxes out of peat are affected by water table has been recorded elsewhere (i.e. McNeil and Waddington, 2003; Price and Whitehead, 2001; Rochefort, 2000) and water table has been shown to be a controlling factor on the vegetative assembly found on ombrotrophic bogs (Pellerin et al., 2009). Moreover, water table was only significantly related to R_{eco} for the bryophyte groups, whose average water tables are relatively shallow when compared with the other groups (figure 3.4.1.1). This finding seems to agree with that of Leppälä et al., (2008) who determined that there is a maximum threshold depth below which water table fluctuation no longer influences R_{eco}.

In the case of this study, this pattern may also be explained in terms of the physiological differences between the rooting graminoid and ericaceous species with shallowly/non-rooting bryophyte species. However, the bare peat datasets, where the water table was deepest (on average) and soil respiration dominated, were also unaffected by water table fluctuations. This suggests that there are additional factors, besides plant physiology, which determine why water table fluctuations could be ineffective below a threshold depth. One possibility is that peat becomes more recalcitrant with depth (Charman, 2002, pp 44-45) and as such water table fluctuations within the deeper levels of a peat profile may have effects on only a negligible rate of decay going on at those depths.

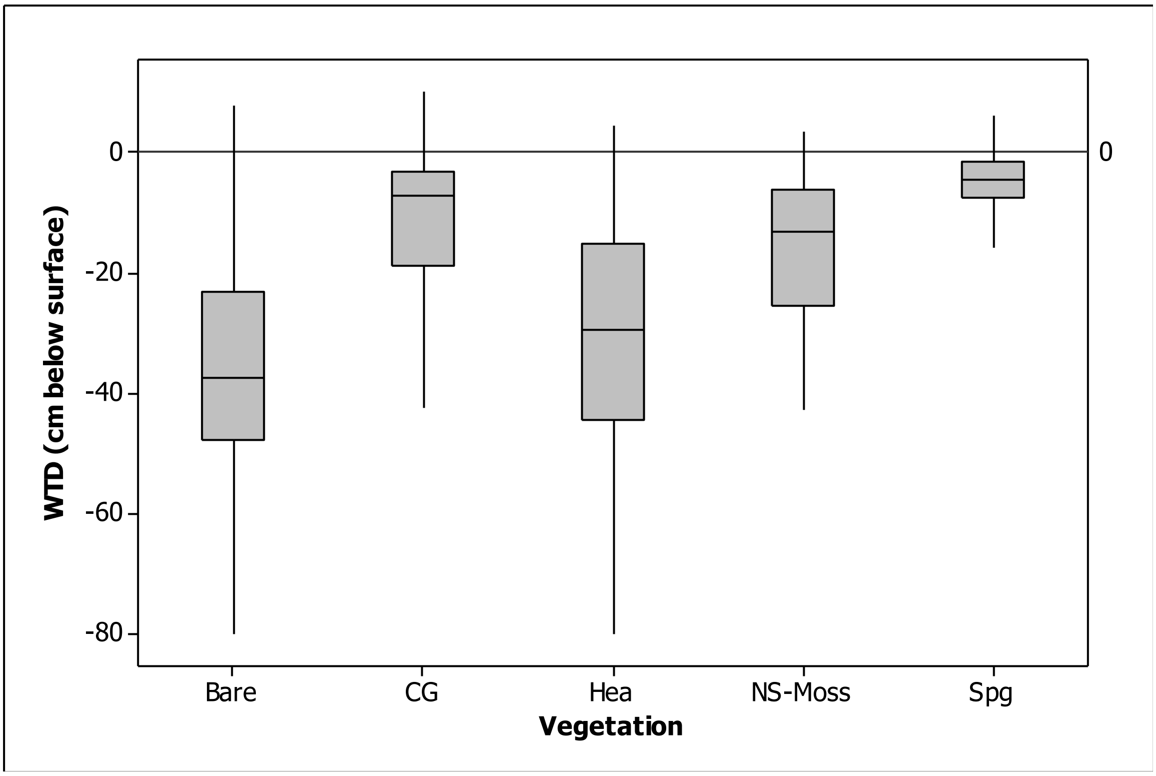


Figure 3.4.1.1 – Boxplot showing the dataset variation within the water table depth (WTD) dataset by vegetative group.

While most models were best fitting where P_g was included, it is important to note that significant relationships between R_{eco}/NEE and water table, air temperature and PAR were demonstrated. This underlines the primary importance of exogenous environmental variables in driving carbon cycling within terrestrial ecosystems. Indeed, while P_g may explain a large fraction of dataset variation, its real effect (i.e. that not due to self-correlation) will only be a response to the exogenous variables which control photosynthesis.

3.4.2 – The Effects of Altitude

It is evident that altitude, when used as a covariate/predictor variable, can have a statistically significant relationship to both R_{eco} and NEE fluxes. The results of the analyses performed will be discussed for each dataset (i.e. R_{eco} and NEE) and experiment individually.

For experiment I R_{eco} the MLR analysis suggested that altitude was effective on the all data, bare peat, *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* moss datasets (i.e. that H_1 could be accepted in these cases). The mean sensitivity to altitude across the datasets, where an effect was identified, was -0.00056 ΔF m^{-1} asl. Examination of the standard errors of the partial regression coefficients (figure 3.3.3.1) suggests that there are significant differences between the bryophyte datasets and some/all of the rest. For non-*Sphagnum* moss a significant difference with bare peat is apparent, whereas for *Sphagnum* spp. a significant difference with all other datasets, with the exception of non-*Sphagnum* moss is identified (figure 3.3.3.1). The importance (i.e. % of dataset variation explained by altitude) of altitude was 4.20, 7.70, 1.50, 3.90 and 13.90% respectively for the all data, bare peat, *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* spp. datasets respectively.

The results of the ANOVA and altitude analysis suggested that fewer datasets (all data and bare peat) had satisfied H_1. The mean sensitivity of these datasets to altitude was -0.00022 ΔF m^{-1} asl. Examination of the standard errors of the partial regression coefficients (figure and table 3.3.3.1) suggested that there were significant differences between sensitivities of the all data and bare peat datasets to altitude. However, there were no apparent significant differences in sensitivity between the MLR and ANOVA analyses for the datasets where significant relationships had been found in both. The importance of the relationships found increased nearly two fold between the MLR and ANOVA results (table 3.3.3.1) with values of 8.20 and 13.03% for all data and bare peat respectively.

The results of the ANCOVA excluding P_g approach demonstrated that H_1 could be accepted for the all data, bare peat and *Sphagnum* spp. datasets. The mean sensitivity to altitude across these datasets was -0.00079 with significant differences in standard errors (figure and table 3.3.3.1) between all datasets. Once again there were no significant differences between the three approaches so far reported within the results for each dataset. The importance of altitude in the datasets was 9.07, 13.48 and 10.38% for all data, bare peat and *Sphagnum* spp. respectively.

The results of the ANCOVA including P_g approach demonstrated that H_1 could be accepted in the all data, *Eriophorum* spp. non-*Sphagnum* moss and *Sphagnum* spp. datasets. The mean sensitivity to altitude across the datasets accepting H_1 was -0.00069 $\Delta F\ m^{-1}$ asl. The relationship identified between R_{eco} and altitude in the bare peat dataset in all previous analyses seems to have been explained by the combination of variance in P_g and variance explained by inter-locational differences (table 3.3.3.1). Significant differences in dataset sensitivity to altitude (as shown by the standard errors in figure and table 3.3.3.1) were identified between bryophyte and all data/*Eriophorum* spp. datasets. No other significant differences were apparent between the datasets. However, no significant differences between the estimations of sensitivity to altitude (where a relationship was significant) can be seen in the individual datasets for any statistical approach taken. The importance of the altitude relationships identified in this approach was 8.50, 1.63, 3.20 and 10.38% for all the data, *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* spp. datasets respectively.

Aside from the fact that altitude is always shown to cause a decrease in R_{eco} with increasing altitude, there are two important features of the comparison between the results of the different statistical approaches taken for experiment I R_{eco}. Firstly, it is apparent that where the relationship with altitude identified was weak (i.e. not very important) it was much more likely to be found by the addition of covariates, either in a MLR or ANCOVA format (i.e. the results for *Eriophorum* spp. or non-*Sphagnum* moss). This makes sense as including these significant covariates will normalise for their effects and remove large amounts of, possibly confounding, dataset variability, making subtler effects more apparent. Secondly, the comparison between the MLR and ANCOVA plus P_g results yielded sensitivities to altitude that were within errors of each other and that had importances that were of similar or larger magnitude in the ANCOVA plus P_g results. This implies that the dataset variability attributed to altitude in the datasets in the MLR approach was not subsequently accounted for by the factors considered in the ANOVA approaches. The exception to this is the unvegetated bare peat dataset, where a combination of P_g and differences in the factor levels of locality appeared to explain the altitudinal effect observed. The reason for this exception for bare peat may be explained in terms of differences in amounts of vegetative biomass of the soil surrounding the bare collars by locality. For instance, Bleaklow Summit was dominated by bare peat left as a result of wild fire/gully incision whereas the bare peat on Green Withens was found in hollows between *Molinia caerulea* hummocks, and thus the peat around these collars was more likely to have plant roots (and therefore enhanced root respiration) than the Bleaklow Summit plots. The bare Green Withens plots were found a lower altitude than the bare Bleaklow Summit plots and as such it is evident that an altitudinal effect may have been artificially introduced by this effect. This kind of limitation does not affect the vegetated datasets as the plots of these were selected and installed in areas dominated by the vegetation type in question. This line of reasoning is supported by the fact that bare peat was the only dataset where locational factors (i.e. locality, region) were significant after the use of covariates in the ANCOVA approaches. This suggests, therefore, that the use of environmental covariates (i.e. air temperature, water table depth) is able to deal with inter-locational differences in the individual and amalgamated vegetated datasets used within this chapter. This is demonstrated by the fact that locational factors were not present in any of the significant ANCOVA models of R_{eco} in experiment I for the individual or all data datasets, with the exception of bare peat, the reasons for which have been discussed above. This finding is in agreement with a meta-analysis by Couwenberg et al. (2011), who suggest that vegetation itself should be used as a proxy for greenhouse gas flux in order to take account spatial variability of greenhouse gas fluxes across restored peatlands in Belarus, as vegetation itself is reflective of long term site attributes like water table, management etc.

For R_{eco} in experiment II no relationship with altitude was identified in any of the analyses conducted (MLR or ANOVA). Given the fact that altitude sensitivity appears to be greater in plots containing non/shallowly rooting bryophytes it could be that the extensive root system possessed by degenerate *C. vulgaris* made it insensitive to altitude. It could also be that the altitudinal range, of 69 m, for the transect in experiment II, was not sufficient. This notion is supported by the fact that the datasets with comparable altitudinal ranges (i.e. non-*Sphagnum* moss and *Sphagnum* spp.) have the largest standard errors on their R_{eco} estimated sensitivities to altitude.

For NEE in experiment I relationships with altitude were found within the same datasets as R_{eco} in the MLR analysis (i.e. all data, bare peat, *Eriophorum* spp. non-*Sphagnum* moss and *Sphagnum* spp.). The importance of altitude in these MLR models of NEE is comparable to the corresponding importance within R_{eco} models, with values of 4.60, 7.40, 2.00, 6.20 and 15.00% for the all data, bare peat, *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* spp. datasets respectively (table 3.3.3.2). The significant differences between datasets are similar to the corresponding R_{eco} MLR analysis.

The pattern of results changes markedly between MLR and ANOVA approaches with all data, bare peat, *C. vulgaris* and non-*Sphagnum* moss showing relationships between NEE and altitude. However the importance of the relationships identified was generally much lower than in the MLR approach, with values of 0.19, 1.81, 0.14 and 14.50% for all data, bare peat, *C. vulgaris* and non-*Sphagnum* moss respectively. The exception to this pattern was non-*Sphagnum* moss which increased in importance. The sign of the relationship of NEE to altitude was found to be positive for the bare peat and *C. vulgaris* datasets, the opposite of the direction determined in the MLR analysis. All other altitude relationships found were negative.

For the ANCOVA approach excluding the same datasets as in the ANOVA results were found to be significantly related to altitude. The importance of altitude in these models was similar to the ANOVA approach and was relatively low when compared to the MLR approach with values of 0.11, 1.94, 0.14 and 15.85% for the significant datasets respectively. The direction of the relationship between NEE and altitude in the bare peat dataset was found to be negative in this analysis, but, it was also of a magnitude much greater than the other datasets considered and when compared to the other statistical approaches taken (figure and table 3.3.3.2). This was the only dataset where significant differences in sensitivity to altitude were observed between the statistical approaches taken.

For the ANCOVA approach including P_g, only three datasets were shown to have accepted H_1. These were all data, *Eriophorum* spp. and non-*Sphagnum* moss. All these relationships have a negative sign with respect to altitude. The sensitivities of NEE to altitude in these datasets are within errors of those estimated for R_{eco} by the same statistical approach. The big difference between the R_{eco} and NEE results for this analysis is that the *Sphagnum* spp. dataset was not found to have a significant relationship with altitude. Moreover, the importance of altitude, when NEE is being modelled, was lower than that found in the MLR results in the ANCOVA including P_g approach. Again with the exception to this pattern is the non-*Sphagnum* moss dataset. The importance values were 0.01, 0.83 and 18.40% for the all data *Eriophorum* spp. and non-*Sphagnum* moss datasets respectively.

It is apparent that altitude is less important in the NEE datasets than the R_{eco} datasets. The important exception to this pattern is the non-Sphagnum moss dataset where importance increased between the MLR and ANCOVA approaches markedly (from 6.20% to 18.40%), while the estimates of sensitivity to altitude remained within errors. This increase in importance suggests that variation related to the factors considered in the ANOVA/ANCOVA models was masking the altitudinal effect, and causing its importance to be understated in the MLR results. Furthermore, the importance of altitude within NEE in this dataset is much greater than the corresponding importance of altitude within R_{eco}. This implies that the altitude effect, in this case, is not solely attributable to the observed effect of altitude within R_{eco}. This may, again, reflect dataset ecological limitations, similar to the bare peat dataset, where certain species of moss are more likely to occur at different altitudes (i.e. *Hypnum* spp. on Big Moor and *Polytrichum commune* on Ravenslow). However, while most sensitivity values of NEE to altitude were within errors of each other across the statistical approaches in the individual datasets, there were differences between the methods for bare peat. It appears that the relationships between NEE and altitude identified in the MLR and ANCOVA plus P_g approaches correspond (e.g. sensitivities in the same direction and having magnitudes within errors of the other) to the altitude effects seen the equivalent R_{eco} datasets. This implies that it is the effect on the gross flux R_{eco} that causes the effect seen in the net flux NEE, explaining why altitude was generally less important in the NEE models relative to the R_{eco} models. The exception to this, as discussed above, was the non-*Sphagnum* moss dataset.

Mirroring the R_{eco} results for NEE there were no significant relationships identified with altitude in any of the statistical approaches taken in the experiment II NEE dataset. Reasons for this have been discussed above (i.e. altitudinal range too small or rooting structures). Moreover, as it seems likely that the altitudinal effect is manifest in the R_{eco} component of NEE, it makes sense that no relationship with NEE was identified in experiment II.

While an apparent effect of altitude has been identified in this chapter it is impossible to deduce what controls it without further work. The effects of any potential lapse rate in air temperature were not enough to explain the full magnitude of the effect seen. However, this does not mean that lapse rates in other environmental variables (e.g. rainfall, wind speed, nutrient deposition) are not also effective. Moreover, a number of factors may add to the explanation of the effect observed. For instance, historic management of the uplands may have been more intense at lower altitude resulting in a gradient of disturbance with altitude. This may also be true of grazing animals which may have favoured the sheltered flanks of the hills to the summits. Changes in the hydraulic and structure properties of the peat with altitude/slope position (e.g. Holden 2005a, 2005b; Holden et al., 2007).

3.5 – Conclusions

When considered from a whole dataset perspective, the results of this chapter imply that variation in altitude is effective on R_{eco} fluxes (4-9% of dataset variance explained), with this effect then being reflected, with reduced importance, into the NEE flux dataset also (0.01-4% dataset variance explained).

Splitting the dataset by vegetative/ground cover group assisted in accounting for spatial variability within MLR models. Issues related to the spatial variability in the ecological comparability of the bare peat plots limited the effectiveness of this technique in the bare peat dataset. Nonetheless, the general pattern was that locational factors were insignificant in ANCOVA models where covariates such as air temperature, P_g and water table depth were employed (i.e. in models where variables related to hydro-meteorological variation were accounted for).

There was agreement between all of the methods as to what the sensitivity of R_{eco}, in any given dataset was to altitude (i.e. the estimated sensitivities were within errors of each other). Moreover, the importance of altitude in these R_{eco} models did not change radically between the statistical approaches taken. This implied that the MLR approach, where environmental predictors were used alongside altitude, accounted for potential significant differences that may have been introduced by spatial variation within the individual datasets. Moreover, the fact that the importance of altitude did not vary much between techniques suggests that variation in the vegetated datasets was not erroneously attributed to altitude in the MLR analyses. The caveat on this is that the plots of the dataset needed to be ecologically comparable, which was not the case for bare peat or non-*Sphagnum* moss.

Looking at the pattern of results from the individual dataset perspective, it was apparent that more sophisticated techniques (i.e. MLR and full ANCOVA) employing environmental covariates were more likely to identify an altitudinal trend in the individual datasets than the less sophisticated techniques like ANOVA without covariates, particularly when the importance of the altitude effect found was small. This is explained by the fact that employing covariates in these approaches takes into account (and thus removes the effects of) dataset variation that was potentially masking more subtle altitude effects. This is the primary benefit of both MLR and ANCOVA approaches. In experiment I, both MLR and full ANCOVA (including P_g) methods determined that variation in altitude was effective on the *Eriophorum* spp., non-*Sphagnum* moss and *Sphagnum* spp. datasets. Both methods were in agreement about the sensitivity and importance of the R_{eco}-altitude relationships identified, suggesting variance in the purely empirical MLR approach was not falsely attributed to altitude in the absence of the consideration of categorical factors (i.e. the MLR approach seems to be conservative). The exception to this was the relationship identified in the bare peat dataset, however, as discussed above this seems to be due to dataset rather than methodological limitations. Moreover, the results of the NEE analysis suggested that the altitude effect in the non-*Sphagnum* moss dataset was more important than in the R_{eco} dataset. This implied that altitude was not just effective on the R_{eco} component of this dataset. The reason why this might be the case was not clear and may relate to similar issues of ecological comparability between the plots as are present in the bare peat dataset.

The bryophyte R_{eco} datasets (i.e. non-*Sphagnum* moss and *Sphagnum* spp.) were shown to be significantly more sensitive to altitude than *Eriophorum* spp. The altitude effect was most important in the *Sphagnum* spp. dataset (10-13% of dataset variance explained) when compared with the *Eriophorum* spp. (1.5-1.6% dataset variation explained) or non-*Sphagnum* moss datasets (3-4% dataset variance explained). Another important finding in this chapter is that the incorporation of environmental covariates known to be subject to lapse rates with altitude (i.e. air temperature) were not able to explain the variance attributed to altitude. Moreover, comparison of the observed altitude sensitivities for R_{eco} to those predicted on the basis of an air temperature lapse rate demonstrated that lapse rate effects were predicted to be much smaller than the observed effects.

Thus it can be concluded that, at least some portion, of the altitudinal effects observed are independent of air temperature lapse rate effects. The best fitting models contained P_g as a predictor, it is important to bear in mind the potential for self-correlation when interpreting these results.

4 – The Role of Vegetation

4.1 – Introduction

Blanket peatlands are a poor growing medium for most terrestrial plant species and special adaptation to the environment is needed for plants to survive. The most important factors affecting plant growth were defined by (Charman, 2002, pp 57-58) as:

- Low oxygen availability due to persistent waterlogging;
- Mobilisation of toxic elements (e.g. Fe, Mn, S);
- Low nutrient availability – with nitrogen and phosphorus in very limited supply;
- Acidity – Typical blanket peat pore water pHs are around 3.5-4.

The net effect of these factors has been to produce characteristic communities of species, all adapted to the harsh conditions of blanket bogs. Aside from the environment within the peat itself, blanket peat community composition in the UK is also affected by latitudinal (i.e. growing season length) and precipitational gradients (i.e. rain shadow effects), from north to south and west to east respectively (Simmons, 2003, pp 204-206). These 'natural' forcings are further modified by anthropogenic interventions, principally vegetation management by peatland drainage, sheep grazing and vegetation cutting/burning, which arguably exert the largest controls on many UK blanket peat community compositions (e.g. Holden et al., 2007). Indeed, Tallis et al. (1998b) estimated that of the 22,500 km^2 of blanket bog in the British Isles at least 18,500 km^2 (82%) is substantially modified as a result of management. As such, to assess the role of vegetation in blanket peat carbon cycling it is important to sample a representative sample of the species present and where necessary to sample the effects of management on the vegetation.

4.1.1 – The Ground Cover of Blanket Peat in the Peak District and South Pennines

'Heather' communities are the principal constituents of South Pennines/Peak District blanket bogs, with Phillips et al. (1981, pp 28-34) reporting that *C vulgaris* (*Calluna* heather) dominated communities accounted for 32% of the Peak District's moorlands with *Vaccinium* spp. (Bilberry heather) dominated communities accounting for a further 25% in 1981. However, despite 'heather' communities dominance Bardgett and Marsden (1995) estimated that the West Midlands (i.e. the area including the Peak District) had the largest proportions of "damaged/suppressed" heather, a fact they related to "over-grazing and management neglect" in the area. This finding supports Anderson and Yalden (1981) who demonstrated that a loss of 36% of the heather moorland area in the Peak District had taken place between 1913 and 1981 due to inappropriate and/or over-intensive management interventions. Much of this lost heather moorland has been replaced by sedge (i.e. *Eriophorum* spp.) and grass (especially *Molinia caerulea*) dominated communities. Indeed, Simmons, (2003, pp 207) defined communities dominated by *Eriophorum vaginatum* as "widespread/extensive" in the South Pennines region (including the Peak District).

Sphagna are the bryophytes that account for most of the biomass production that goes to form blanket peat. Clymo and Hayward (1982) estimate that more carbon is held in the biomass of living and dead Sphagnum than is fixed on an annual basis by all other terrestrial vegetation adding up to some 10-15% of the World's terrestrial carbon stock. It is thought that *Sphagna* abundance in the South Pennines/Peak District area is much reduced from pre-industrial times with Moss (1913, pp 163-198) recording 16 common species of *Sphagnum* but Tallis (1964) reporting only five species, of which only one (*S. fallax*) was common. This decline has been attributed primarily to the effects of atmospheric pollutant deposition associated with increased burning of fossil fuels upon the advent of the industrial revolution (Tallis, 1964). Indeed, the South Pennines/Peak District area contains Britain's (and Europe's) largest accumulation of acid deposition (Skeffington et al., 1997), due to its proximity to two major industrial areas (Manchester to the west and Sheffield to the east). However, there have been decreases in the levels of deposition of most atmospheric pollutants (with the exception of nitrogen) in the South Pennines/Peak District areas since the 1970s with the inception of clean air laws. This decline in deposition and large scale ecological restoration efforts in the area have been associated with an increase in the diversity of *Sphagnum* species found in the South Pennines with Carroll et al. (2009) reporting eight species of *Sphagnum*.

In addition to the peat-forming *Sphagnum* mosses, a large number of other bryophytes are present in the Peak District. Bryophytes, including *Sphagna*, occupy specific niches, which are often defined by: hydrology, (e.g. *Polytrichum commune* in boggy areas) and/or vegetative cycles (Gimingham, 1972, pp 125-140). For example, fire mosses (i.e. *Ceratodon purpureus*) are often present after *C. vulgaris* burning with *Hypnum cupressiforme* below mature *C. vulgaris* canopies followed by *Pleurozium schrebei* and *Hylocomium splendens* in degenerate stands. The main point is that bryophytes, as understory vegetation types, are particularly sensitive to changes in the canopy vegetation above them and the water table below them.

While vegetation, of varying types, accounts for most of the land cover in the South Pennines/Peak District, the region is also an area of widespread and heavy erosion, typically by gully incision (e.g. Bower, 1961) (see also chapter 1). This erosion has left an estimated 8% of the blanket peat surfaces completely bare of vegetation (Tallis, 1997). Moreover, Evans et al. (2006) showed that fluxes of particulate organic carbon (POC) from actively eroding South Pennines/Peak District blanket peatlands were the largest losses of carbon from the system.

Therefore, to assess the role vegetation plays in the carbon cycling in the Peak District and South Pennines region it was decided that a cross section sample of all the ground cover types given above was necessary. Moreover, as the vegetation (principally *C. vulgaris*) is heavily managed in the area, a sample of the various conditions this management creates was also deemed to be of importance to the analysis. However, before the aims and objectives of this chapter are formally stated, it is necessary to consider what role vegetation plays in soil carbon cycling.

4.1.2 – Vegetation and Carbon Cycling

Plants give out CO_2 directly (both above- and below-ground) in the form of autotrophic respiration which is defined by Trumbore (2006) to be "CO_2 released by living plant leaves, stems and roots". Secondly, plants supply substrates for micro-organisms to subsequently respire in the form of litter (e.g. Singh and Gupta, 1977) and root exudates (e.g. Boone et al., 1998). These photosynthetic by-products, transferred below ground, are respired by heterotrophs, and contribute to a flux known as heterotrophic respiration. The definition of heterotrophic respiration given by Trumbore (2006) is "CO_2 released during decomposition of non-living organic matter". A heterotroph is defined as an organism that relies upon organic carbon molecules for its supply of metabolic energy and growth tissues (Taiz and Zeiger, 2002, pp 638) whereas an autotroph is defined as being an organism that obtains metabolic energy and growth tissues from CO_2 (or other inorganic carbon molecules). The reduction reaction required to produce tissues from CO_2 is endothermic; thus an external supply of energy is required, which in most cases is obtained from the sun (i.e. photosynthesis) (Taiz and Zeiger, 2002, pp 628). Therefore, all photosynthesising organisms (e.g. plants) are by definition autotrophs. While the term heterotrophic respiration relates to all respiration by heterotrophs, it should be acknowledged that in peatland soils (which are almost entirely composed of organic carbon) heterotrophs will respire substrates derived as products of photosynthesis, either through degradation of dead plant biomass in litters or the peat itself or as respiration of root exudates. Hence, autotrophic and heterotrophic respiration are not in reality discrete fluxes but represent a spectrum of fluxes based on the time elapsed between the respiration of substrates and the substrate's initial derivation from photosynthesis. Nonetheless, it is likely that the autotrophic component of respiration will have the most immediate relationship with photosynthesis (e.g. Gamnitzer et al., 2009), whereas the heterotrophic component of respiration will be subject to potential lags between the production of a substrate by photosynthesis and subsequent respiration of those substrates by heterotrophs.

The sum of these two fluxes (autotrophic and heterotrophic) gives the overall magnitude of ecosystem respiration. However, Bond-Lamberty et al. (2004) acknowledge that partitioning of respiratory fluxes into autotrophic and heterotrophic components is a “gross simplification” of the sources of ecosystem respiration and such portioning may be unable to “capture the processes” that control carbon turnover on long time scales. However, they suggest that the distinction is “very useful” for studies of carbon cycling in soils as it helps estimate root/mycorrhizal respiration rates (i.e. the below-ground autotrophic component) and the size heterotrophic component of ecosystem respiration, allowing for more accurate estimates of net ecosystem production and below ground carbon allocation.

Obviously the role played by vegetation in carbon cycling is complex, firstly, vegetation and the litter it produces can alter the hydrology of peatlands (e.g. Gimingham, 1972; Farrick and Price 2009) thus influencing soil moisture conditions. The quality and quantity of litter produced will vary with species and thus will affect rates of decomposition (e.g. Dorrepaal et al., 2005; 2007; Ward et al., 2010). Provision of differing quantities and qualities of root exudates are known to affect soil microbial community structure (e.g. Chen et al., 2008; Yan et al., 2008). Rates of biomass production and autotrophic respiration vary between species (Gimingham, 1972). Moreover, plant morphology (i.e. lacunae systems in monocotyledonous species and stomatal conductance in general) can affect the rate at which gases are transported from the rhizosphere to the atmosphere (Thomas et al., 1996; Garnet et al., 2005).

Given these effects, vegetation is known to play an important role in global terrestrial carbon cycling, with approximately 10%-17% of atmospheric carbon being cycled through soils, via photosynthesis, every year (Raich and Potter, 1995; Prentice et al., 2001). Indeed, the largest flux of carbon in the terrestrial carbon cycle is photosynthesis, with an estimated magnitude of 104.9 Pg C y^{-1} (Field et al., 1998). Ecosystem respiration of CO_2, is the next largest flux (Raich and Schlesinger, 1992) being ~18 times as large as the fossil fuel contribution to the global carbon budget in the

1990s (Prentice et al., 2001), and can be thought of as made up of heterotrophic and autotrophic respiration. It is thought that correlations observed between the rates of heterotrophic and autotrophic respiration are due to variations in photosynthate supply (Bond-Lamberty et al., 2004), which are mediated by the vegetation present. In fact, the dynamics of ecosystem respiration as whole are also thought to be controlled, in part, by variations in the rate of photosynthesis in forests (e.g. Hogberg et al., 2001; Bhupinderpal-Singh et al., 2003; Tang et al., 2005), multiple ecosystem studies (e.g. Migliavacca et al., 2011), grasslands (e.g. Bahn et al., 2009) and peatlands (e.g. Larsen et al., 2007) and thus coupled with the vegetation present. Ryan et al. (1997; 2004) estimate that between 64-77% of annual photosynthesis is given to autotrophic respiration. There is uncertainty, however, about the partitioning of photosynthate between root exudates (i.e. for heterotrophic respiration) and direct root/mycorrhizal respiration (i.e. autotrophic respiration) (Trumbore, 2006; Metcalfe et al., 2011). Moreover, on a global scale it has been difficult to separate environmental effects from vegetation effects on soil respiration of CO_2 (Raich and Tufekcioglu, 2001).

Nonetheless, on a local scale Ward et al. (2009) have shown that physiological differences between plant functional group affect ecosystem respiration on blanket peat soils in the UK. More broadly, Leppälä et al. (2008) found that differences in CO_2 fluxes along a mire successional gradient in Finland were controlled by differences between plants in terms of phenology. Bubier et al. (1998) found differences in CO_2 dynamics between vegetative communities on a boreal peatland complex in Canada. Furthermore, an in situ UK-based, isotope tracer experiment by Trinder et al. (2008) showed significant differences between vascular species (*Eriophorum* spp. and *Calluna vulgaris*) in terms of shoot respiration, but not soil respiration. This finding was in agreement with an isotope tracer study on temperate grassland in Germany by Gamnitzer et al. (2009) who suggested that autotrophic respiration was closely connected to current photosynthesis while heterotrophic respiration was not. Yan et al. (2008), on the same site as Trinder et al. (2008) demonstrated that differences in root exudate composition between vascular plant species (*Eriophorum* spp. and *Calluna vulgaris*) caused significant differences in the soil microbial community composition under the respective species. In terms of litter, Ward et al. (2010) demonstrated significant differences between upland vascular plants (*Eriophorum* spp. and *Calluna vulgaris*) and bryophytes (*Pleurozium schreberi*) in terms of litter quality and rates of decomposition.

While the processes by which vegetation can control the carbon cycle of peatlands are well established, there are relatively few comparative, in situ studies of the impact of vegetation type on CO_2 flux/carbon dynamics from UK blanket peatlands. Moreover, the studies that exist compare relatively few vegetation types (e.g. Yan et al., 2008, Ward et al., 2009; 2010) and/or have sub-annual time series (McNamara et al., 2008). Moreover, many studies seek to characterise the processes by which vegetation types modify the carbon cycle without necessarily stating what the basic differences between species are in terms of the bulk carbon flux pathways. It is this latter information, however, that would be of value to any attempt to modify the Durham Carbon Model for vegetation type. As such, this study sets out to compare a number of common upland ground cover types, in terms of their impacts on the dynamics of blanket peat CO_2 flux from data gathered for at least twelve months (per plot) on a once monthly basis. The methods available to carry out this study limit the extent to which a process based understanding of impacts of specific vegetation types in peatland carbon cycling can be obtained (i.e. no tracers or below-ground monitoring equipment etc. can be employed). Instead, this chapter will focus on whether plots dominated by differing vegetation types have differing rates of CO_2 flux and differing concentrations of soil pore water DOC, when variation due to other potentially confounding factors and covariates is controlled for. If differences are found that are unexplained by other factors/covariates, this will imply that it is empirically justifiable to modify the existing Durham Carbon Model to take into account any statistically significant differences in carbon cycling by vegetation type that cannot be explained by the predictors already used in the model (i.e. air temperature, water table depth etc.).

4.1.3 – Aims and Objectives

Thus, the broad aim of this chapter is to:

- Characterise whether differences exist between common upland vegetation types in terms of CO_2 flux (i.e. R_{eco} and NEE) and soil pore water DOC concentrations and whether such differences are reflected in efficacy of various CO_2 flux modelling techniques relative to vegetation type.
- Determine whether there are significant differences between canopy heights, and thus whether this would be an appropriate method of considering moorland vegetation management in the DCM.

The overall objective of this research is to provide insight into the role of vegetation and its management in the blanket peat carbon cycle of the Peak District/South Pennines. In the same way as chapter 3, the results of this chapter will be considered (in chapter 7) with respect to the Durham Carbon Model and whether vegetation type would provide a useful modifying sub-model.

4.2 – Experimental Design

Data acquisition and laboratory analysis for this chapter follows the methods given in chapter 2 for all field and laboratory derived data. The following data were gathered for this analysis: CO_2 (NEE, P_g and R_{eco}) and CH_4 fluxes, air temperature, PAR, water table depth and soil pore water DOC concentration. In addition heather canopy height data (taken from a July 2009 vegetation survey) is included. To measure canopy height a steel tape measure was held on the peat/litter surface in the centre of each collar containing and the height to which the canopy reached relative to the tape measure was recorded. This measurement is not a direct measure of stem length (as stems may have been bent over by the wind etc.) and is only a measure of the canopy height in any given plot.

The study sites used within this chapter are listed in table (4.2.1). It is important to note that many sites used in this analysis were not originally instrumented for the purposes of this vegetation study; although some were, more detail is given in chapter 2 and table 4.2.1. As such, the datasets for the respective vegetation types are populated on a plot by plot basis, i.e. the vegetation within each collar is assessed and that defines its classification within this study rather than the dominant vegetation of the site. On occasions when the collars of a site contain differing vegetation types the site is split up and the collars are put into the dataset of their respective vegetation types. This introduces the limitation of poor replication of some vegetation types on the site scale. However, it is ecologically unfeasible to expect every vegetation type to occur within every site (i.e. ecosystems do not always lend themselves to being a fully cross-classified experiment). Moreover, some vegetation types (i.e. bare) were cross-classified with respect to higher order spatial factors like locality and region while some types (i.e. non-*Sphagnum* moss) were nested within them instead (i.e. present on only one area and/or locality). As such, vegetation can both, potentially, be considered as a nested factor within locality and/or region or as a fixed factor (excluding locality/region from the analysis). Neither method is ideal. The benefit of analysing vegetation as a nested factor within locality and region is that it avoids the potential for variance being attributed to vegetation when it should be allocated to locality and/or region, the downside to this approach is that it will not produce estimates of the main effects of vegetation type, as the same vegetation types on differing localities/regions will be considered to separately in the model. This limits the interpretability of the results with respect to the research aims posed. Treating vegetation as a fixed factor allows main effects to be estimated; however, due to the lack of cross-classification with respect to locality and region, the factors locality and region cannot be used in such a model. As such, it was decided that vegetation would be considered as both a nested factor within locality and region and as a fixed factor (without locality and region) in separate analyses. If the importance (i.e. the ω^2 value) of vegetation is equally or less important in the fixed model than the nested model then it can be said that no variance attributable to locality and/or region has been erroneously ascribed to vegetation. Where this is the case the main effects of vegetation determined in the fixed model can be trusted to be unbiased with respect to locality and region. Despite the spatial limitations of the dataset the factors vegetation and month are fully cross-classified and thus datasets were always analysed in terms of these factors. To avoid issues of pseudo-replication all vegetation types in the model had to be present at more than one site. That said, no site contained all vegetation types and a number of sites only have one replicate of a given vegetation type. This means that site was not a useable factor in the analyses undertaken and this limitation should be borne in mind when considering the results to this study

The primary statistical method used for this analysis was GLM-ANCOVA (see chapter 2). When comparing vegetation types the models produced considered a number of potential factors: vegetation (inside collar), month, locality, morphology, orientation, region and year. As discussed previously vegetation was tested as both a fixed factor and a nested factor within locality and/or region, in separate ANCOVA model runs. In addition, locality was always first considered as a nested factor with region, and if region was insignificant locality was then considered as a fixed factor in its own right. Orientation, morphology and year have differing numbers of factor levels between the factor levels of vegetation and as such are considered in the model as random factors (i.e. representing a random sample of the population of all potential factor levels). The additional fixed factor of canopy height range was considered in the *C. vulgaris* dataset. The canopy height range factor was produced by taking the heather canopy height data measured during the vegetation survey in June 2009 and grouping into four categories of canopy heights from 0-10, 10-20, 20-30 and 30-40 cm. These ranges correspond to the maximum and minimum values in the dataset. The following potential covariates were considered in each model, where appropriate: air temperature (K), P_g (g CO_2 m^{-2} hr^{-1}), photosynthetically active radiation (μmol m^{-2} s^{-1}), slope angle (^{o} from horizontal) and water table depth (cm). ANCOVA models were produced by inputting all potential factors and covariates and removing insignificant factors/covariates iteratively until a model containing only significant predictors remained. As mentioned in chapters 2 and 3, there is the potential for self-correlation in regressions between P_g versus R_{eco} and/or NEE. As such, this chapter follows the method adopted in chapter 3 whereby models of R_{eco} and NEE are produced with and without P_g as a predictor.

Table 4.2.1 – Sites and Numbers of Collars Used for Each Vegetation Dataset in this Chapter

Vegetation	Site	Collar(s)	Locality	Region
Bare	BVD	1	Bleaklow Plateau	Peak District
	JPG	1		
	Pen	2		
	TE	5		
	TN	6		
	TS	6		
	Moss	1	Goyt Valley	
	S2:b	1	Green Withens	South Pennines
	S2:c	1		
	S2:d	1		
	BA:b	1	Keighley Moor	
	BB:d	1		
Bilberry	BVD	1	Bleaklow Plateau	Peak District
	WM	1		
	WR	1		
	GS3	2	Goyt Valley	
	Moss	1		
	Pat	3		
	UB	1		
	BB:d	1	Keighley Moor	South Pennines
Cotton Grass	BVD	4	Bleaklow Plateau	Peak District
	Ori	6		
	Pen	4		
	Ben	1	Goyt Valley	
	GS1	1		
	Kra	2		
	Moss	2		
	Nep	4		
	Pat	1		
	Pos	3		
	BB:a	1	Keighley Moor	South Pennines
	BB:b	1		
	SB	1		
Hea	WM	2	Bleaklow Plateau	Peak District
	WR	5		
	Ben	2	Goyt Valley	
	BN	2		
	BS	3		
	Kra	1		
	Nep	1		
	OB	5		
	Prom	4		
	BA:a	3	Keighley Moor	South Pennines
	BA:c	2		
	BA:d	2		
	BB:a	2		
	BB:b	2		
	BB:c	2		
	BB:d	1		
Lawn Grass	JPG	5	Bleaklow Plateau	Peak District
	TE	1		
	TW	6		
Molinia	Pos	3	Goyt Valley	Peak District
	S2:a	2	Green Withens	South Pennines
	S2:b	2		
	S2:c	2		
	S2:d	2		
	S4:b	3		
	S4:c	3		
NS - Moss	BN	1	Goyt Valley	Peak District
	GS1	5		
	GS3	1		
	Kra	3		
	LA	2		
	LB	3		
	Moss	2		
	Pat	1		
	UB	1		
Sphagnum	BVD	3	Bleaklow Plateau	Peak District
	Dory	3	Goyt Valley	
	Nemo	3		
	Nep	1		
	BA:c	1	Keighley Moor	South Pennines
	BB:c	1		
	SA	3		
	SB	2		

- *Bare – bare peat*
- *Bilberry – Vaccinium spp.*
- *Cotton Grass – Eriophorum spp.*
- *Hea – Calluna vulgaris*
- *Lawn Grass – a mixture of common UK lawn grass seeds sown to aid site revegetation*
- *Molinia – Molinia caerulea*
- *NS-Moss – any bryophyte that isn't of the Sphagnum genus*
- *Sphagnum – Sphagnum spp.*

4.2.1 – Comparative Vegetation Study

This analysis seeks to identify whether differing functional groups of vegetation are significantly different in terms of (1) their CO_2 exchange, (2) their DOC production and (3) in a more limited sense their methane flux rates.

Data gathered for this study were obtained from the plots given in table 4.2.1, and split into groups by vegetation type as described above. The vegetation types sampled for this study were chosen on the basis of the literature review in section 4.1 and subsequent field reconnaissance to give a representative sample of the common and/or ecologically important upland functional groups. The groups investigated are given below, and the titles to each section are the terms used to describe these groups in the text henceforward:

- *Bare Peat* – as the name suggests bare peat is defined as a peat surface bare of any living vegetation. The main occurrences of bare peat were sampled on Bleaklow Plateau, with less extensive occurrences sampled in the Goyt Valley and both South Pennines localities.
- *'Bilberry' (Vaccinium spp.)* – is a genus of shrub, of the family *Ericaceae*, that has an affinity for acidic soils like blanket bog and are a common heathland vegetation type (e.g. Gimingham, 1972; Simmons, 2003). Bilberry was mostly found in the heavily managed Goyt Valley with some collars sampling it on Bleaklow Plateau and a single collar in the South Pennines.
- *'Cotton Grass' (Eriophorum spp.)* – is an herbaceous perennial, of the family *Cyperaceae* (i.e. sedges), which is commonly found in heathland communities (e.g. Gimingham, 1972). The two main species found in the Peak District are *Eriophorum angustifolium* and *Eriophorum vaginatum. E. angustifolium* is primarily associated with wetter areas of bogs, close to ponds, streams and *Sphagnum* lawns. *E. vaginatum* (more common in this dataset) is found further away from areas of standing water, frequently forming hummocks and is distinguished from *E. angustifolium* by having single flowered spikelets. Cotton grass is known to have internal lacunae which permit the transport of

carbon gases from the rhizosphere to the surface, controlled on a diurnal scale by the opening and closing of stomata (Thomas et al., 1996). Cotton grass is mainly found in the Peak District, with even numbers of collars between Bleaklow Plateau and the Goyt Valley, a small number of collars in the South Pennines at Keighley Moor.

- *'Heather' (Calluna vulgaris)* – is a species of shrub, of the family *Ericaceae*, which is the dominant heathland vegetation type in the UK (e.g. Gimingham, 1972; Bardgett et al., 1995). It has a four stage growth cycle; juvenile phase, with shoots 0 – 10 cm; building phase, becoming dominant, with shoots 10 – 20 cm; mature phase, sub-dominant to dominant, with a canopy height 20 – 30 cm; degenerate phase, dominance declining with a decreasing amount of living green material and breaks opening in the canopy, canopy height 30 – 40 cm. Note that the canopy height measurements given above are based on measurements from the plots used in this study. The life cycle of heather is typically reset by fire, either wildfire or more commonly managed burning as part of upland management practice for game bird shooting. Heather was sampled in all localities except Green Withens in the South Pennines.
- *'Lawn Grass' (Agrostis spp., Deschampsia spp. and Festuca spp.)* – is a collective term given to three common grass genera whose seeds were sown to help re-vegetate heavily eroded blanket peat on the summit of Bleaklow Plateau. While these genera are not naturally common on blanket peat in the uplands, restoration of heavily eroded peat is becoming common practice in the area and as such this group is of ecological interest. Lawn grasses were only sampled on Bleaklow Plateau.
- *'Molinia' (Molinia caerulea)* – is an herbaceous perennial, of the family *Poaceae* (i.e. grasses). These grasses can tolerate high acidity levels and grow to upwards of 90 cm in height. *Molinia caerulea*, like Cotton Grass, contains an internal lacunae system which permits transfers of rhizosphere gases to the surface (Thomas et al., 1996). *Molinia* tends to be found in wetter areas of the Peak District/South Pennines and is present in the wet heath

part (Ravenslow) of the Goyt Valley locality and in Green Withens. Note that the sites on Green Withens were established specifically to sample *Molinia*.

- *'Non-Sphagnum Moss' (e.g. Hypnum spp. and Polytrichum spp.)* – is taken by this study to be a collective term for all bryophytes sampled that are not the peat-forming *Sphagnum* mosses. The most common genera sampled in this study are given in brackets. While not composed of bryophytes of the same genera this group is typically non/minimally peat forming and thus the comparison with the peat forming *Sphagnum* mosses (i.e. the bulk of biomass preserved in ombrotrophic bogs is derived from *Sphagnum* spp., e.g. Clymo and Hayward, 1982) is considered to be worthwhile in this regard. Functionally, *Sphagnum* and non-*Sphagnum* mosses may be similar (relative to graminoids or ericaceous groups), however, *Sphagnum* litters, due to high concentrations of phenolic compounds (e.g. lignin), are much less decomposable than other peatland vegetation (e.g. Verhoeven and Toth, 1995). As such, differing rates of decomposition between *Sphagnum* and non-*Sphagnum* moss plots may be expected to cause differences between these groups in some or all of the datasets analysed.
- *'Sphagnum' (Sphagnum spp.)* – are bryophytes, of the family *Sphagnaceae.* They are the principal peat-forming biomass in blanket peat in the UK due to high concentrations of phenolic compounds within their cellular structure which retards microbial degradation (e.g. Verhoeven and Liefveld, 1997; Rydin et al., 2006). This means that *Sphagnum* litters may well be less decomposable than those of none peat-forming mosses and other vegetation types. *Sphagnum* mosses have an affinity for highly acidic areas with very shallow water tables or even areas of ponded water. Their affinity for wet areas is due to the fact that they are hydrophytes (i.e. confined to living within centimetres of a free water surface) (Richardson, 1981, pp 25). Moreover, they are ectohydric (Richardson, 1981, pp 25), drawing up moisture by external capillary systems with little ability to move moisture around internally. As such they are sensitive to fluctuations in moisture conditions. The refractory nature of *Sphagnum* biomass may lead to different (likely lower level) fluxes of CO_2 when

compared with other vegetation types. *Sphagnum* has been sampled on Bleaklow Plateau, the Goyt Valley and Keighley Moor. In all these locations it is found in close proximity to surface water, be that ponds or flowing streams.

4.2.2 – Heather Canopy Height Study

Heather is frequently managed by burning and to a lesser, but increasing, extent by cutting, in order to create a suitable habitat for red grouse (*Lagopus lagopus scotica*) (Holden et al., 2007). This creates a mosaic pattern of differing canopy heights within the same broad area. As such a sub-aim of this chapter is to identify whether significant differences exist between areas of heather with varying canopy heights.

Canopy height measurements were taken for all sites/collars containing heather. The data from the heather group have been ordered into factors delimited by canopy height (as described above), with four factor levels: 0 – 10 cm, 10 – 20 cm, 20 – 30 cm and 30 – 40 cm canopy heights. These levels correspond to the growth phases of the heather given in section 4.2.1.

4.2.3 – Modelling Carbon Cycling

This analysis aims to compare the effectiveness of several differing modelling approaches in terms of their predictive ability with respect to CO_2 fluxes by vegetation type. These approaches are either process-based (i.e. stemming from physical/biochemical theories of reaction rate/photosynthesis) or empirical techniques. All models are fitted by regression, either linear or non-linear.

Ecosystem respiration and exchange of CO_2 has been modelled in the past using both empirical (backward – model created on the basis of gathered data) and process-based (forward – model created on the basis of established theory) modelling techniques. Lloyd and Taylor (1994) produced a model (equation 4.1) of ecosystem respiration based on an exponential relationship between chemical reaction rate and temperature, first proposed by Arrhenius (1889). This model is frequently used to describe ecosystem respiration (e.g. Worrall et al, 2009) from peat soils and as such it has been selected for use in this chapter. A model similar in form to this but with an added term relating to the gross photosynthetic rate (equation 4.2) was proposed by Larsen et al. (2007) as an improvement to temperature only models like Lloyd and Taylor (1994) and as such is the next model being considered with respect to ecosystem respiration in this chapter.

$$\mathrm{R} = \mathrm{R}_{10}\mathrm{e}^{\mathrm{E}_0\left(\frac{1}{56.02}-\frac{1}{\mathrm{T}-227.13}\right)} \qquad \textit{Equation 4.1}$$

$$\mathrm{R} = (\mathrm{R}_0 + \lambda \mathrm{P}_\mathrm{g})\mathrm{e}^{\mathrm{b}_\mathrm{m}\mathrm{T}} \qquad \textit{Equation 4.2}$$

Where: R = ecosystem respiration, R_0 = basal respiration at 0°C, R_{10} = respiration rate at 10°C, E_0 = parameter associated with activation energy, T = temperature (K or °C), λ = fraction of P_g instantly respired at 0°C (g CO_2 m^{-2} h^{-1}), P_g = gross photosynthesis (g CO_2 m^{-2} h^{-1}) and b_m = temperature sensitivity. All unknown constants are fitted by a least squares, non-linear process.

In addition to ecosystem respiration of CO_2, this analysis will compare two literature models of net ecosystem exchange of CO_2. The first model to be considered is that of Bubier et al., (1998) which takes the general form NEE = P_g + R. This model uses a rectangular hyperbola fitting technique with respect to PAR, based on the theory of Thornley and Johnson (1990), to estimate P_g, the overall model equation is given in equation 4.3. The next model considered, that of Nykänen et al. (2003) is similar in form to Bubier et al. (1998) but takes a slightly different approach to estimating P_g, with a rectangular hyperbola, than Thornley and Johnson (1990). The overall model equation is given in equation 4.4.

$$\mathrm{NEE} = \frac{\mathrm{P_{gmax}}\alpha\mathrm{PAR}}{\alpha\mathrm{PAR}+\mathrm{Pg_{max}}} + \mathrm{R}$$ *Equation 4.3*

$$\mathrm{NEE} = \frac{\mathrm{P_{gmax}PAR}}{(\mathrm{PAR+K})} + \mathrm{b_0} + \mathrm{tT_{air}} + \mathrm{R}$$ *Equation 4.4*

where R = respiration (g CO_2 m^{-2} h^{-1}), P_{gmax} = the maximum rate of gross photosynthesis (g CO_2 m^2 h^{-1}), α = the initial gradient of the rectangular hyperbola, PAR = photosynthetically active radiation (μmol m^{-2} s^{-1}), T_{air} = air temperature (^oC), b_0, t is a temperature sensitivity coefficient fitted by a least squares, non-linear process. K is the half saturation parameter for P_g with respect to PAR, estimated by linear regression.

The models above represent forward, process-based modelling; however, this study also aims to investigate how well empirical, regression based modelling can predict CO_2 flux, both in an absolute sense and in a comparative sense with respect to forward modelling techniques. Therefore, MLR of the individual vegetation group CO_2 flux datasets will be undertaken, with one third of the data held back for later model validation. MLR models will be produced on both untransformed and natural log transformed datasets, with the best fit (i.e. highest R^2) model being selected. In order to validate the models produced by MLR, they will be fitted to the excluded data. Model validation will help to determine how well the empirical models can be used to predict data not used in their own construction. Moreover, following the convention established in chapter 3, MLR models with and without P_g as a predictor will be produced. The models produced by MLR in this study are generated in a similar manner to the MLR models of photosynthesis and respiration produced for a boreal peatland in Bubier et al. (1998). Moreover, the MLR approach to carbon fluxes has been employed in a number of studies in the UK in similar peatland environments (e.g. Clay et al., 2012; Worrall et al., 2009a).

In addition to comparing model performance, this study will also compare modelled measures of temperature sensitivity in the form of the Q_{10} factor (equation 4.5) and an estimation of activation energy derived from (equation 4.6).

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{\left(\frac{10}{T_2 - T_1}\right)} \qquad \textit{Equation 4.5}$$

$$E_a = U\frac{dR}{dT^{-1}} \qquad \textit{Equation 4.6}$$

where: Q_{10} = the factor by which respiration changes with a 10°C change in temperature, R = respiration (g CO_2 m^2 h^{-1}), U = universal gas constant (J K^{-1} mol^{-1}), T = temperature (K), E_a is the activation energy of respiration (kJ mol^{-1}).

4.3 – Results

Prior to the more sophisticated analyses undertaken later in this section, it is important to consider the dataset as a whole and the relationships between the response variables and their potential predictors. The main objective of this chapter is to investigate whether there are significant differences between plots containing differing vegetation types in terms of CO_2 and soil pore water DOC concentrations. As such, interval plots of the CO_2 flux and DOC data have been created (figures 4.3.1-4.3.3 respectively) which show whether the standard errors of the means for each vegetation type overlap. In order to minimise the potential for type 1 like errors (i.e. observing a difference where none in fact exists), the error bars on all interval plots represent plus/minus three standard errors of the mean. For R_{eco} (figure 4.3.1) it appears that *Molinia* is has a significantly greater rate of R_{eco} than the other vegetation types considered and bare peat has a significantly lower rate of R_{eco}

than the rest. For NEE (figure 4.3.2) the only vegetation type which appears to be a significant sink (i.e. error bars always less than zero) is lawn grass, with *Sphagnum* looking like it is also likely to be a sink. *Molinia* is a large significant source and is also appears to be significantly different to cotton grass, lawn grass and *Sphagnum*. For DOC (figure 4.3.3) bilberry appears to have significantly higher soil pore water DOC concentrations than bare peat, cotton grass, lawn grass, *Molinia* and *Sphagnum*.

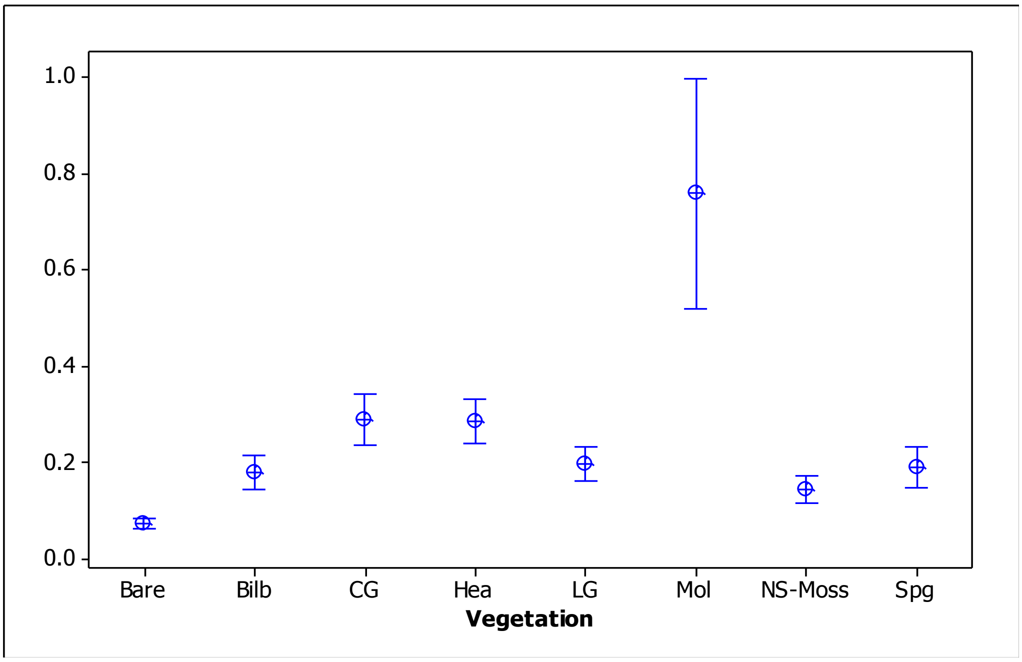


Figure 4.3.1 **–** Interval plot of R_{eco} (g CO_2 m^{-2} h^{-1}) versus vegetation type. The interval bars represent ±3 standard errors of the mean and the circles represent the mean value. Bare = bare peat, Bilb = Bilberry, CG = Cotton Grass, Hea = Heather, LG = Lawn Grass, Mol = *Molinia*, NS-Moss = Non-*Sphagnum* moss and Spg = *Sphagnum*.

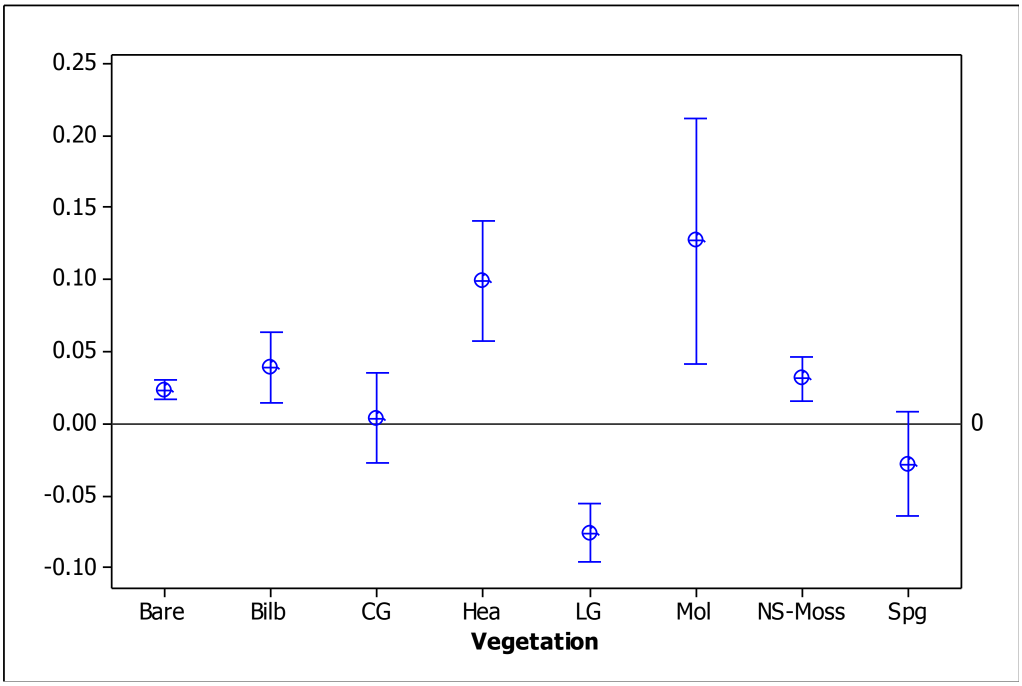


***Figure 4.3.2* –** Interval plot of NEE (g CO_2 m^{-2} h^{-1}) versus vegetation type. The interval bars represent ±3 standard errors of the mean and the circles represent the mean value.

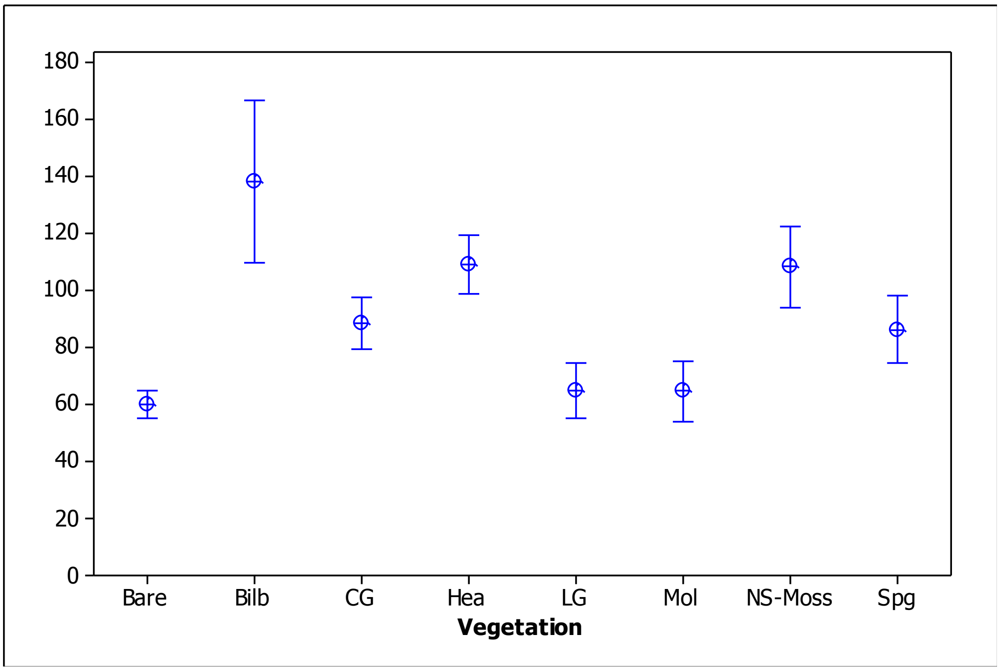


***Figure 4.3.3* –** Interval plot of DOC (mg C l^{-1}) versus vegetation type. The interval bars represent ±3 standard errors of the mean and the circles represent the mean value.

A matrix plot showing the bivariate relationships between R_{eco}, NEE and DOC (i.e. the response variables of interest) and important potential predictors of these datasets has been included below (figure 4.3.4). For R_{eco} it can be seen that significant bivariate relationships have been identified between R_{eco} and air temperature, P_g and water table depth, with P_g being having the strongest relationship with R_{eco} (R^2 = 64.9%) followed by air temperature (R^2 = 16.1%), with water table having only a weak effect (R^2 = 0.4%). For NEE a weak but significant relationship was identified only between NEE and air temperature (R^2 = 0.5%). For DOC a weak but siginificant relationship was identified between DOC and water table depth (R^2 = 1.3%) and DOC and P_g (R^2 = 0.5%).

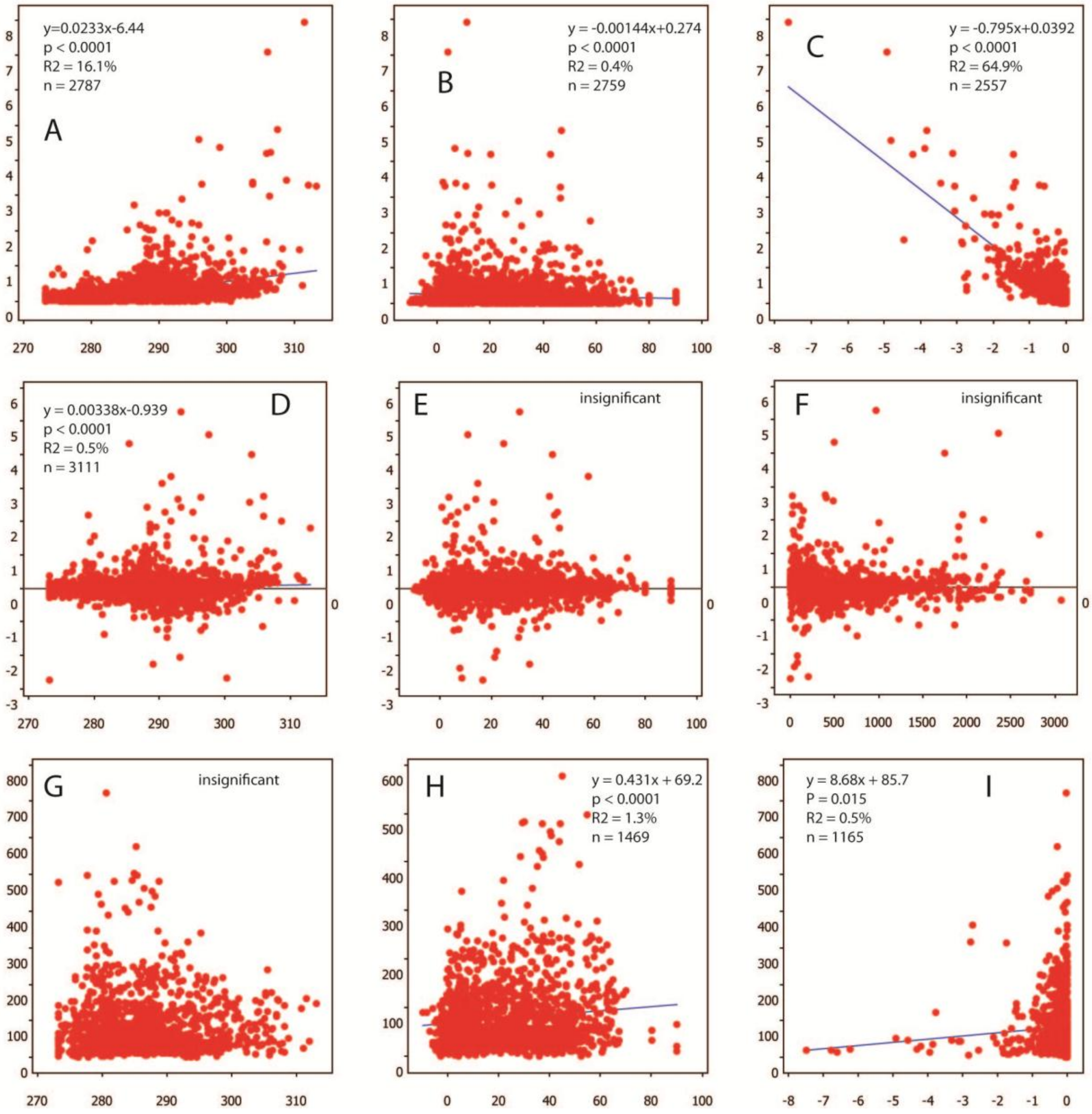


Figure 4.3.4 **–** Matrix plot of R_{eco} (g CO_2 m^{-2} h^{-1}, panels A-C), NEE (g CO_2 m^{-2} h^{-1}, panels D-F) and DOC (mg C l^{-1}, panels G-H) versus air temperature (K, panels A,D and G), water table depth (cm, panels B,E,H), P_g (g CO_2 m^{-2} h^{-1}, panels C and I) and PAR (μmol m^{-2} s^{-1}, panel F). Blue lines represent significant linear regression lines.

It is known that water table conditions can control the surface vegetation present on peatlands (e.g. Bragazza and Gerdol, 1996; Breeuwer et al., 2009; Lavoie et al., 2005; Pellerin et al., 2009). Indeed, vegetation can is actively being used as a predictor of peatland hydrological conditions (e.g. Harris and Bryant, 2009). As such, boxplots of the distribution of the water table data set by vegetation type are given in figure 4.3.5. It can be seen from figure 4.3.5 that the graminoid and bryophyte groups tend to have shallower water tables than ericaceous groups and areas of bare and restored peat.

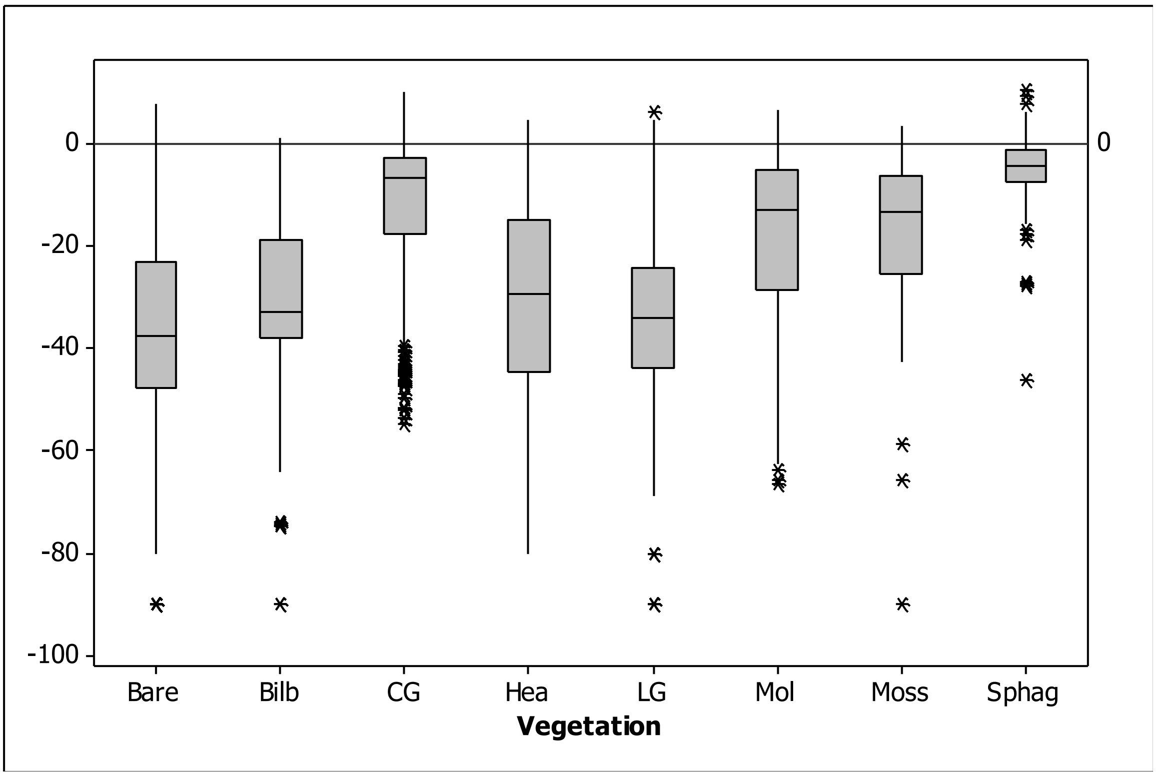


Figure 4.3.5 **–** Boxplots of the distribution of the water table depth dataset (units: cm below the soil surface) versus vegetation group. The asterisks represent outliers.

4.3.1 – Comparative Vegetation Study

Before considering the results of the more sophisticated statistical analysis of the vegetation dataset it is important to consider the size of each dataset and what the raw data for each vegetation type look like on a monthly basis. Table 4.3.1.1 show the dataset sizes for each vegetation type for R_{eco}, NEE, P_g and DOC. The mean monthly values for each vegetation type are displayed for R_{eco}, NEE and soil pore water DOC concentration in figures 4.3.1.1., 4.3.1.4 and 4.3.1.8 respectively.

Table 4.3.1.1 – Number of Data by Vegetation Type and Carbon Flux/Species

Vegetation	n			
	R_{eco}	NEE	P_g	DOC
Bare	649	800	567	354
Bilb	180	190	167	60
CG	570	596	518	306
Hea	593	623	506	281
LG	387	425	385	208
Mol	195	201	159	112
NS-Moss	276	313	252	145
Sphag	202	237	212	113

A visual inspection of figure 4.3.1.1 reveals that *Molinia* has a much larger annual respiratory flux than the other vegetation types. Moreover, it is also clear that bare peat has a lower R_{eco} flux than the vegetated sites; however, its flux is not zero. Cotton grass and heather tend to have similar fluxes with bilberry, non-*Sphagnum* moss and *Sphagnum* having similar magnitudes also.

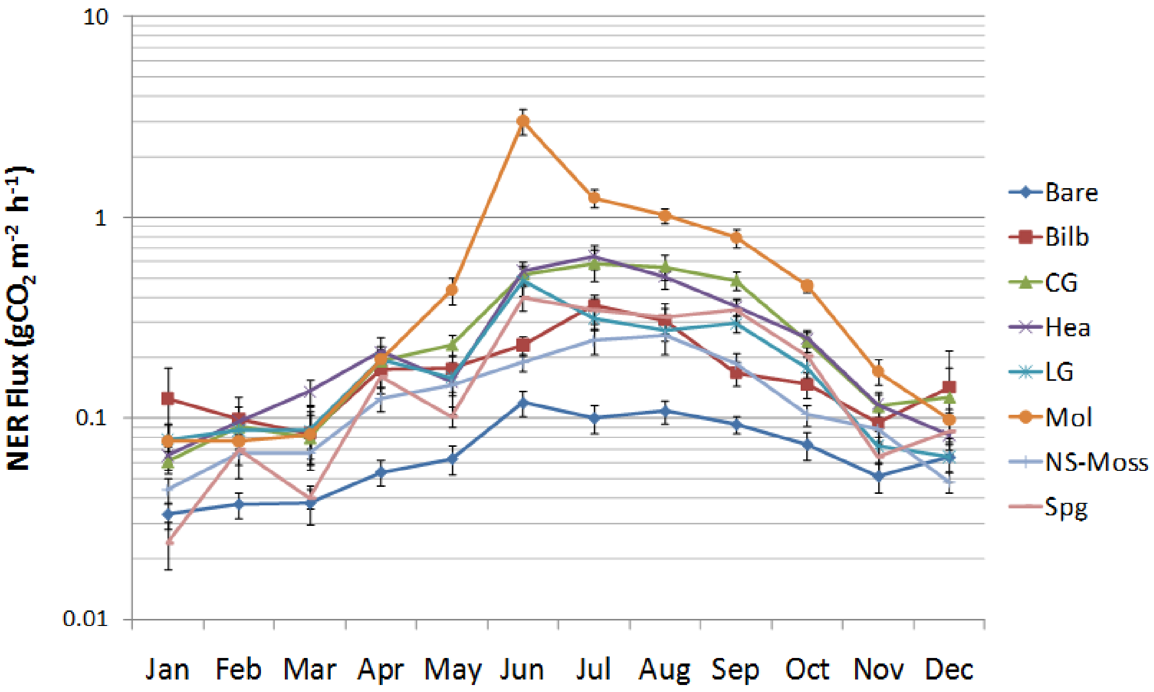


Figure 4.3.1.1 **–** Mean monthly ecosystem respiration value for each vegetation dataset. The error bars represent the standard error of the mean.

As described in section 4.2, the R_{eco} data were analysed by ANCOVA with vegetation considered as (i) a fixed factor and (ii) a nested factor within the regions and localities of the plots forming the datasets. Given the data distribution apparent in figure 4.3.1.1, it is not surprising that a natural-log-transformed R_{eco} dataset provided the best model fits. The results for $\ln(R_{eco})$ are stated in table 4.3.1.2. Of the factors originally tested (summarised in section 4.2), the following were significant in all ANCOVA outputs regardless of model setup: month, orientation, vegetation (nested within locality or as a fixed factor) and year. Of these factors vegetation was most important explaining between 8.00-17.46% of $\ln(R_{eco})$ dataset variation depending on whether P_g was included as a covariate or not. While vegetation was significant both as a fixed factor and as a nested factor within locality, the importance of vegetation remained similar between both model setups (table 4.3.1.2), i.e. no/very little variation ascribed to vegetation as a fixed factor is actually variation that should really be ascribed to locality. Moreover, the importance of locality as factor was low (ω^2 =

1.79-3.23%) in comparison to the importance of vegetation. Thus the main effects of vegetation, determined as a fixed factor, can be thought of as representing a good estimation of the general effects of the vegetation types on R_{eco} fluxes despite dataset limitations regarding differing spatial ranges of each vegetation type considered.

The vegetation main effects (both with and without P_g as a covariate) and the *post hoc* Tukey comparisons groupings are shown in figure 4.3.1.2. It can be seen in figure 4.3.1.2 that the *post hoc* tests confirm the results of the visual inspection of figure 4.3.1.1 with *Molinia* having, generally, greater magnitude fluxes that the rest and bare peat having consistently lower magnitude fluxes. The use of P_g as a covariate (i.e. once its variance is taken into account) caused inter-vegetation differences to be somewhat reduced, such that cotton grass and heather were no longer statistically different to *Molinia*. Taking a more general look at covariates, apart from P_g (table 4.3.1.2), the only other variable significant in all ANCOVA approaches was air temperature. Moreover, air temperature was the most important predictor of $\ln(R_{eco})$ (ω^2 = 24.69-27.17%) dataset variability. Slope (i.e. slope angle from vertical) was found to be a significant predictor of $\ln(R_{eco})$ in all but one ANCOVA model, however, its importance, as determined by the ω^2 statistic was negligible (ω^2 = 0.01 – 0.05%).

It is clear, from chapter 2, that the sites used in this chapter are subject to a number of land management techniques, such as burning, cutting, restoration etc. The residuals from the ANCOVA model of $\ln(R_{eco})$ with vegetation unnested including P_g as a covariate have been plotted as box plots by management type in order to characterise whether there are obvious differences between the management types (figure 4.3.1.3). It can be seen from figure 4.3.1.3 that the variance of the residuals by management type does not seem to vary greatly with management, i.e. it appears that management is not important in terms R_{eco} fluxes or that variance due to management has been captured by other covariates and/or factors.

Table 4.3.1.2 – ANCOVA Results for Reco (nested/unnested vegetation and with/without Pg)

ANCOVA (Nested Vegetation)								
			ln R_{eco} - without P_g					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	20.23	< 0.0001	0.05	0.0446	0.0099		
Cov	Air Temperature	137.64	< 0.0001	24.69	0.0438	0.0037		
NF	**Vegetation (Locality)**	**33.58**	**< 0.0001**	**17.41**				
FF	Locality	20.53	< 0.0001	3.23			54.95%	2724
FF	Month	38.91	< 0.0001	6.18				
RF	Orientation	4.29	< 0.0001	0.38				
RF	Year	33.9	< 0.0001	2.21				
			ln R_{eco} - with P_g					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	15.66	< 0.0001	0.01	0.0383	0.0097		
Cov	Air Temperature	50.54	< 0.0001	27.17	0.0261	0.0037		
Cov	Pg	326.26	< 0.0001	16.98	-0.8427	0.0467		
NF	**Vegetation (Locality)**	**20.37**	**< 0.0001**	**8.75**			62.11%	2294
FF	Locality	10.58	< 0.0001	1.79				
FF	Month	29.11	< 0.0001	4.64				
RF	Orientation	5.04	< 0.0001	0.50				
RF	Year	22.95	< 0.0001	1.48				

ANCOVA (Un-nested Vegetation)								
			ln R_{eco} - without P_g					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	5.86	0.016	0.05	0.0194	0.0080		
Cov	Air Temperature	150.11	< 0.0001	24.69	0.0462	0.0038		
FF	**Vegetation**	**104.39**	**< 0.0001**	**17.46**				
							52.83%	2724
FF	Month	36.7	< 0.0001	5.88				
RF	Orientation	6.26	< 0.0001	0.65				
RF	Year	42.97	< 0.0001	3.55				
			ln R_{eco} - with P_g					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Air Temperature	59.81	< 0.0001	27.17	0.0287	0.0037		
Cov	Pg	333.64	< 0.0001	16.74	-0.8595	0.0471		
FF	**Vegetation**	**55.71**	**< 0.0001**	**8.00**			60.08%	2294
FF	Month	26.83	< 0.0001	4.22				
RF	Orientation	8.57	< 0.0001	0.93				
RF	Year	28.17	< 0.0001	2.46				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor

RC = regression coefficient

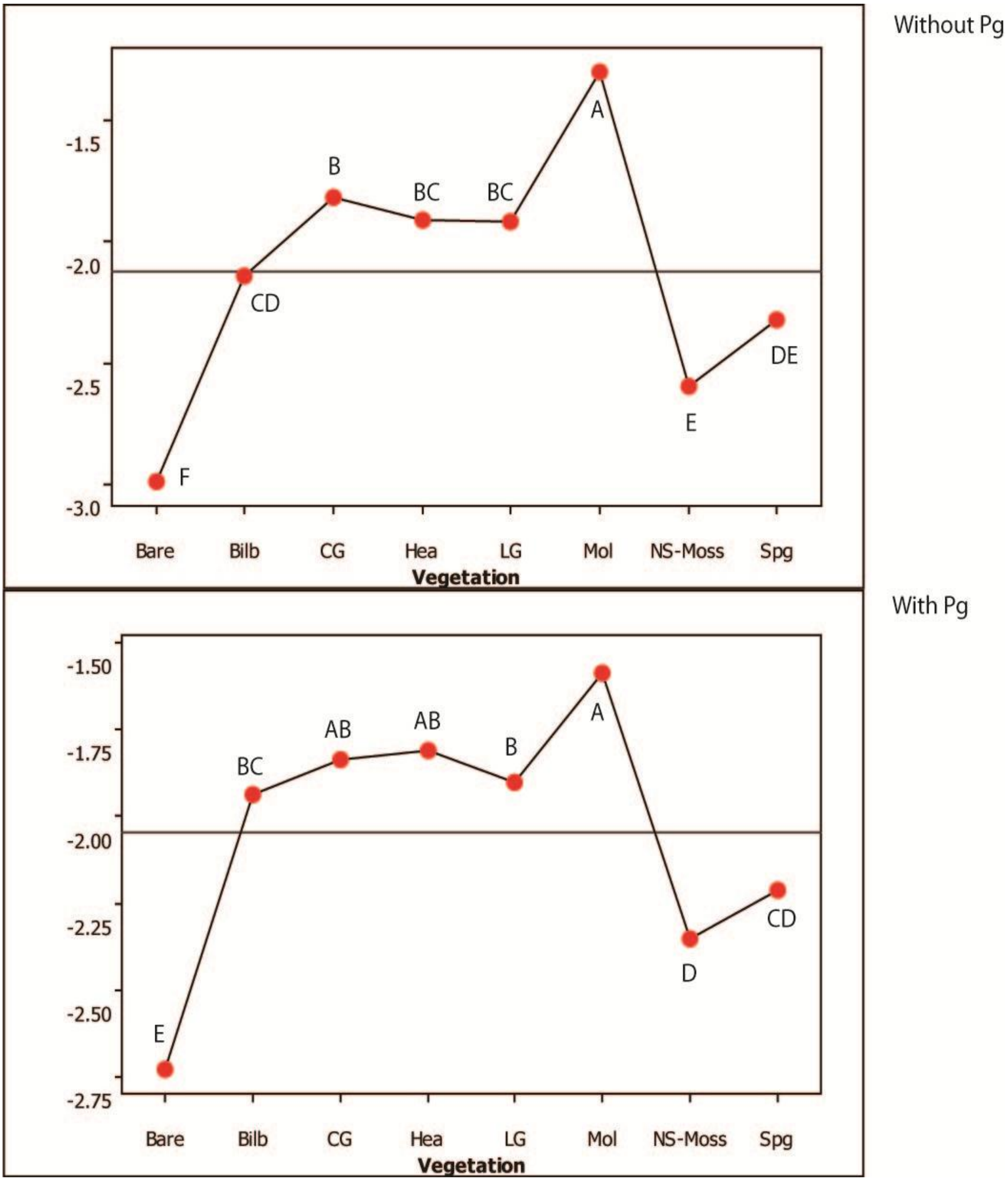


Figure 4.3.1.2 **–** Main effects plots of ln(R_{eco}) (units = ln(g CO_2 m^{-2} h^{-1})) for models both with and without P_g as a covariate. The letters in proximity to each data point represent the groupings determined by *post hoc* Tukey's pairwise comparisons. Any group sharing a letter with another group is not statistically different to that group.

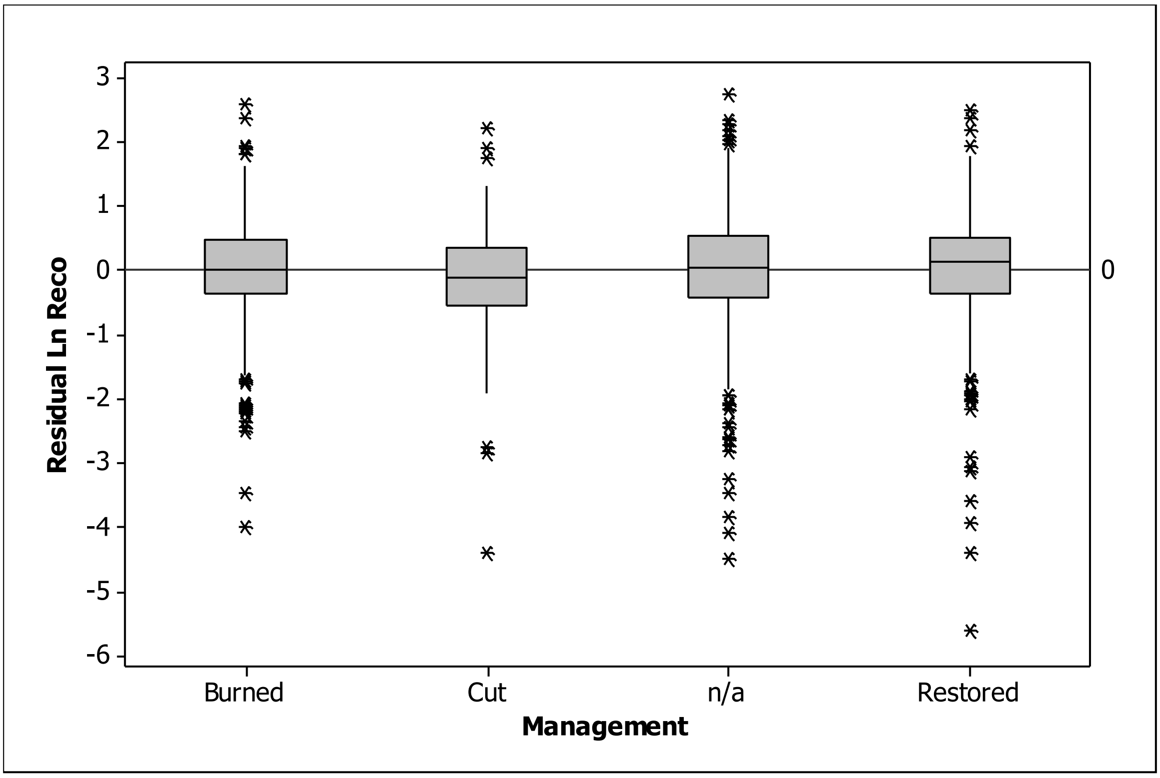


Figure 4.3.1.3 **–** Boxplot showing dataset distribution of the residual variance of the ln(R_{eco}) ANCOVA model (with vegetation as an unnested-fixed factor within locality and P_g as a covariate) versus land management technique. Where: burned = heather burned, cut = heather cut, n/a = means no known management within five years prior to site installation and restored = areas of bare peat restored by reseeding and/or slope stabilisation and/or water table restoration. Asterisks represent outlying data points.

Similar to R_{eco} the NEE fluxes out of the various vegetation types tend to be different in magnitude and, in this case, direction (figures 4.3.1.4 - 4.3.1.5). The largest magnitude fluxes (regardless of direction) were recorded under heather, Molinia and to a lesser extent Sphagnum. It appears that bryophytes and graminoids are more likely to be net sinks of CO_2 than ericaceous genera, with Molinia as a clear exception to this rule, this is in agreement with figure 4.3.2. Bare peat tends to vary around zero, with a small increase in source strength in the middle of the growing season.

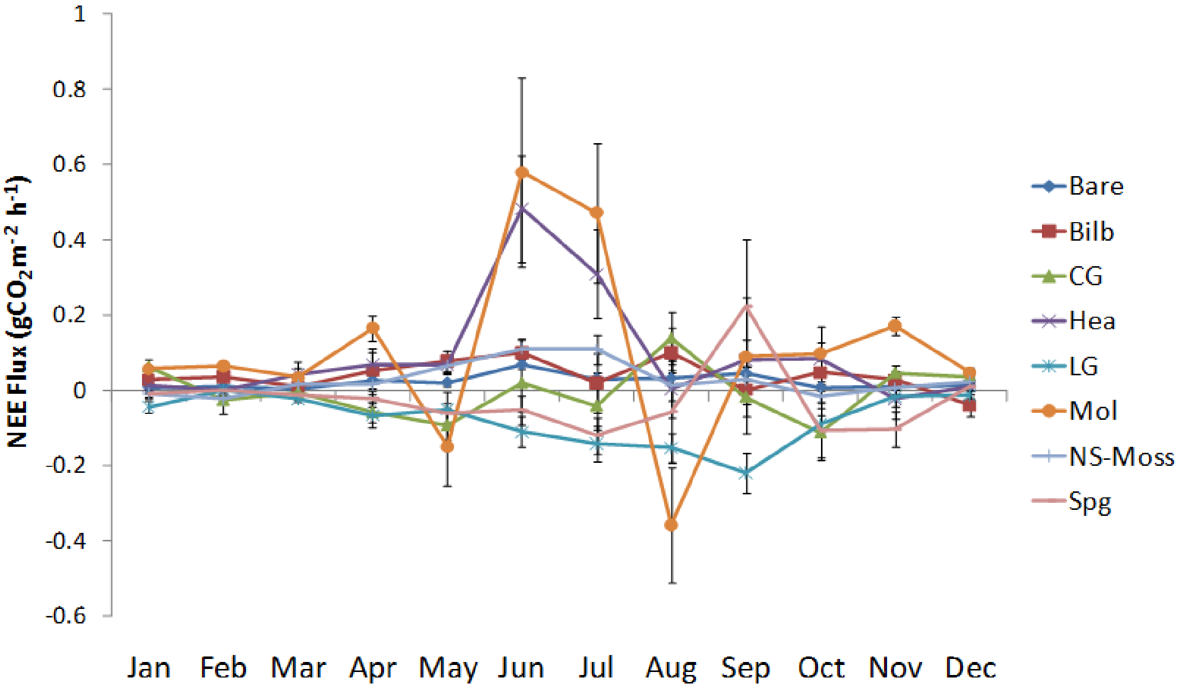


Figure 4.3.1.4 **–** Mean monthly R_{eco} value for each vegetation dataset. The error bars represent the standard error of the mean.

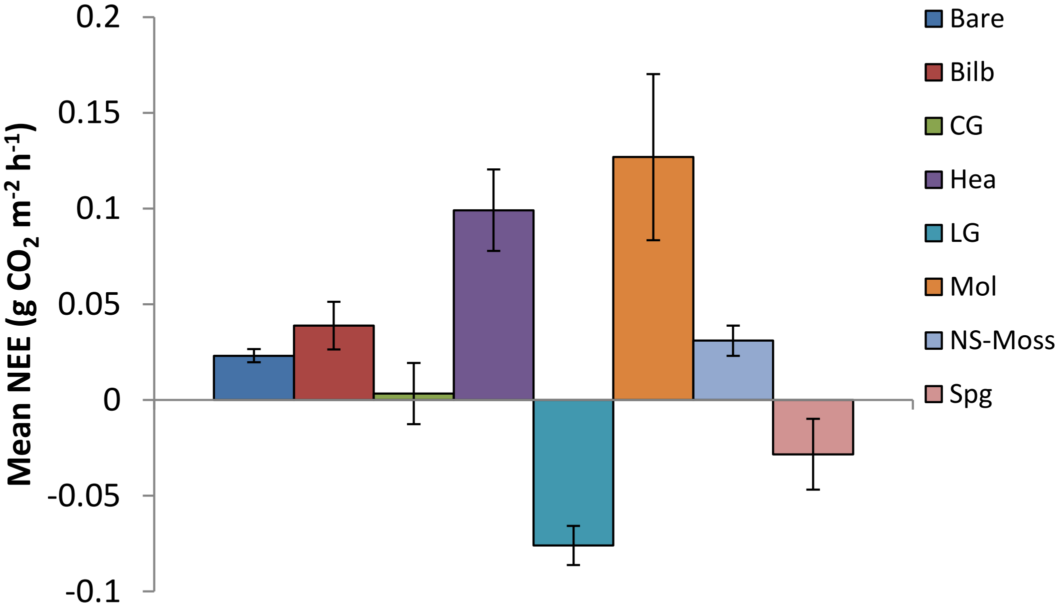


Figure 4.3.1.5 –Mean NEE for each vegetation type. The error bars represent the standard error of the mean.

The results from the ANCOVA approaches taken for NEE are stated in table 4.3.1.3. The striking difference between these results and those of R_{eco} is that the model R^2s are much smaller for NEE. The following factors were significant in all ANCOVA models regardless of approach taken: month, orientation and vegetation. Vegetation is the most important factor explaining variation in the NEE dataset (ω^2 = 2.53-7.42), regardless of whether vegetation is nested within locality and region or whether P_g is used as a covariate. The importance of vegetation decreases somewhat when vegetation is considered as an unnested-fixed factor relative to models where vegetation is nested within locality and region. Therefore, there is no evidence that NEE dataset variance is being erroneously attributed to vegetation when, in fact, it belongs to locality or region. Moreover, the factors locality and region are less important (ω^2 = 0.40-0.75% and ω^2 = 0.47-0.82% respectively) in the ANCOVA models than vegetation. Consequently the main effects of vegetation, as determined using vegetation as a fixed factor, can be thought of as being unbiased by inter-locality/regional variation. The use of P_g as a covariate increases the importance of vegetation in the ANCOVA models, suggesting that accounting for variance attributable to P_g allows less important effects to become more apparent. The variables ln(PAR) and air temperature are significant predictors of NEE in all ANCOVA approaches taken; however, their importance is low relative to that of vegetation (ω^2 = 0.08-1.15% and ω^2 = 0.12-1.11% respectively).

The main effects of vegetation (i.e. vegetation as an unnested-fixed factor) are shown in figure 4.3.1.6 for models with and without P_g as a covariate. It can be seen that, in general, the results of the *post hoc* testing on the datasets confirm what is evident from visual inspection of figure 4.3.1.4 and 4.3.1.5, that the overall rates of NEE from most vegetation types are comparable, with the exception of *Molinia* which is a considerably larger net source of CO_2 than the rest. Indeed, the results for models where P_g was used as a covariate show that, once P_g is taken into account, all vegetation types are not significantly different to each other with the exception of *Molinia*, which is different to all other vegetation types.

Once again, a set of box plots of the residual NEE dataset after ANCOVA with vegetation unnested and P_g included as a covariate versus management type have been produced (figure 4.3.1.7). These boxplots demonstrate that variance in the NEE residuals does not appear to vary with management type, with the exception that the range of values for cut heather and restored areas is less than burned heather and no management. This suggests that management is either not effective on NEE or that the effects of management have already been explained by the significant factors or covariates considered.

Table 4.3.1.3 – ANCOVA Results for NEE (nested/unnested vegetation and with/without P_g)

ANCOVA (Nested Vegetation)

NEE - without P_g

Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Ln PAR	31.54	< 0.0001	0.08	-0.0382	0.0068		
Cov	Air Temperature	11.28	0.001	1.11	0.0049	0.0015		
NF	**Vegetation (Locality Region)**	**3.71**	**< 0.0001**	**4.29**				
NF	Locality (Region)	4.56	0.003	0.40			9.34%	2938
FF	Region	8.61	< 0.0001	0.47				
FF	Month	4.46	< 0.0001	1.21				
RF	Orientation	3.11	0.003	0.46				

NEE - with P_g

Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Ln PAR	55.18	< 0.0001	0.40	-0.0409	0.0055		
Cov	Air Temperature	68.67	< 0.0001	0.87	0.0098	0.0012		
Cov	Pg	461.28	< 0.0001	12.73	0.2940	0.0137		
NF	**Vegetation (Locality Region)**	**4.04**	**< 0.0001**	**7.42**			27.13%	2393
NF	Locality (Region)	9.67	< 0.0001	0.75				
FF	Region	10.19	< 0.0001	0.82				
FF	Month	6.76	< 0.0001	1.96				
RF	Orientation	4.84	< 0.0001	0.83				

ANCOVA (Un-nested Vegetation)

NEE - without P_g

Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Ln PAR	26.97	< 0.0001	0.76	-0.0355	0.0068		
Cov	Air Temperature	11.21	0.001	0.43	0.0050	0.0015		
FF	**Vegetation**	**5.2**	**< 0.0001**	**2.53**				
							6.83%	2938
FF	Month	4.21	< 0.0001	1.09				
RF	Orientation	6.16	< 0.0001	1.16				

NEE - with P_g

Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Ln PAR	49.4	< 0.0001	1.15	-0.0390	0.0056		
Cov	Air Temperature	68.92	< 0.0001	0.12	0.0100	0.0012		
Cov	Pg	492.87	< 0.0001	12.73	0.3051	0.0137		
FF	**Vegetation**	**19.44**	**< 0.0001**	**6.38**			24.46%	2393
FF	Month	6.5	< 0.0001	1.84				
RF	Orientation	6.97	< 0.0001	1.33				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor

RC = regression coefficient

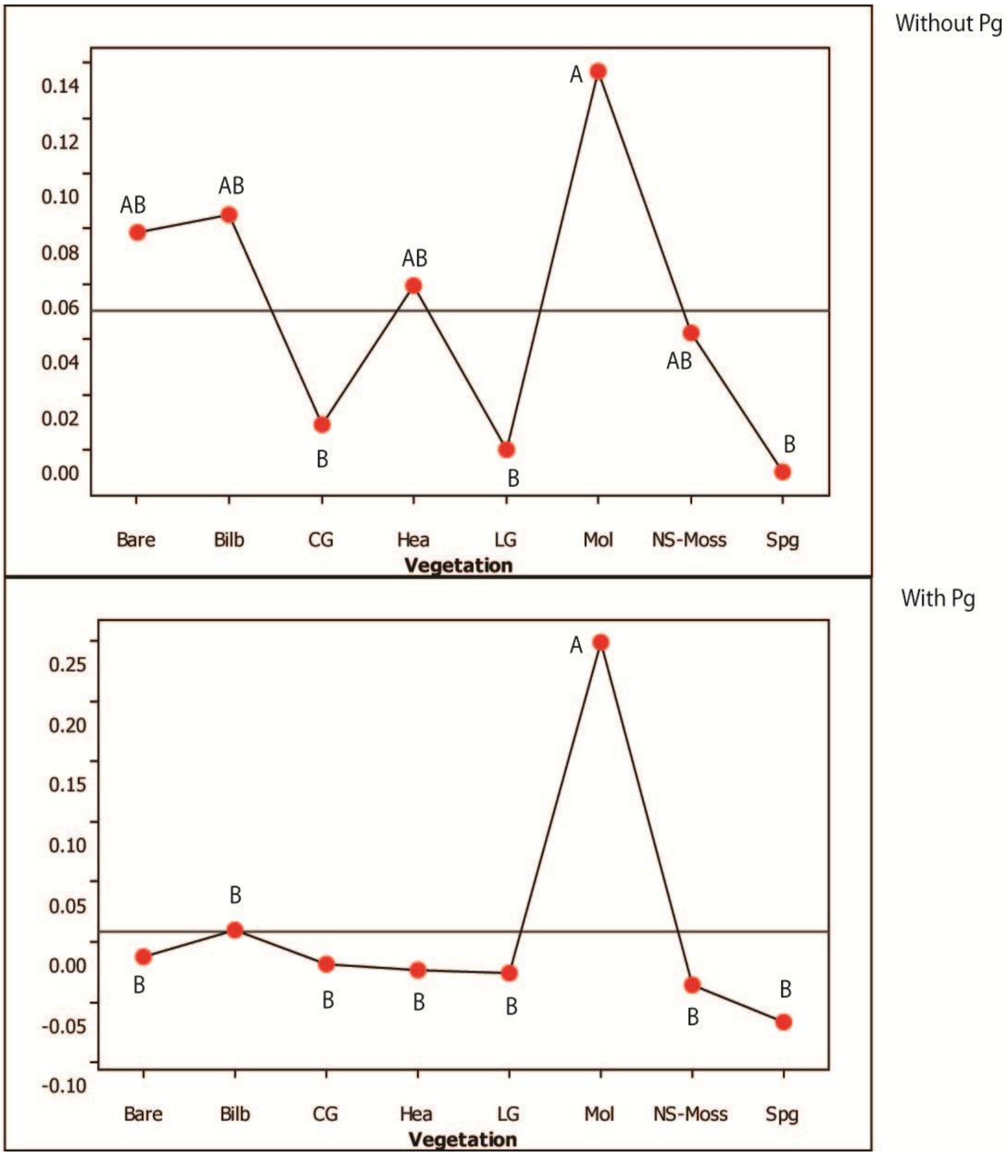


***Figure 4.3.1.6* –** Main effects plots of NEE (units = g CO_2 m^{-2} h^{-1}) for models both with and without P_g as a covariate. The letters in proximity to each data point represent the groupings determined by *post hoc* Tukey's pairwise comparisons. Any group sharing a letter with another 7group is not statistically different to that group.

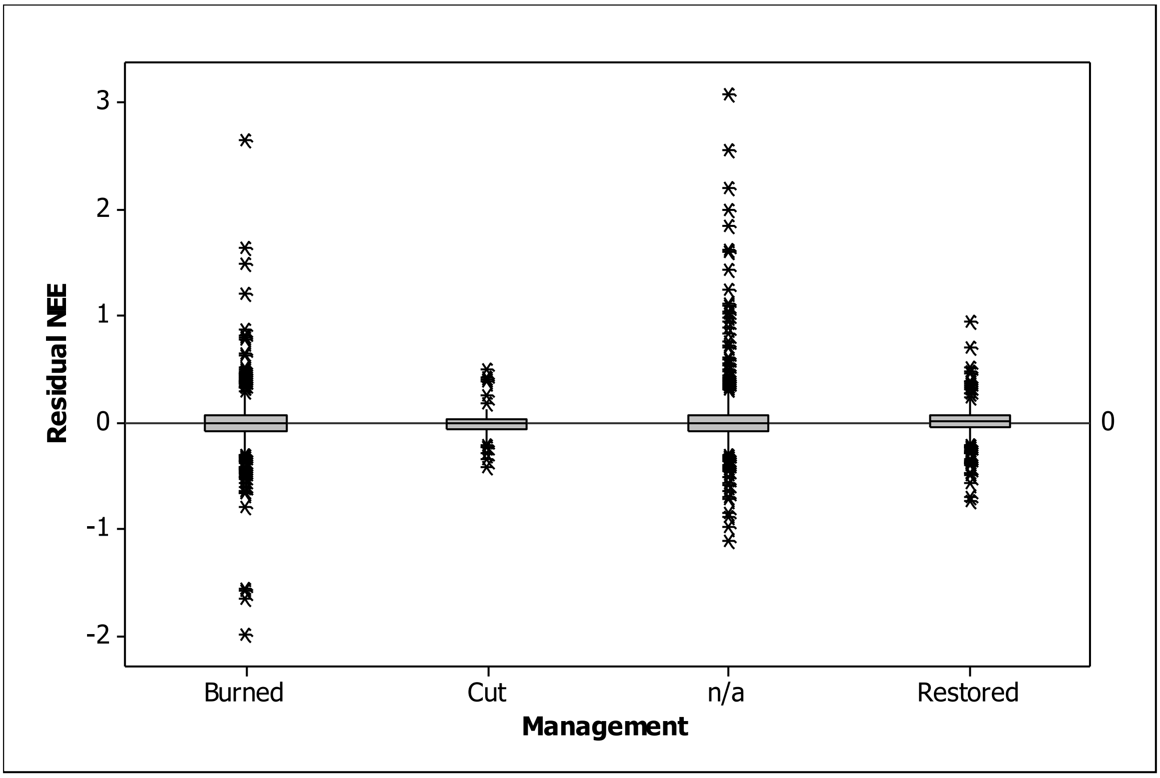


Figure 4.3.1.7 – Boxplot showing dataset distribution of the residual variance of the NEE ANCOVA model (with vegetation as an unnested-fixed factor and P_g as a covariate) versus land management technique. Where: burned = heather burned, cut = heather cut, n/a = means no known management within five years prior to site installation and restored = areas of bare peat restored by reseeding and/or slope stabilisation and/or water table restoration. Asterisks represent outlying data points.

Soil pore water DOC concentrations have more inter- and intra-monthly variation across the year than the CO_2 fluxes; however, many of the datasets show a peak (particularly bilberry) around late autumn/early winter (October and November) (figure 4.3.1.8), with an additional apparent pulse in early spring (March).

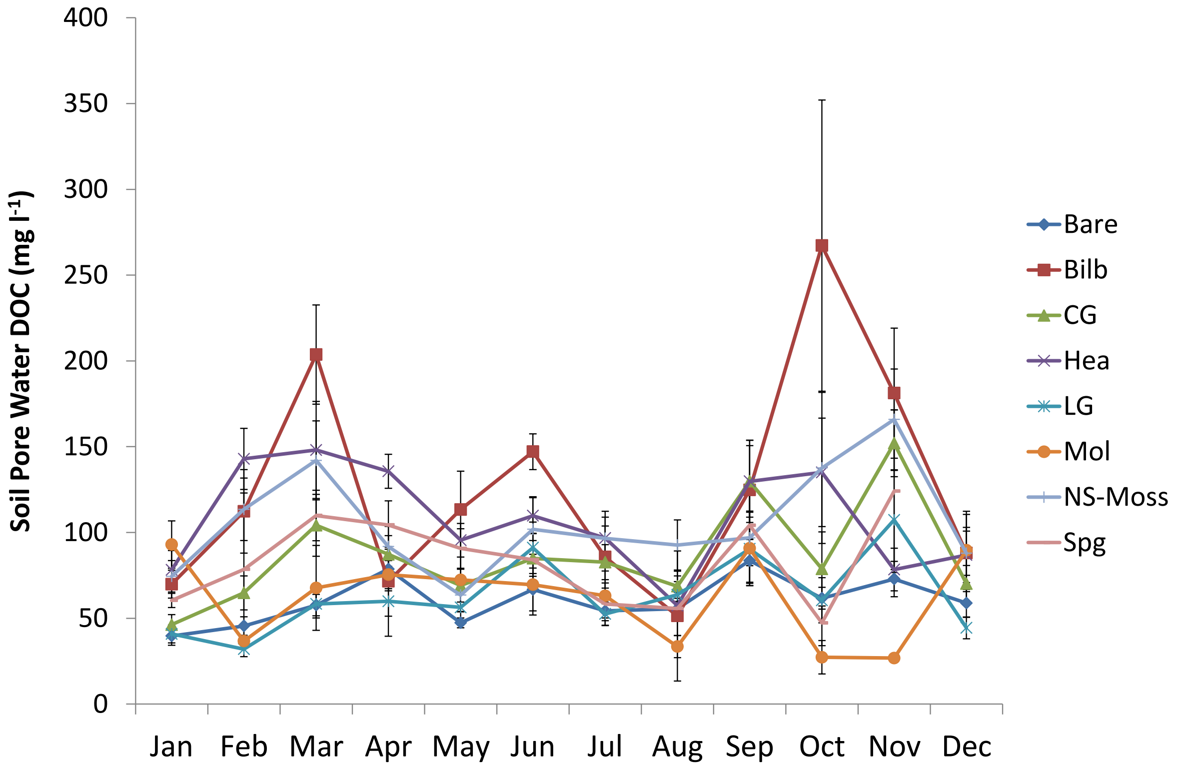


Figure 4.3.1.8 –Mean monthly soil pore water DOC concentration value for each vegetation dataset. The error bars represent the standard error of the mean.

The results of the ANCOVA approaches for the DOC dataset are presented in table 4.3.1.3. The model fit of the unnested vegetation ANCOVA (i.e. the only significant model) was 20.73%, which is much lower than the equivalent ln(R_{eco}) model but similar to the fit of the comparable NEE model. Of the factors originally tested (see section 4.2), the following were significant in the model: month, orientation, vegetation and year. Vegetation was the most important factor accounting for 10.64% of dataset variation. The fact that neither locality nor region were significant in the model means that it is reasonable to consider vegetation as a fixed factor and that the main effects therein are not biased by variance that should really be attributed to locality and/or region.

The main effects of, and *post hoc* Tukey pairwise comparisons for, vegetation are shown in figure 4.3.1.9. It is evident from figure 4.3.1.9 that, as was discernible from figure 4.3.1.8, bilberry has significantly higher soil pore water DOC concentrations than many vegetation types and bare peat, lawn grass and *Molinia* have significantly lower soil pore water DOC concentrations than many other vegetation types.

Once again boxplots of the DOC ANCOVA model residual dataset variation by management type has been created (figure 4.3.1.10). It is clear from figure 4.3.1.10 that the residuals of the DOC ANCOVA do not vary with management type.

Table 4.3.1.3 – ANCOVA Results for Soil Pore Water DOC Concentration (vegetation as a nested factor and as an unnested-fixed factor)

ANCOVA (Nested Vegetation)								
DOC								
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
No significant nested model								

ANCOVA (Un-nested Vegetation)								
DOC								
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Water Table Depth	25.71	< 0.0001	1.29	0.0045	0.001438	20.73%	1469
FF	**Vegetation**	**8.15**	**< 0.0001**	**10.64**				
FF	Month	7.17	< 0.0001	3.69				
RF	Year	4.78	0.001	1.04				
RF	Orientation	7.24	< 0.0001	2.41				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor
RC = regression coefficient

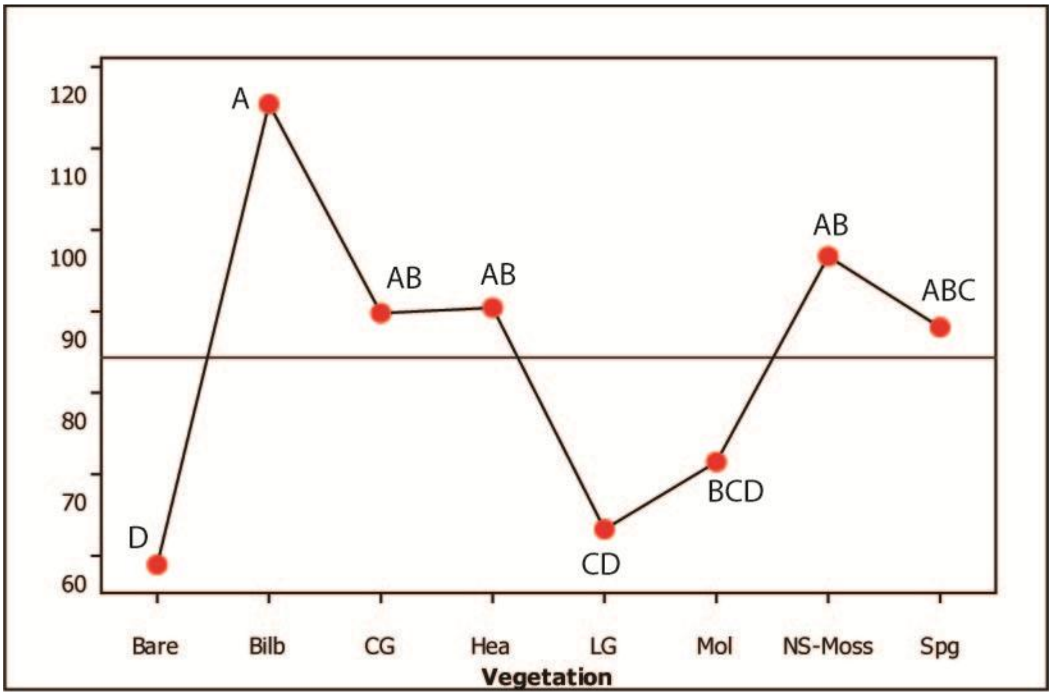


***Figure 4.3.1.9* –** Main effects plots of DOC (units = mg C l1). The letters in proximity to each data point represent the groupings determined by *post hoc* Tukey's pairwise comparisons. Any group sharing a letter with another group is not statistically different to that group.

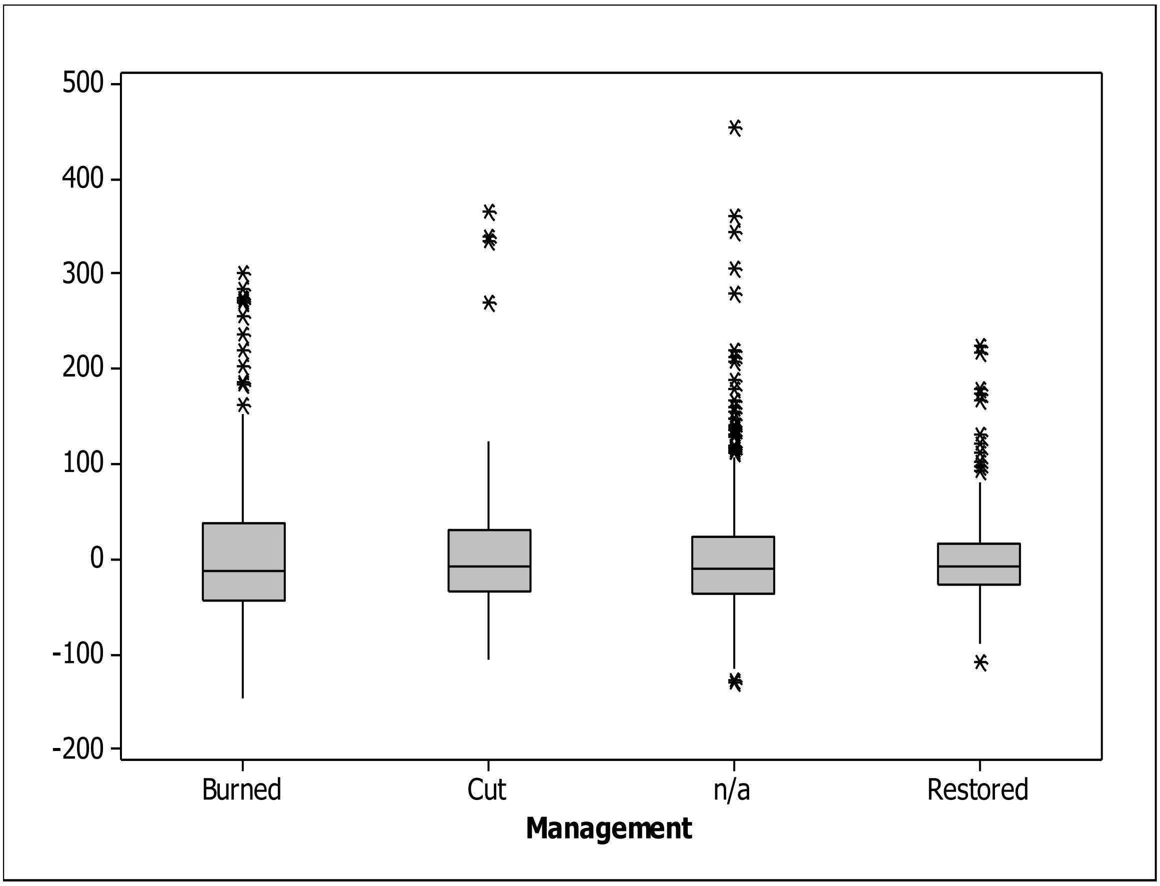


Figure 4.3.1.10 **-** Boxplot showing dataset distribution of the residual variance of the DOC ANCOVA model versus land management technique. Where: burned = heather burned, cut = heather cut, n/a = means no known management within five years prior to site installation and restored = areas of bare peat restored by reseeding and/or slope stabilisation and/or water table restoration. Asterisks represent outlying data points.

Methane flux was recorded for all vegetation types during three campaigns (January 2009, September 2009 and January 2010) the results of which are shown in figure 4.3.1.11. This chart, as with the DOC data, shows a high degree of variability both within and between the groups. However, it is clear that in general the magnitude of methane flux is higher in the September campaign, relative to the January campaigns. Due to the relative paucity of the methane data gathered, it was not possible to carry out any further statistical analyses on the data.

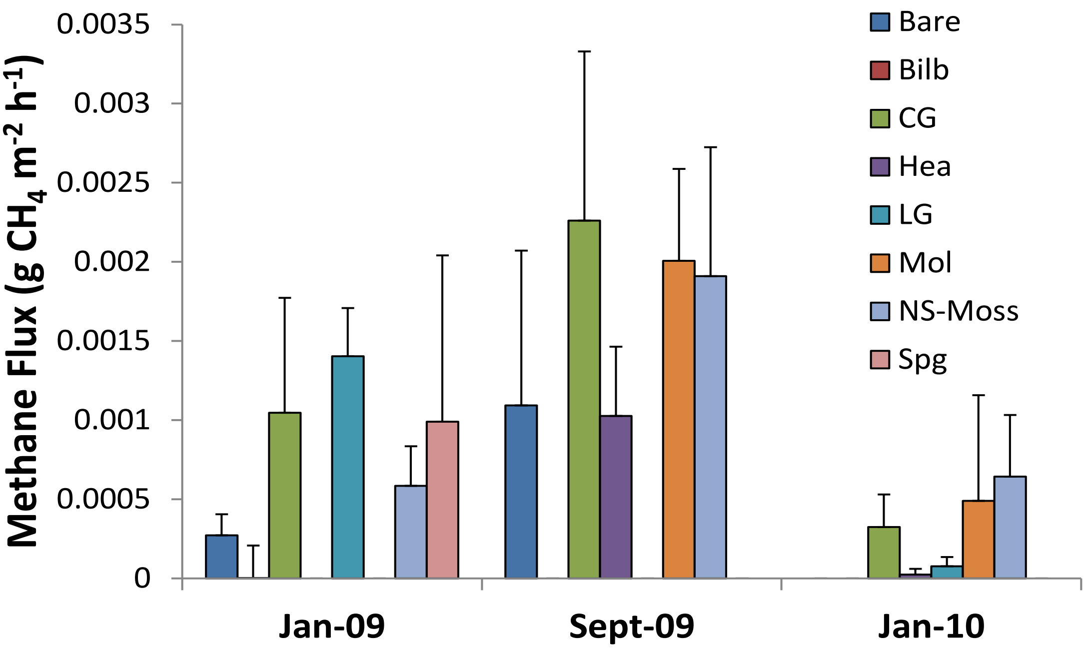


Figure 4.3.1.11 – Mean CH_4 flux from each vegetation type on each of the three data gathering campaigns. Where no bar is present for a given vegetation type this denotes that the there was, on average, no measureable flux (subject to gas chromatograph detection limits) of methane from that vegetation type on that campaign. The error bars shown are the standard error of the mean.

4.3.2 – Canopy Height Study

The mean rates of R_{eco} for each month across the four height categories (figure 4.3.2.1) have peak values during the early to mid-growing season (June and July). R_{eco} increases and decreases across the year in a highly asymmetric fashion with a sudden increase around the start of the growing season (May/June) to its peak value followed by a gradual decrease from July onwards levelling out in late autumn/early winter (November).

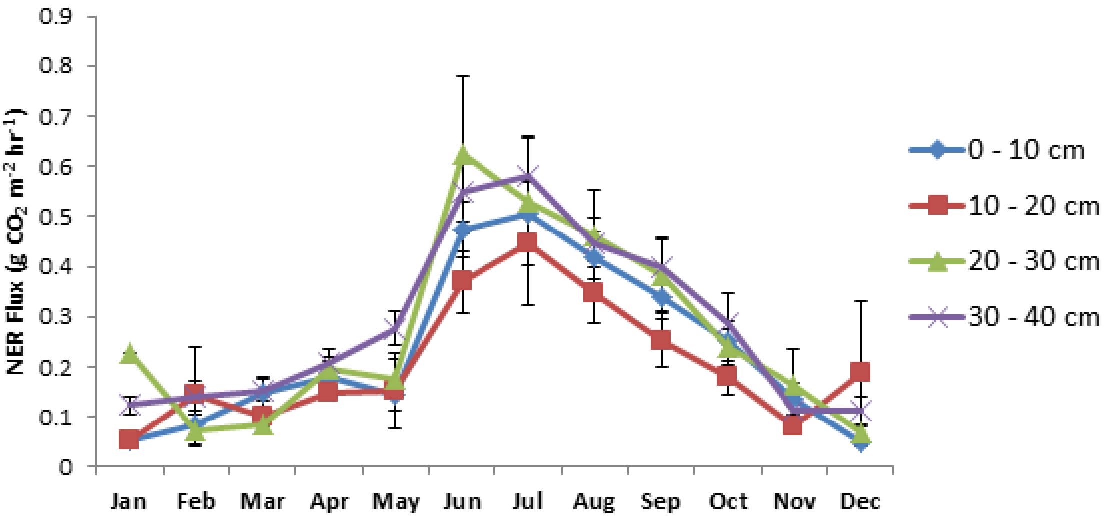


Figure 4.3.2.1 **–** Mean monthly R_{eco} value for each heather height category. The error bars represent the standard error of the mean.

Following the convention adopted earlier in this chapter and chapter 3 the results of the ANCOVA analyses are reported both with and without P_g as a covariate. The results for ln(R_{eco}) are given in table 4.3.2.1. The following factors were significant in all ANCOVA approaches: canopy height, month and locality. The most important factor was month, explaining between 10.54-11.92% of ln(R_{eco}) dataset variation. Canopy height was less important overall explaining between 3.13-6.02% of dataset variation. The inclusion of P_g as a covariate resulted in heather canopy height being more important in the model, once again showing that controlling for variation related to P_g allows less important effects to become more apparent. Air temperature was the most important covariate in all models, accounting for between 34.40-36.30% of ln(R_{eco}) dataset variation. Slope was also significant in all models but was of little importance (ω^2 = 0.98-1.41%).

The main effects for canopy height are given in figure 4.3.2.2 alongside the *post hoc* Tukey groupings. It can be seen from figure 4.3.2.2. that for both ANCOVA models the canopy height range between 30-40 cm had a significantly greater rate of respiration than all other canopy height ranges. Furthermore the other canopy height ranges (i.e. 0-30 cm) had no significant differences amongst themselves. In the same way as in section 4.3.1 the residuals of the ANCOVA model using P_g as a covariate were made into boxplots against the management types the plots used in the study had been subject to (figure 4.3.2.3). It is apparent from figure 4.3.2.3 that, whilst burned plots appear to have a wider spread of residuals, the median values (i.e. lines in the centre of the boxes) are not greatly different.

Table 4.3.2.1 – ANCOVA Output for ln(R_{eco}) in the Canopy Height Study (with and without P_g)

			ln Reco (without P_g)					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	15.68	< 0.0001	1.41	-0.1439	0.0363	53.75%	542
Cov	Air Temperature	11.8	0.001	34.40	0.0287	0.0084		
NF	Locality (Region)	3.94	0.048	0.89				
FF	Region	6.47	0.011	0.38				
FF	Month	12.13	< 0.0001	11.92				
FF	**Canopy Height**	**12.78**	**< 0.0001**	**3.12**				
			ln Reco (with P_g)					
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	12.45	< 0.0001	0.98	-0.1209	0.0343	63.91%	436
Cov	Air Temperature	4.04	0.045	36.30	0.0158	0.0008		
Cov	Pg	83.13	< 0.0001	8.53	-1.1192	0.1227		
FF	Locality	4.22	0.015	0.16				
FF	Month	9.36	< 0.0001	10.54				
FF	**Canopy Height**	**24.18**	**< 0.0001**	**6.01**				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor
RC = regression coefficient

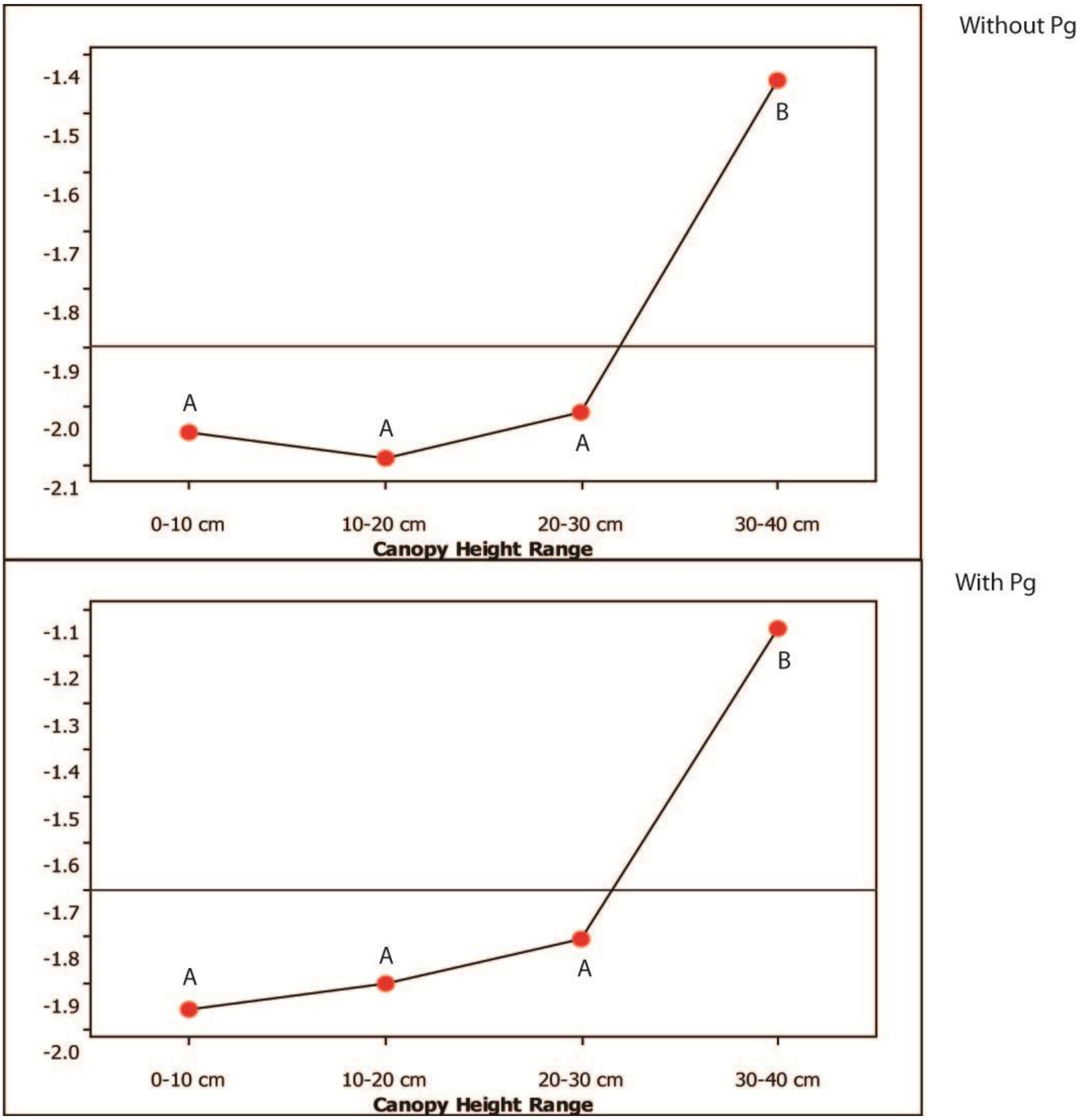


***Figure 4.3.2.2* –** Main effects plots for ln(R_{eco}) (units = ln(g CO_2 m^{-2} h^{-1}) by heather canopy height range. The letters in proximity to each data point represent the groupings determined by post hoc Tukey's pairwise comparisons. Any group sharing a letter with another group is not statistically different to that group.

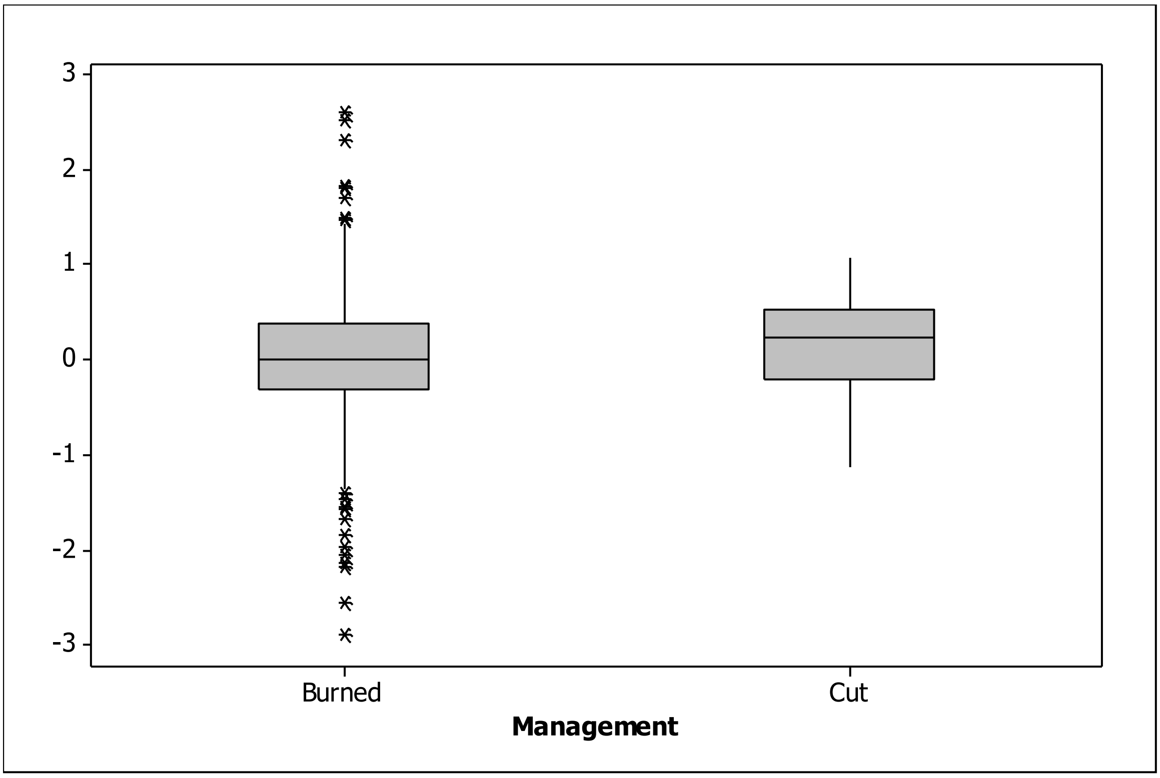


Figure 4.3.2.3 – Boxplot of ln(R_{eco}) residuals (ANCOVA including P_g model) from the canopy height study versus management type. Where: burned = the heather had been managed by burning and cut = the heather had been managed by cutting.

The mean monthly NEE plot (figure 4.3.2.4) shows a much different pattern than the R_{eco} plot (figure 4.3.2.1). The 0-10 cm dataset is the most frequent sink of CO_2 only being a net source in June. The next most frequent sink is the 20-30 cm dataset, which is a sink on four months; however, these months appear to be randomly distributed throughout the year. The 10-20 cm dataset is a sink for two months of the year during the late growing season (August and September). There are no months where the 30-40 cm dataset was a net sink. Figure 4.3.2.4 suggests that a net sink of CO_2 is more likely when R_{eco} is low/not peak and/or when the heather canopy is less than 30 cm.

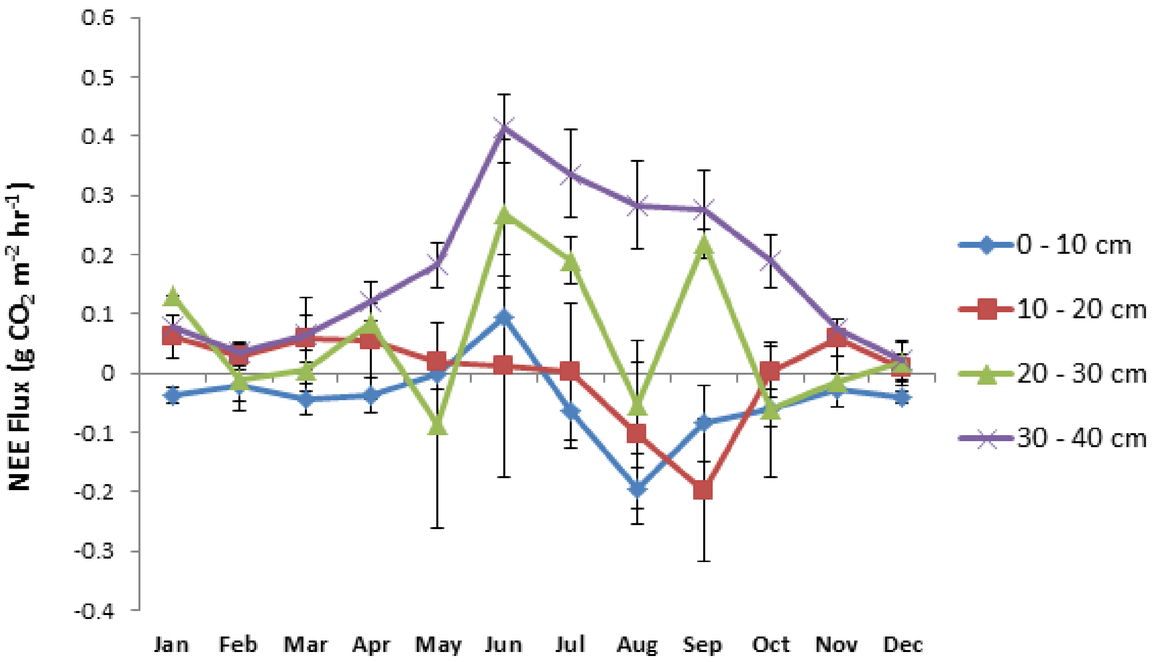


Figure 4.3.2.4 **–** Mean monthly NEE value for each heather height category. The error bars represent the standard error of the mean.

The results of the ANCOVA analyses for NEE are given in table 4.3.2.2. The model of NEE without P_g has a low R^2 of 11.39% whereas the model including P_g is comparable to the ln(R_{eco}) models (R^2 = 66.26%). The following factors are significant in all ANCOVA models: canopy height and month. Month is the most important factor (ω^2 = 4.45-5.22%) with canopy height explaining between 1.71-2.01% of dataset variation. The most important covariate, aside from P_g, was slope; however, this was of only minor importance (ω = 0.08-0.65%). The introduction of P_g into the model gave rise to a significant relationship between NEE and air temperature being found; however, this was of minor importance (ω^2 = 0.21%). P_g when used as a covariate explained most of the dataset variability in NEE (ω^2 = 58.61%).

The main effects of NEE versus heather canopy height are given in figure 4.3.2.5 for both models with and without P_g. It is evident from this that, once again, the 30-40 cm heather canopy height range is significantly greater than most or all of the other ranges. When P_g is not considered, the 20-30 cm range is not significantly different to any other range whereas the 30-40 cm range is significantly different to the ranges between 0-20 cm. When P_g is considered as a covariate, the *post hoc* results mirror those for R_{eco}. The residuals of the ANCOVA model with Pg as a covariate have been made into boxplots versus land management type (figure 4.3.2.6). It is clear from figure 4.3.2.6 that the residuals are distributed in the same way as the R_{eco} residuals and there do not appear to be large differences between residuals across management types.

Table 4.3.2.2 – ANCOVA Output for NEE in the Canopy Height Study (with and without P_g)

NEE (without P_g)								
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	11.81	0.001	0.60	-0.0166	0.0072	11.39%	613
FF	Month	4.13	< 0.0001	5.22				
FF	**Canopy Height**	**5.97**	**0.001**	**2.03**				
RF	Year	2.87	0.036	0.84				

NEE (with P_g)								
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	Slope	6.33	0.012	0.08	-0.0082	0.0033	66.26%	455
Cov	AbsAT	5.5	0.019	0.21	0.0046	0.0019		
Cov	Pg	659.24	< 0.0001	58.61	0.7271	0.0283		
FF	Month	5.01	< 0.0001	4.45				
FF	**Canopy Height**	**5.01**	**< 0.0001**	**1.71**				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor
RC = regression coefficient

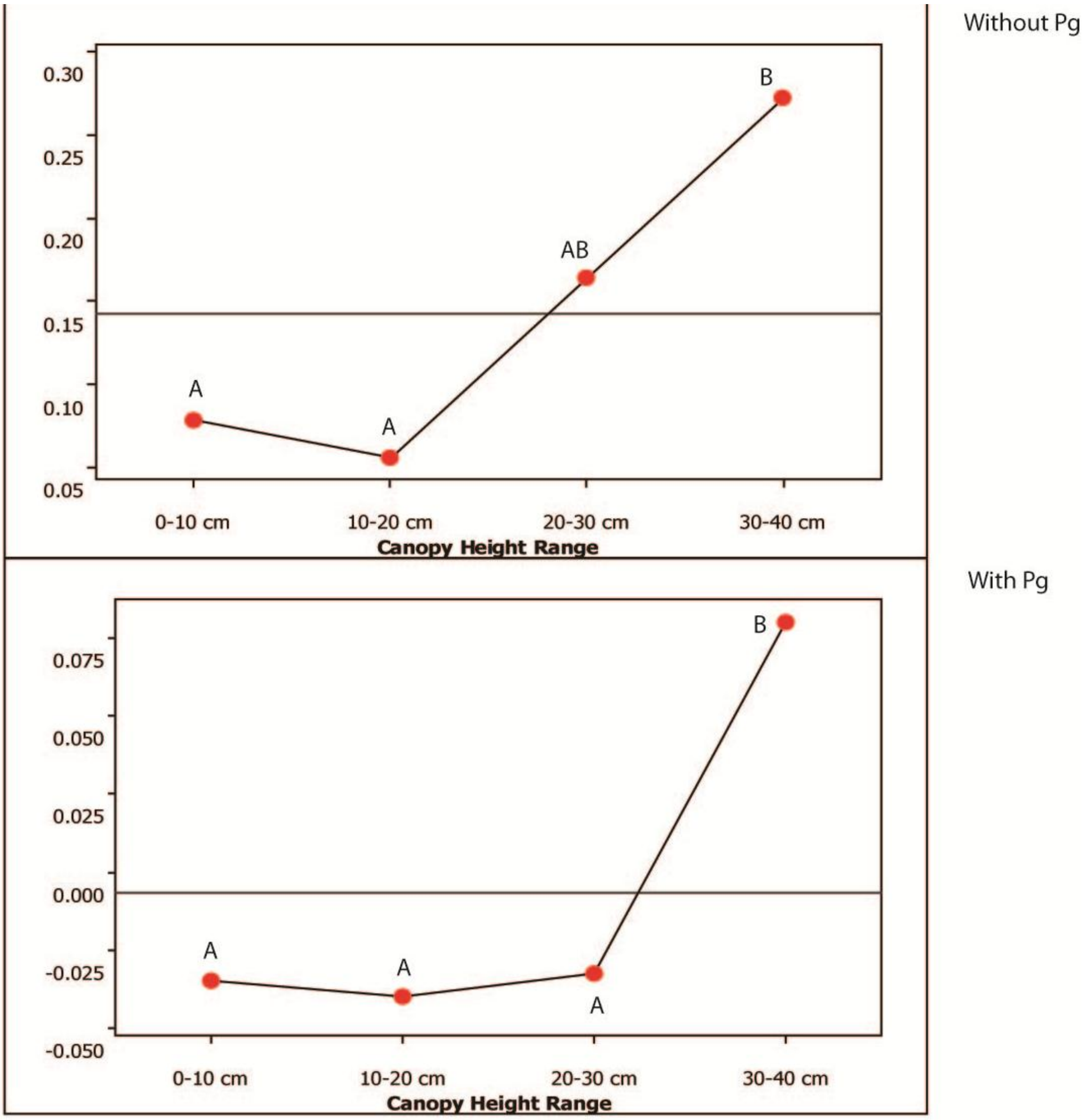


Figure 4.3.2.5 **-** Main effects plots for NEE (units = g CO_2 m^{-2} h^{-1}) by heather canopy height range. The letters in proximity to each data point represent the groupings determined by *post hoc* Tukey's pairwise comparisons. Any group sharing a letter with another group is not statistically different to that group.

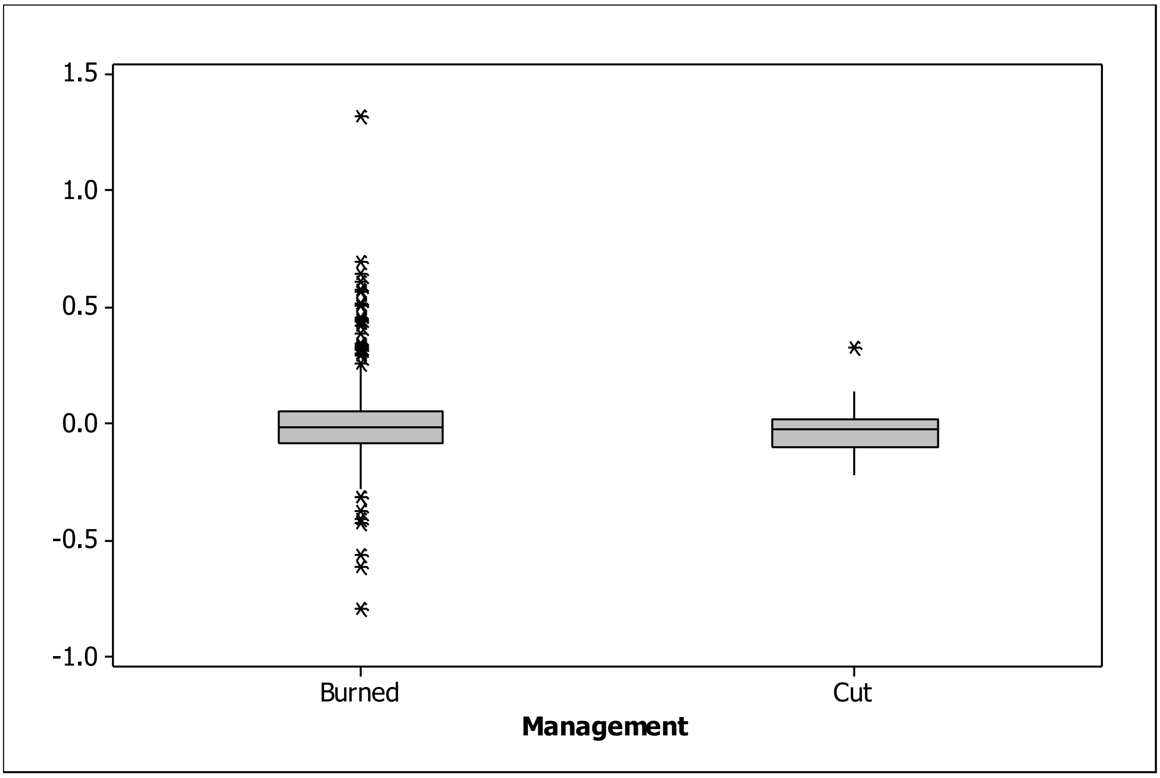


Figure 4.3.2.6 **-** Boxplot of NEE residuals (ANCOVA including P_g model) from the canopy height study versus management type. Where: burned = the heather had been managed by burning and cut = the heather had been managed by cutting.

The monthly mean DOC plot (figure 4.3.2.7) shows a highly variable pattern of soil pore water DOC concentration across the year and between the canopy height factor levels. The error bars are very large in many cases and as such it is difficult to draw clear conclusions from the observed data distribution. That said it appears that the 30-40 cm group frequently has the greatest production of soil pore water DOC. Moreover, 20-30 cm heather most frequently has the lowest DOC concentrations. 0-10 cm and 10-20 cm are broadly similar, with an outlier point in December for 10-20 cm, which is very much greater than the rest of the data points.

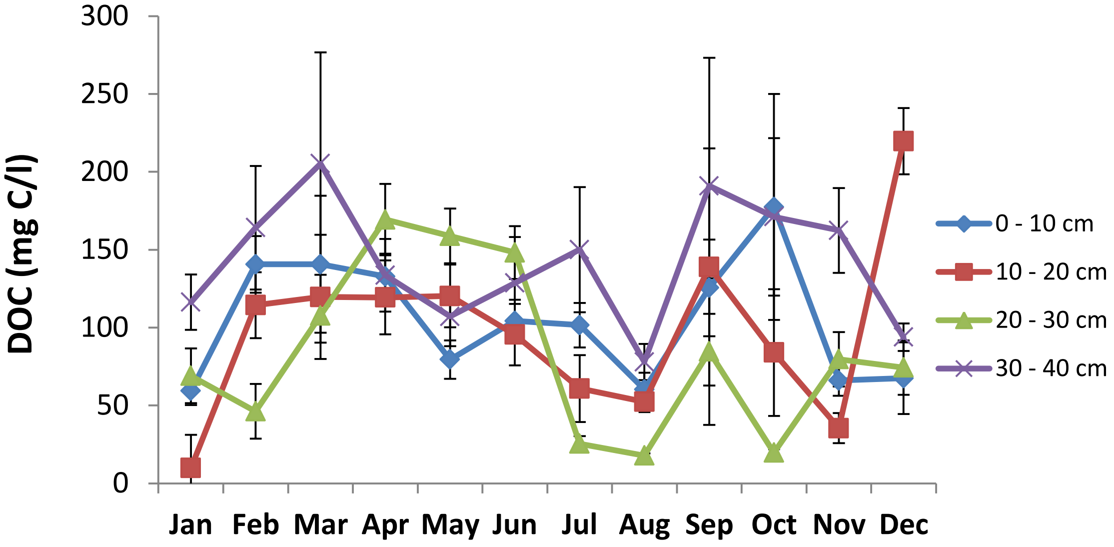


Figure 4.3.2.7 **–** Mean monthly DOC concentration value for each heather height category. The error bars represent the standard error of the mean.

The results of the ANCOVA model for ln(DOC) are given in table 3.2.3.3. It is evident from table 3.2.3.3 that the following factors were significant in the ANCOVA model for ln(DOC): canopy height, locality and month. Month was the most important factor, explaining 12.87% of dataset variation. This was followed by locality explaining 7.25% with canopy least important explaining 2.85% of dataset variation. The only significant covariate was water table depth, which explained 3.39% of dataset variation.

The main effects plot including *post hoc* Tukey results for heather canopy height range in the DOC ANCOVA model is given in figure 4.3.2.8. It can be seen from figure 4.3.2.8 that the only differences existing between the factor levels are between the 30-40 cm range and the rest (i.e. 0-30 cm). The 30-40 cm height range appears to have significantly greater soil pore water DOC concentrations than the rest. The residuals of the ANCOVA model when plotted against treatment (figure 4.3.2.9) do not appear to vary between management types.

Table 4.3.2.3 – ANCOVA Output for ln(DOC) in the Canopy Height Study

ln(DOC)								
Coding	Source	F	P	ω^2	RC	RC Error	R^2	n
Cov	WTD	3.91	0.049	3.39	0.0078	0.0040	31.33%	257
FF	Locality	8.21	< 0.0001	7.25				
FF	**Canopy Height**	**4.32**	**0.005**	**2.85**				
FF	Month	5.51	< 0.0001	12.87				

Coding: Cov = covariate, NF = nested factor, FF = fixed factor, RF = random factor
RC = regression coefficient

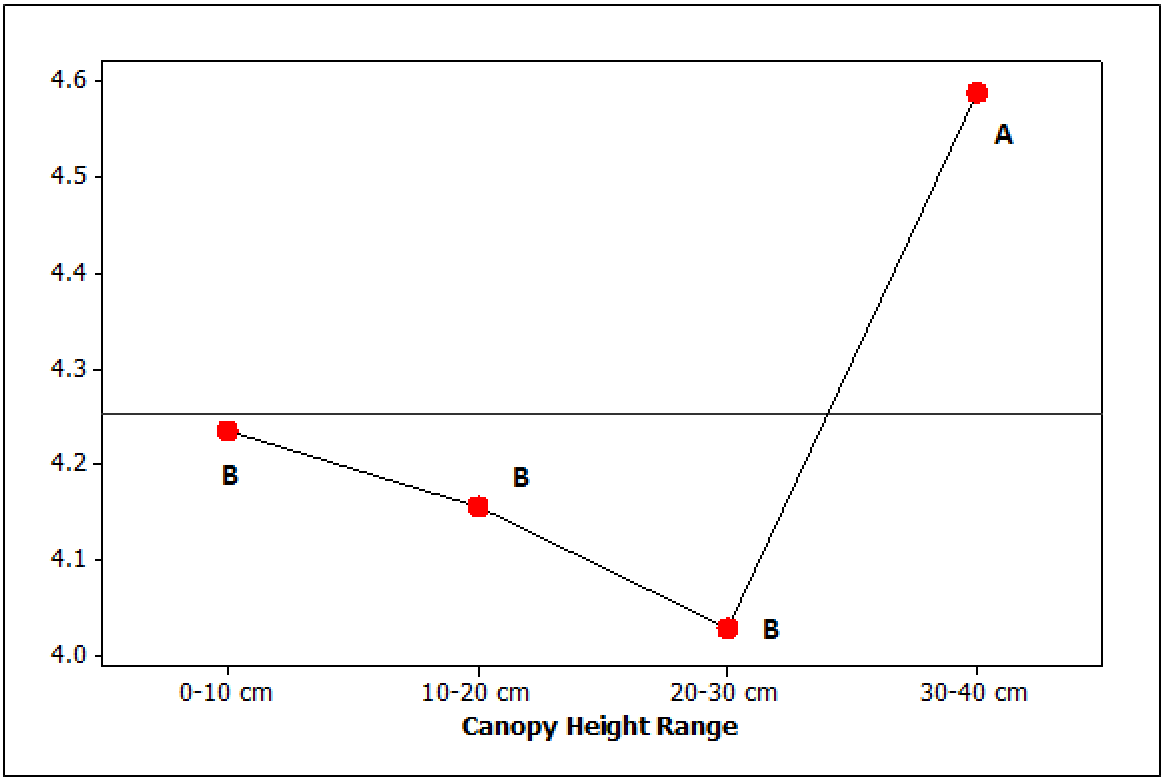


Figure 4.3.2.8 **–** Main effects plots for ln(DOC) (units =ln(mg C l^{-1})) by heather canopy height range. The letters in proximity to each data point represent the groupings determined by *post hoc* Tukey's pairwise comparisons. Any group sharing a letter with another group is not statistically different to that group.

Figure 4.3.2.9 **-** Boxplot of ln(DOC) residuals (ANCOVA model) from the canopy height study versus management type. Where: burned = the heather had been managed by burning and cut = the heather had been managed by cutting.

4.3.3 – Modelling Carbon Cycling

The results of the modelling carried out in this section are summarised in table 4.3.3.1. This table gives the model fit (R^2) for each model, showing both the fitted MLR and validation (i.e. tested on data not used in the model construction) MLR results for approaches with and without P_g as a predictor. Fitted and validation MLR model fits are displayed in figures 4.3.3.1 – 4.3.3.2, with the best fit MLR model equations being shown in tables 4.3.3.2 and 4.3.3.3. In addition, the calculated temperature sensitivity parameters (E_a and Q_{10}) are presented. Results for the individual vegetation types are detailed below.

Table 4.3.3.1 – Model Fits and Temperature Sensitivity Parameters for All Vegetation Type

	R_{eco} Model Fits (R^2)						**NEE Model Fits (R^2)**						**Temperature Sensitivity**		
			Without P_g		**With P_g**				**Without P_g**		**With P_g**				
Vegetation	**Lloyd and Taylor, (1994)**	**Larsen et al., (2007)**	**MLR (fitted)**	**MLR (validation)**	**MLR (fitted)**	**MLR (validation)**	**Bubier et al., (1998)**	**Nykanen et al., (2003)**	**MLR (fitted)**	**MLR (validation)**	**MLR (fitted)**	**MLR (validation)**	**E_a (kJ/mol)**	**± S.E. E_a (kJ/mol)**	**Q_{10}**
Bare	12.80%	21.60%	15.70%	12.93%	40.90%	27.80%	19.90%	0.30%	5.60%	1.23%	22.40%	27.13%	36.5	5.91	1.8
Bilberry	19.50%	40.70%	30.20%	4.96%	50.90%	63.79%	33.40%	10.90%	-	-	63.20%	48.06%	30.7	7.19	1.6
Cotton Grass	21.50%	51.40%	52.10%	42.06%	66.10%	60.33%	31.20%	1.10%	8.20%	1.70%	16.00%	53.66%	19.4	5.66	2.1
Heather	15.70%	38.70%	51.30%	21.64%	59.50%	37.04%	26.90%	0.80%	-	-	42.10%	67.98%	40.4	4.55	1.8
Lawn Grass	17.60%	55.40%	24.60%	35.64%	54.60%	48.79%	43.40%	0.90%	12.70%	8.57%	38%	58.02%	22.8	5.23	2.0
Molinia	60.60%	78.80%	79.70%	71.66%	84.50%	69.12%	2.70%	8.50%	15.30%	7.27%	21.20%	28.36%	36.7	6.34	3.5
Non-*Sphagnum* Moss	26.90%	39.00%	26.00%	27.13%	42.10%	67.23%	34.40%	14.00%	22.90%	12.76%	38.80%	30.67%	26.5	10.33	1.9
Sphagnum	47.60%	70.40%	50.30%	19.27%	71.70%	70.22%	34.40%	6.60%	-	-	49.50%	48.60%	27.8	8.15	2.3
Mean	**27.78%**	**49.50%**	**41.24%**	**29.41%**	**58.79%**	**55.54%**	**28.29%**	**5.39%**	**12.94%**	**6.31%**	**36.40%**	**45.31%**	**30.1**	**6.7**	**2.1**
Median	**20.50%**	**46.05%**	**40.25%**	**24.38%**	**57.05%**	**62.06%**	**32.30%**	**3.85%**	**12.70%**	**7.27%**	**38.40%**	**48.33%**	**29.25**	**6.12**	**1.95**
			n							**n**					
Bare	624	462	590	268	469	209	462	462	752	271	538	209	624		624
Bilberry	164	142	164	53	142	47	126	126	-	-	142	47	164		164
Cotton Grass	505	442	463	165	406	165	417	442	494	170	444	156	505		505
Heather	540	438	538	184	438	147	438	438	-	-	441	142	540		540
Lawn Grass	370	342	363	141	339	141	342	342	384	133	366	122	370		370
Molinia	181	147	185	66	150	66	146	144	188	64	149	46	181		181
Non-*Sphagnum* Moss	209	169	182	74	169	65	169	169	201	68	189	65	209		209
Sphagnum	188	172	187	67	168	54	172	172	-	-	188	54	188		188

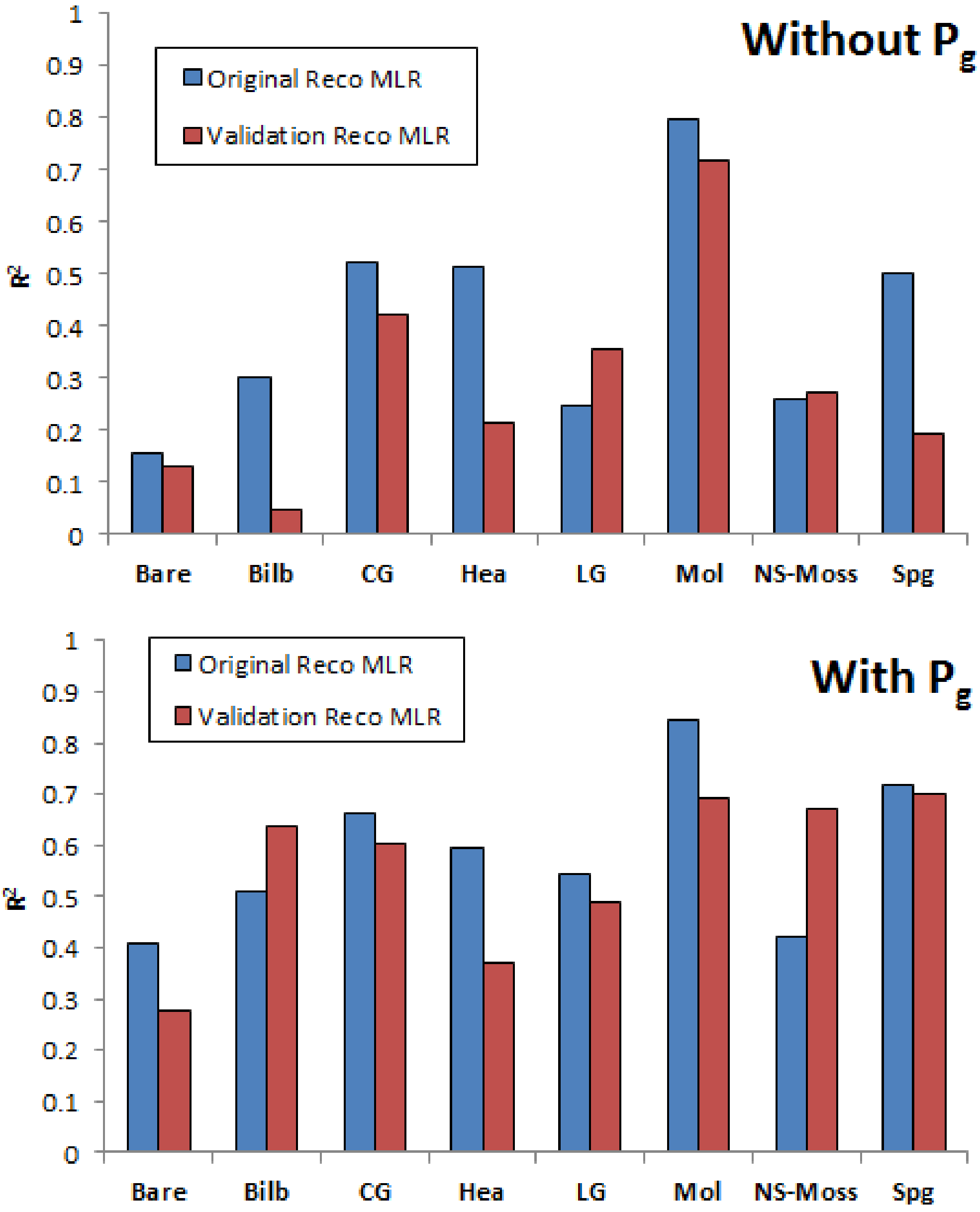


***Figure 4.3.3.1* –** Model fit (in blue) for the MLR R_{eco} models created on two thirds of the data for each vegetation group. The red bars represent the model fit when this model was tested against the validation third of the data not used to create the model. Models with and without P_g, as a predictor, are presented.

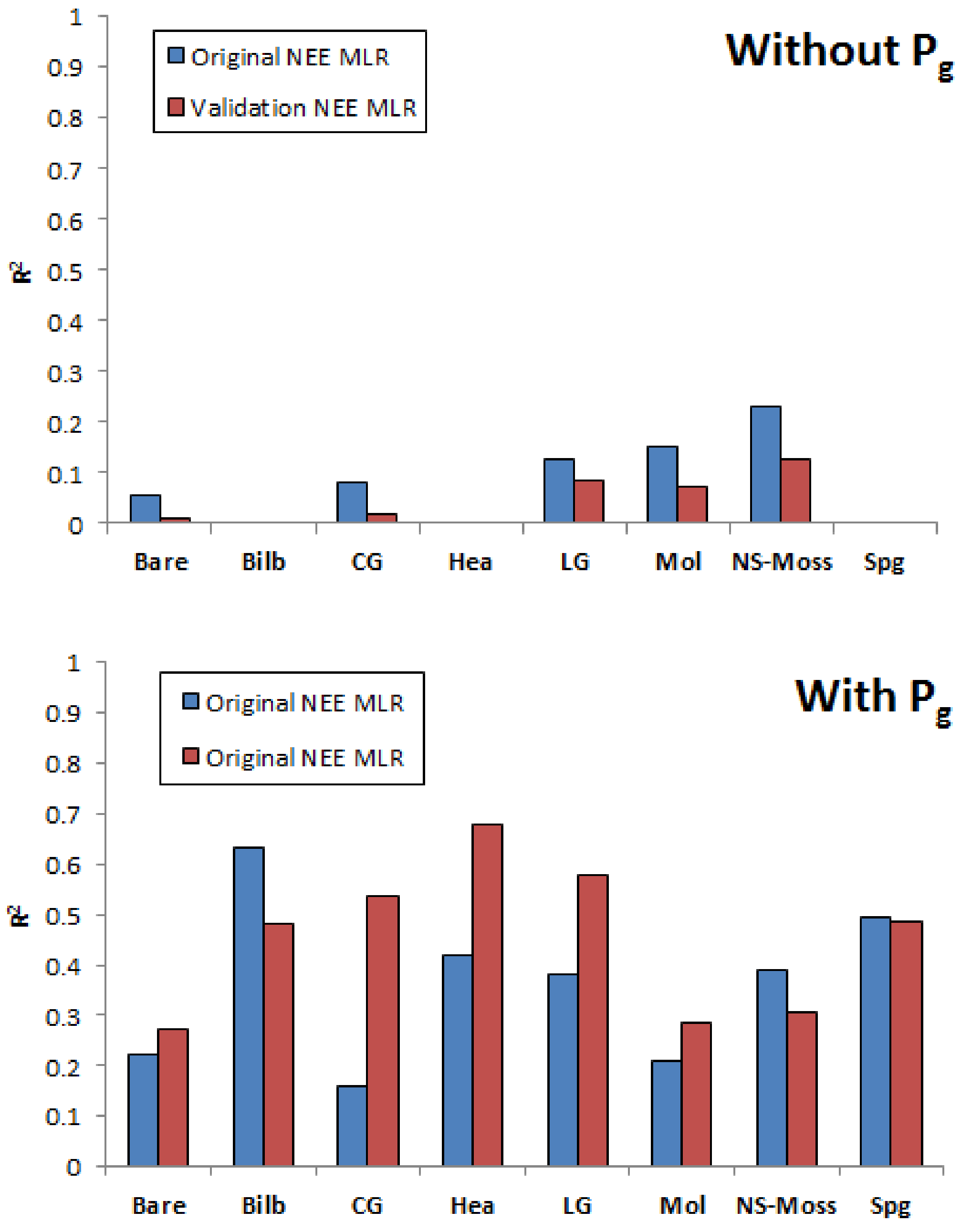
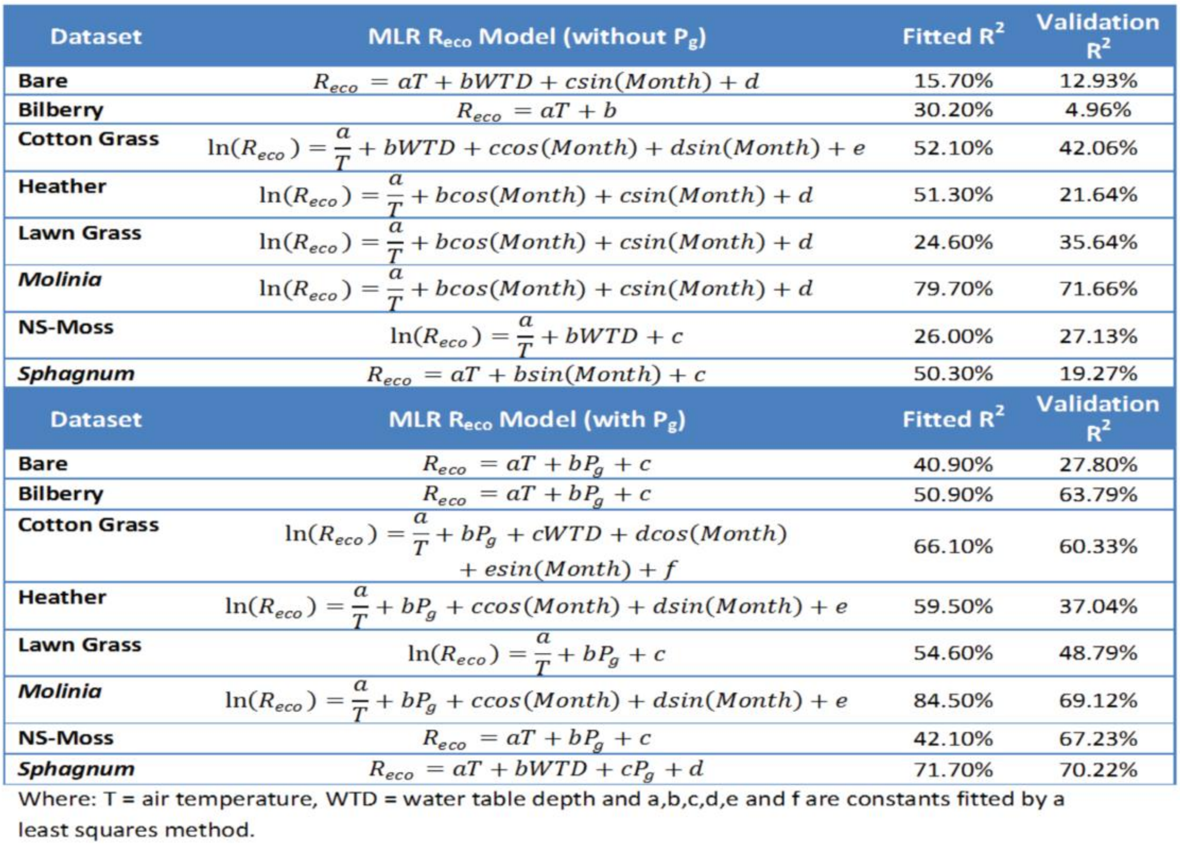


Figure 4.3.3.2 – This figure shows the model fit (in blue) for the NEE MLR models created on two thirds of the data for each vegetation group. The red bars represent the model fit when this model was tested against the validation third of the data not used to create the model. Models with and without P_g, as a predictor, are presented.

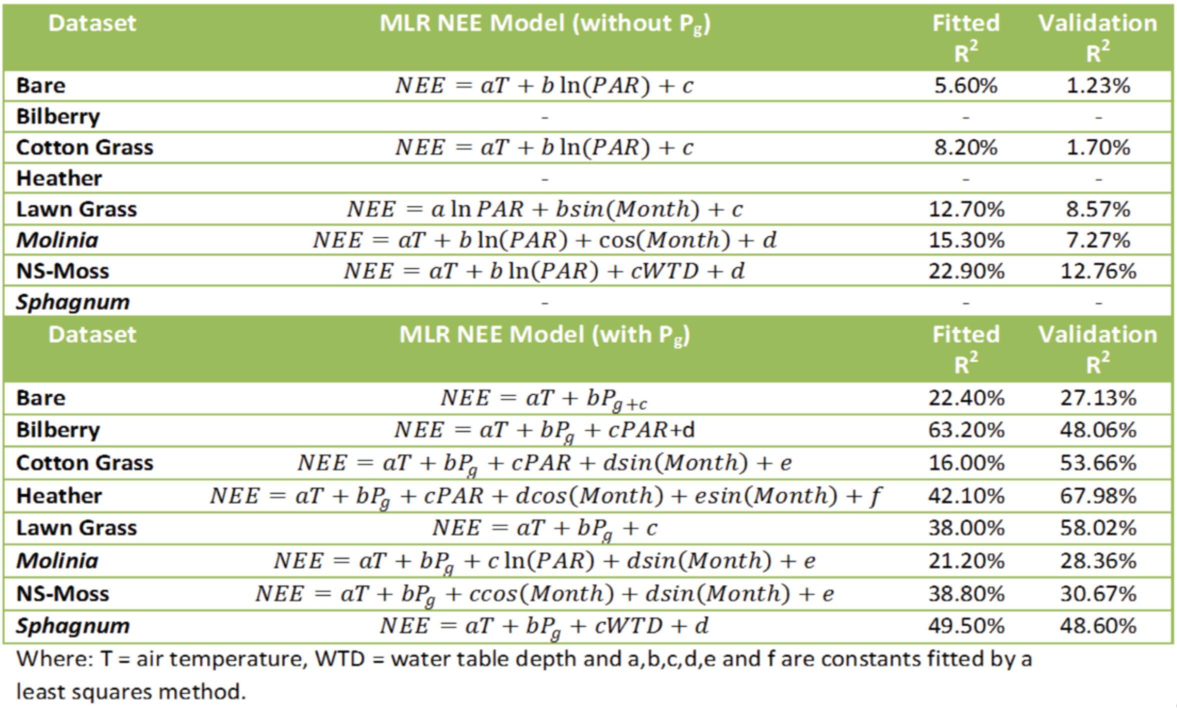
Table 4.3.3.2 – MLR Models for R$_{eco}$



Dataset	MLR R$_{eco}$ Model (without P$_g$)	Fitted R^2	Validation R^2
Bare	$R_{eco} = aT + bWTD + csin(Month) + d$	15.70%	12.93%
Bilberry	$R_{eco} = aT + b$	30.20%	4.96%
Cotton Grass	$\ln(R_{eco}) = \frac{a}{T} + bWTD + ccos(Month) + dsin(Month) + e$	52.10%	42.06%
Heather	$\ln(R_{eco}) = \frac{a}{T} + bcos(Month) + csin(Month) + d$	51.30%	21.64%
Lawn Grass	$\ln(R_{eco}) = \frac{a}{T} + bcos(Month) + csin(Month) + d$	24.60%	35.64%
Molinia	$\ln(R_{eco}) = \frac{a}{T} + bcos(Month) + csin(Month) + d$	79.70%	71.66%
NS-Moss	$\ln(R_{eco}) = \frac{a}{T} + bWTD + c$	26.00%	27.13%
Sphagnum	$R_{eco} = aT + bsin(Month) + c$	50.30%	19.27%
Dataset	**MLR R$_{eco}$ Model (with P$_g$)**	**Fitted R^2**	**Validation R^2**
Bare	$R_{eco} = aT + bP_g + c$	40.90%	27.80%
Bilberry	$R_{eco} = aT + bP_g + c$	50.90%	63.79%
Cotton Grass	$\ln(R_{eco}) = \frac{a}{T} + bP_g + cWTD + dcos(Month)$ $+ esin(Month) + f$	66.10%	60.33%
Heather	$\ln(R_{eco}) = \frac{a}{T} + bP_g + ccos(Month) + dsin(Month) + e$	59.50%	37.04%
Lawn Grass	$\ln(R_{eco}) = \frac{a}{T} + bP_g + c$	54.60%	48.79%
Molinia	$\ln(R_{eco}) = \frac{a}{T} + bP_g + ccos(Month) + dsin(Month) + e$	84.50%	69.12%
NS-Moss	$R_{eco} = aT + bP_g + c$	42.10%	67.23%
Sphagnum	$R_{eco} = aT + bWTD + cP_g + d$	71.70%	70.22%

Where: T = air temperature, WTD = water table depth and a,b,c,d,e and f are constants fitted by a least squares method.

Table 4.3.3.3 – MLR Models for NEE



Dataset	MLR NEE Model (without P$_g$)	Fitted R^2	Validation R^2
Bare	$NEE = aT + b\ln(PAR) + c$	5.60%	1.23%
Bilberry	-	-	-
Cotton Grass	$NEE = aT + b\ln(PAR) + c$	8.20%	1.70%
Heather	-	-	-
Lawn Grass	$NEE = a\ln PAR + bsin(Month) + c$	12.70%	8.57%
Molinia	$NEE = aT + b\ln(PAR) + \cos(Month) + d$	15.30%	7.27%
NS-Moss	$NEE = aT + b\ln(PAR) + cWTD + d$	22.90%	12.76%
Sphagnum	-	-	-
Dataset	**MLR NEE Model (with P$_g$)**	**Fitted R^2**	**Validation R^2**
Bare	$NEE = aT + bP_{g+c}$	22.40%	27.13%
Bilberry	$NEE = aT + bP_g + cPAR+d$	63.20%	48.06%
Cotton Grass	$NEE = aT + bP_g + cPAR + dsin(Month) + e$	16.00%	53.66%
Heather	$NEE = aT + bP_g + cPAR + dcos(Month) + esin(Month) + f$	42.10%	67.98%
Lawn Grass	$NEE = aT + bP_g + c$	38.00%	58.02%
Molinia	$NEE = aT + bP_g + c\ln(PAR) + dsin(Month) + e$	21.20%	28.36%
NS-Moss	$NEE = aT + bP_g + ccos(Month) + dsin(Month) + e$	38.80%	30.67%
Sphagnum	$NEE = aT + bP_g + cWTD + d$	49.50%	48.60%

Where: T = air temperature, WTD = water table depth and a,b,c,d,e and f are constants fitted by a least squares method.

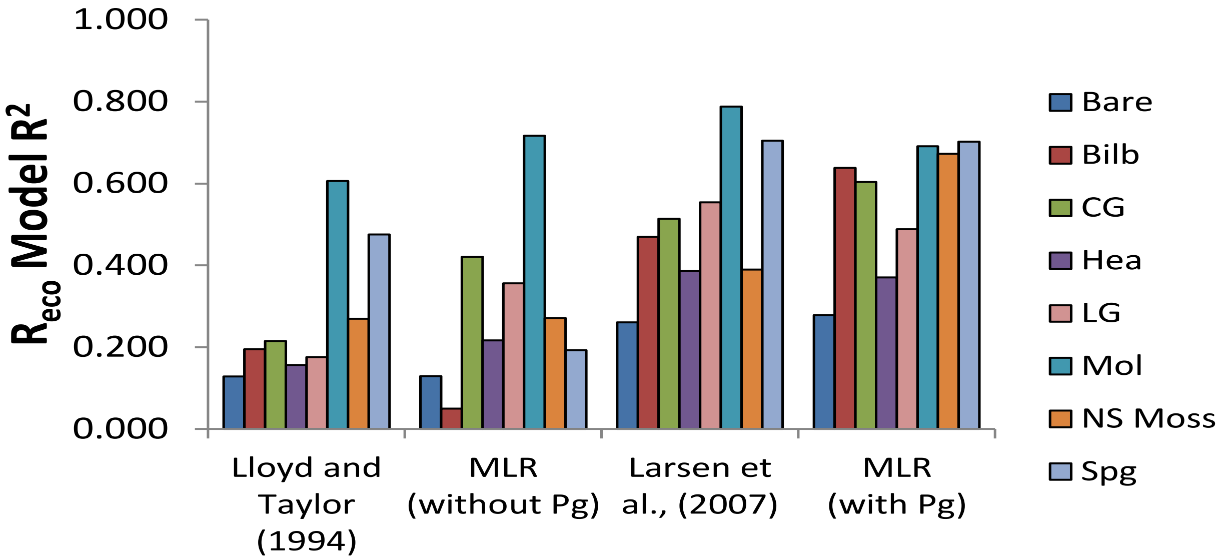


Figure 4.3.3.3 **–** Comparison between the model fits of the two literature and two empirical (MLR) models used to predict R_{eco}. The model fits cited for the MLR models are the model fits to the validation data.

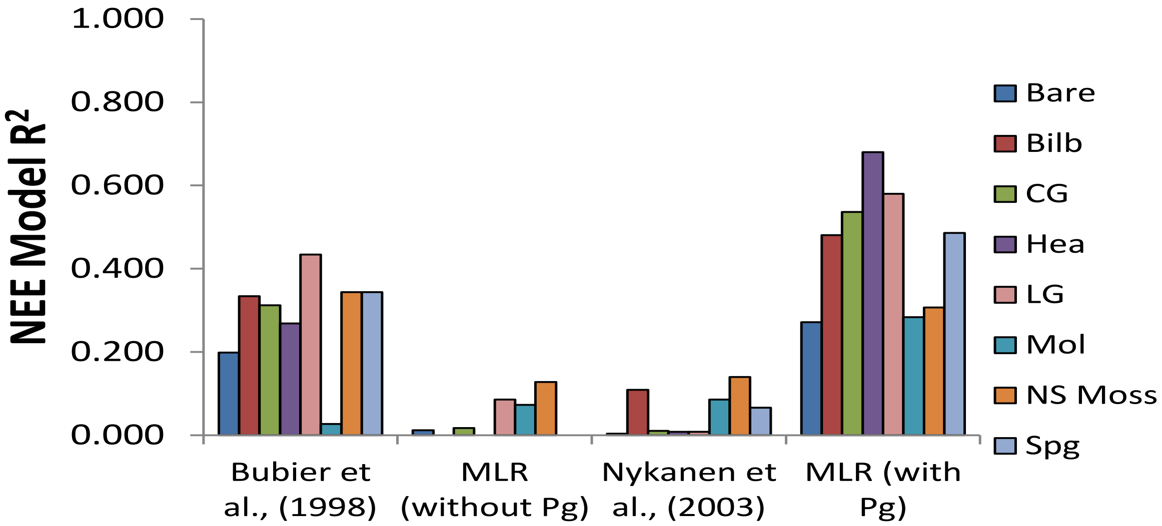


Figure 4.3.3.4 **–** Comparison between the model fits of the two literature and two empirical (MLR) models used to predict R_{eco}. The model fits cited for the MLR models are the model fits to the validation data.

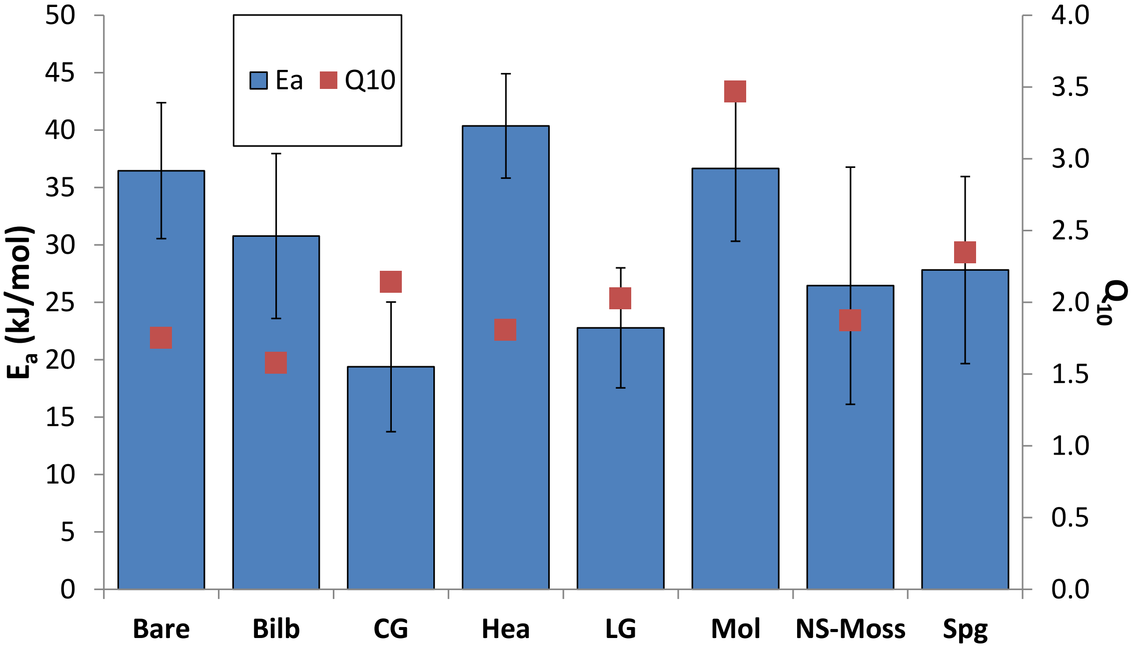


Figure 4.3.3.5 – Comparison of temperature sensitivity parameters of activation energy (E_a) and Q_{10} calculated for each vegetation type. The error bars represent one standard error, and apply only to the E_a values.

Looking at table 4.3.3.1 it is plain that models that use photosynthesis as a predictor account for more variation within the dataset than those that do not. For R_{eco} the MLR (with P_g) approach provided the best mean and median model fits (using validation data) of 55.54% and 62.06% respectively. This model was followed by Larsen et al. (2007) with mean and median model fits of 49.50% and 46.05% respectively. Following this was the MLR (without P_g) approach with mean and median model fits of 29.41% and 24.38% respectively. Finally, the Lloyd and Taylor (1994) was the least well-fitting with mean and median fits of 27.78% and 20.50% respectively. For NEE the MLR (with P_g) model was best fitting (using validation data) with mean and median fits of 45.31% and 48.33% respectively. The next best fitting model was that of Bubier et al. (1998) with mean and median 28.29% and 32.20% respectively. Following this was the MLR (without P_g) approach with mean and median fits of 6.31% and 7.27% respectively. Finally, the model of Nykanen et al. (2003)

which was least well-fitting with mean and median fits of 5.39% and 3.85% respectively. The mean and median activation energy (E_a) from table 4.3.3.1 are 30.1 ± 6.7 and 29.25 ± 6.12 kJ/mol respectively. There are differences (i.e. non-overlapping) error bars between vegetation types visible in figure 4.3.3.5. These differences are between bare and heather (higher) versus cotton grass and lawn grass (lower), also between cotton grass (lower) and *Molinia*. The mean and median Q_{10} factors were 2.1 and 1.95 respectively.

Carbon dioxide flux from bare peat was relatively poorly modelled by all of the methods considered. For R_{eco} the Lloyd and Taylor (1994) model produced a fit (R^2) of only 12.8%. This was improved slightly with the MLR (without P_g) model (tested on the validation data) giving a 12.93% fit. Inclusion of P_g, either in the Larsen et al. (2007) model or the MLR (with P_g) model, provided much better fits (R^2 = 21.60% and 27.80% respectively) than models without P_g. Bare peat had an above average (between group mean = 30.1 ± 6.7 kJ/mol) activation energy (figure 4.3.3.5) of 36.5 ± 5.9 kJ/mol but a below average (between group mean = 2.1) Q_{10} factor (figure 4.3.3.5) of 1.8 for ecosystem respiration. Modelling net ecosystem exchange of CO_2 on bare peat typically gave even lower model fits. The best fitting model for NEE was the MLR (with P_g) approach (R^2 = 27.13%). Following this was 0the Bubier et al. (1998) model which predicted 19.9% of dataset variation. Next was the MLR (without P_g) (R^2 = 1.23%). Finally, the Nykanen et al. (2003) model predicted only 0.3% of dataset variation (i.e. the model does not fit the data).

Modelling of bilberry R_{eco} gave the following outputs from the Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) models of (figure 4.3.3.3); 19.5%, 40.7%, 4.96% and 63.79% respectively. NEE had lower model fits for the Bubier et al. (1998), Nykanen et al. (2003) and MLR models (figure 4.3.3.4) of; 33.4%, 10.9% and 48.06% respectively, with no significant MLR (without P_g) model. The activation energy (figure 4.3.3.5) for bilberry was estimated to be 30.7 ± 7.1 kJ/mol, which is very close to the between group mean of 30.1 ± 6.7 kJ/mol. The Q_{10} factor of Bilberry was calculated as 1.57 which is low when compared to the inter group mean of 2.1.

The model fits for the cotton grass R_{eco} models are 21.50%, 51.40%, 42.06% and 60.33% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) respectively (figure 4.3.3.3). The fits for the Bubier et al. (1998), Nykanen et al. (2003), MLR (without P_g) and MLR (with P_g) NEE models are 31.20%, 1.10%, 1.70% and 53.60% respectively (figure 4.3.3.4). The activation energy was below average (19.4 ± 5.6 kJ/mol), the Q_{10} factor was average at 2.1.

R_{eco} model fits calculated for heather are 15.70%, 38.70%, 21.64% and 37.04% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) respectively (figure 4.3.33). NEE model fits are 26.90%, 0.80% and 67.98% for Bubier et al. (1998), Nykanen et al. (2003) and MLR (with P_g) models respectively (figure 4.3.3.4), there was no significant MLR (without P_g) model. The activation energy for heather is above average (40.4 ± 4.5 kJ/mol) and the Q_{10} factor is below average at 1.8 (figure 4.3.3.5).

Model fits for lawn grass R_{eco} were 17.60%, 55.40%, 35.64% and 48.79% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) models respectively (figure 4.3.3.3). NEE model fits for Bubier et al. (1998), Nykanen et al. (2003), MLR (without P_g) and MLR (with P_g) models were 43.40%, 0.90%, 8.57% and 58.02% respectively (figure 4.3.3.4). The activation energy was below average at 22.8 ± 5.23 kJ/mol and the Q_{10} factor was also (slightly) below average at 2.0 (figure 4.3.3.5).

Model fits for *Molinia* were uniformly highest in all R_{eco} models with values of 60.60%, 78.80%, 71.66% and 69.12% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) models respectively (figure 4.3.3.3). This pattern does not recur for NEE with *Molinia* having among the lowest fits for all models with values of 2.70%, 8.50%, 7.27% and 28.36% for Bubier et al. (1998), Nykanen et al. (2003), MLR (without P_g) and MLR (with P_g) models respectively (figure 4.3.3.4). *Molinia* has above average values of both activation energy (36.7 ± 6.34 kJ/mol) and Q_{10} (3.5), with Q_{10} being very much above average and far greater than the other vegetation types.

The R_{eco} model fits for non-*Sphagnum* moss were 26.90%, 39.00%, 27.13% and 67.23% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (with P_g) models respectively (figure 4.3.3.3). The model fits for NEE are generally greater than most of the other vegetation types with values of 34.40%, 14.00%, 12.76% and 30.76% for Bubier et al. (1998), Nykanen et al. (2003), MLR (without P_g) and MLR (with P_g) respectively. Activation energy (26.5 ± 10.33 kJ/mol) and Q_{10} (1.9) values are below average.

The R_{eco} model fits for *Sphagnum* moss are relatively high with values of 47.60%, 70.40%, 19.27% and 70.22% for Lloyd and Taylor (1994), Larsen et al. (2007), MLR (without P_g) and MLR (without P_g) models respectively. NEE model fits are general middling with values of 34.40%, 6.60% and 48.60% for Bubier et al. (1998), Nykanen et al. (2003) and MLR (with P_g) models respectively, there was no significant MLR (without P_g) model. R_{eco} activation energy was slightly below average (27.8 ± 8.15 kJ/mol). The Q_{10} factor, however, is slightly above average at 2.3.

For comparison the Lloyd and Taylor (1994) model has been solved over a 30 K temperature range for each vegetation type and the solutions are displayed in figure 4.3.3.6. A similar process has been undertaken for the Larsen et al. (2007) model, however, this time the rate of P_g has been changed (figure 4.3.3.7).

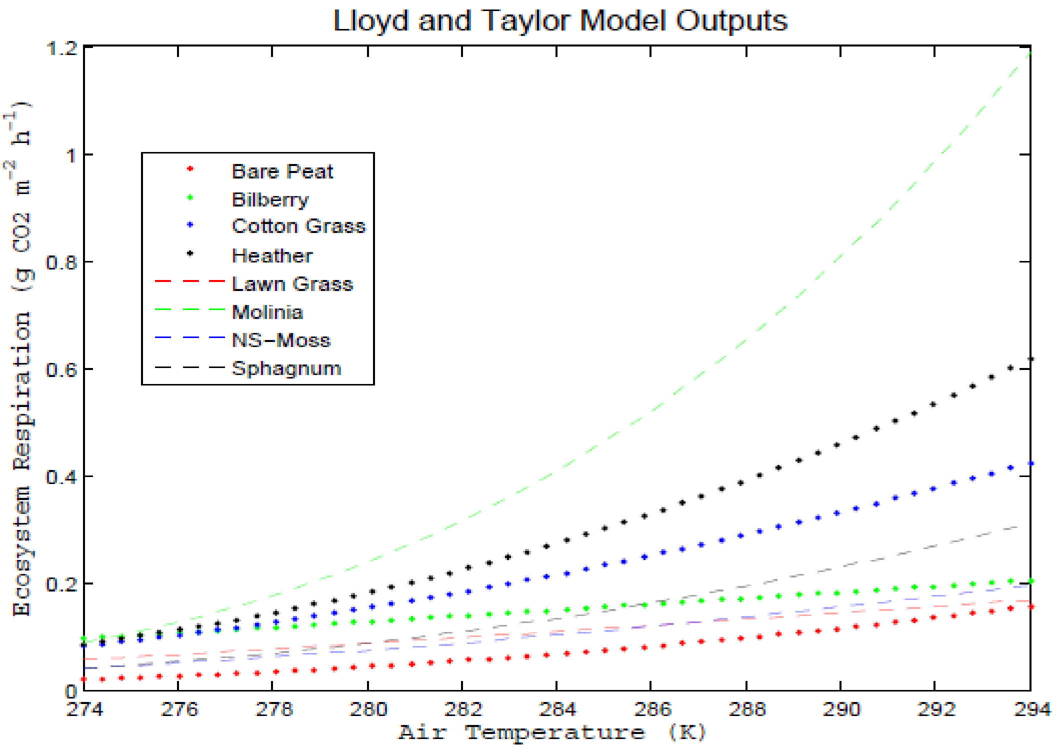


***Figure 4.3.3.6* –** Solutions to the Lloyd and Taylor (1994) Reco models produced in this analysis over a 30 K temperature range using the parameters fitted for each vegetation type by multiple non-linear regressions with an iterative solution.

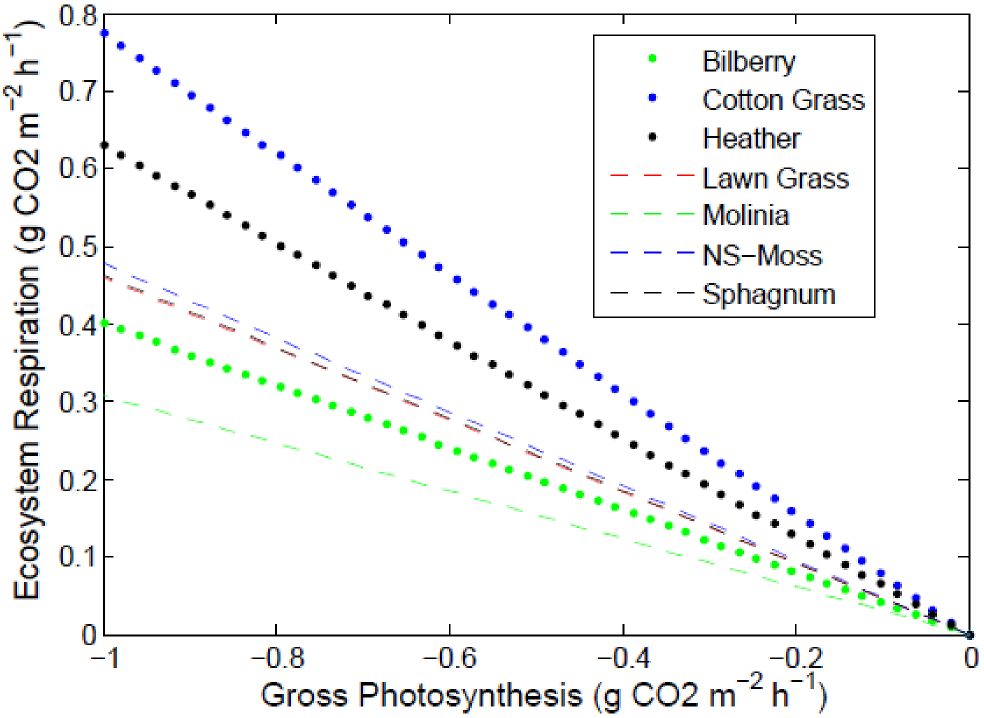


Figure 4.3.3.7 **–**Solutions to the Larsen et al. (2007) model for each vegetation type across a range of P_g rates. To aid visual comparability of the functions basal respiration at 0°C (R_{0m}) was assumed to be 0 and a constant temperature of 10°C was assumed for all functions.

4.4 – Discussion

4.4.1 – Comparative Vegetation Study

Seasonality is clearly important in R_{eco} across all vegetation types (figure 4.3.1.1); however, it is plain, from noting that R_{eco} is plotted on a logarithmic axis, that there are large differences in flux magnitudes between the vegetation types. Ecosystem respiration is fairly low for all vegetation types from November through to March (i.e. during the winter senescent period). From April onward R_{eco} generally increases until each vegetation type reaches its peak respiration flux. The timing of these peaks differs between groups, with some peaking in the early growing season around June (notably *M. caerulea*) and others peaking in the middle of the growing season around July/August. From this point all the vegetation respiratory fluxes decrease back to their winter minima, which occur between November and January.

It is apparent from the interval plots of R_{eco} by vegetation type (figure 4.3.1) that large differences between groups exist in terms of R_{eco}. It is most striking in the interval plots of R_{eco} (figure 4.3.1) that *Molinia* appears to have much larger magnitude fluxes than the rest of the groups and that bare peat has lower magnitude fluxes than the rest of the groups. This interpretation is confirmed by the ANCOVA and *post hoc* results, excluding P_g, which demonstrate that vegetation type was the most important factor controlling R_{eco} fluxes (ω^2 = 17.41-17.46%) with *Molinia* being significantly greater in terms of R_{eco} than the rest and bare peat being significantly lower than the rest. That *Molinia* should have greater R_{eco} fluxes than other vegetation types is not unexpected; indeed, Aerts et al. (1992) demonstrated that *Molinia* has greater rates (i.e. 2-3x) of root biomass production and turnover than *Calluna vulgaris* and *Dechampsia flexuosa*. This enhanced rate of production and subsequent turnover of biomass, relative to *Calluna vulgaris* and *Dechampsia flexuosa*, would be expected to contribute to enhanced R_{eco} flux rates in comparison to these species. Aside from these major differences, other smaller differences between vegetation types are evident. The bryophytes have significantly lower rates of R_{eco} than cotton grass, heather and lawn grass. This pattern of results complements the results of a comparative study of vegetation productivity in the North Pennines (Forrest and Smith, 1975), where *Sphagnum* spp. had the lowest production rates (156 g m^{-2} y^{-1}), followed by *Eriophorum vaginatum* (191 g m^{-2} y^{-1}), with *Calluna vulgaris* being most productive (391 g m^{-2} y^{-1}), i.e. where productivity is high, so too is respiration.

Inclusion of P_g as a covariate in the ANCOVA models explained over half of the variance that was attributed to vegetation in the ANCOVA model without P_g. Assuming the relationship between P_g and R_{eco} present in this dataset is primarily real and not entirely an artefact induced by self-correlation this result would imply that more productive groups tend to have higher rates of R_{eco} when compared to less productive groups. This view accords with the idea that the rates of photosynthesis and respiration are correlated in peatlands (e.g. Bubier et al., 1998; Larsen et al., 2007, Clay et al., 2012) and other ecosystems (e.g. Bahn et al., 2009; Bhupinderpal-Singh et al. 2003; Hogberg et al., 2001; Migliavacca et al., 2011; Tang et al., 2005) across multiple timescales. The mechanism to explain the observed correlation between R_{eco} and P_g is not readily identifiable in this study given that no isotopic/radioactive tracers or below ground equipment could be used. Moreover, no specific process-based explanation of the relationship observed between R_{eco} and P_g in the Larsen et al. (2007) study was provided, with the authors simply stating that as it improves the predictive ability of a regular thermodynamic model it should be incorporated into future models of CO_2 flux from temperate heathlands (i.e. the authors were less concerned with understanding processes than they were with improving model outcomes, in other words it was enough to know the relationship is expected without necessarily being able to directly explain it). While not providing a mechanism to explain the relationship, Larsen et al., (2007) provide several references (e.g. Hogberg et al., 2001, Tang et al., 2005) which suggest that photosynthate allocation to the plant roots could explain part of the observed correlation. Moreover, it is likely that on short time-scales photorespiration (e.g. Lambers et al., 2006, pp 14) and mitochondrial respiration, which utilises glycine generated in photorespiration (Taiz and Zeiger, 2002, pp 245) could account for some of the relationship between R_{eco} and P_g observed. Moreover, as photosynthates can be allocated to the rhizosphere within minutes in vascular plants (e.g. Dilkes et al., 2004), it may be expected that enhanced rates of root respiration and root exudation-driven heterotrophic/mycorrhizal-respiration may be evident on short time scales. Indeed, Moyano et al. 2007, demonstrated that mychorrizal-respiration and rhizosphere-respiration rates were significantly related on a daily-time scale to cumulative photosynthesis estimated from the previous day in vascular crops in a temperate environment. The data for this study were gathered on a monthly basis, however, and as such the correlations observed between R_{eco} and P_g need to be explained on this time-scale. Perhaps, changes in the average amount of photosynthate present in the rhizosphere vary with season (i.e. greater amounts present in late summer than early spring etc.) which would explain the correlation on this time-scale. There is no evidence available within the gathered in this study to test this hypothesis directly however. Nonetheless, Davidson et al. (2006) demonstrate a clear seasonal cycle (low in spring, high in winter) within the ratio of soil respiration to ecosystem respiration from a mature conifer forest in the temperate USA. Furthermore, these effects could not be explained by temperature variability alone. This seasonal cycle of soil respiration to ecosystem respiration was attributed in part to variations in allocation, storage and respiration of photosynthetically derived substrates both above and below-ground. This demonstrates that longer-term (i.e. monthly/annual) variations in the relationship between R_{eco} and P_g are to be expected, due to seasonal variations in the allocation and use of photosynthetically derived substrates.

Seasonality is, again, clearly important for NEE flux across all the vegetation types studied; however, the pattern is more complex across the seasonal cycle. Fluxes tend to be close to zero for all vegetation types between the months of December to March. After this the groups diverge with some becoming sinks and others becoming sources of CO_2. However, vegetation types that become sources early in the growing season (April to June), like Molinia, sometimes become net sinks later in the season (August to September). Moreover, vegetation types that become net sinks of carbon early on can also become net sources later in the season (e.g. Sphagnum). A satisfactory ecological explanation for these apparent differences in growing season CO_2 dynamics between groups is not clear and may, to some extent, be accounted for by sampling biases in the datasets. This study has assumed that the monthly readings taken on the sampling day(s) are broadly representative of the month as a whole. This assumption is more problematic when a group had been sampled for only 12 months as it will only have one set of readings per month. If the day(s) sampled in a given month were unusual with respect to the average monthly pattern, then bias will have been introduced into the dataset. Nonetheless the expected gross seasonal cycle within the CO_2 datasets is visible, implying that this potential bias is not fatal to the interpretation of the results.

Examination of the interval plot of NEE versus vegetation type (figure 4.3.2) demonstrates that significant differences between groups were likely to exist. Indeed, the results of the ANCOVA analyses confirm this assessment. As exected the pattern of the main effects differed markedly between models with and without P_g as a predictor. In the model without P_g the differences between groups were found between cotton/lawn grass and Sphagnum versus Molinia, with Molinia being significantly greater than these groups. However, the model including P_g as a predictor showed, that, once variations in NEE attributable to P_g are taken into account that Molinia is significantly greater than all other groups. The importance of vegetation in the models increases when P_g is used as a predictor. A possible explanation for this is that by explaining a large fraction of the total variability in the dataset with P_g as a covariate, more subtle effects become more apparent. However, as ever, the use of P_g as a predictor requires the assumption that the relationship identified between NEE and P_g is real, and not simply an artefact of self-correlation. For NEE this would seem to be a straight forward assumption as NEE is by definition $R_{eco} + P_g$ (i.e. P_g is a constituent flux of NEE) and as such NEE cannot be thought to be independent of P_g thus a relationship between these two variables is to be expected. There remains the issue of the shared error component which may introduce some self-correlation. However, as discussed in chapters 2 and 3, this error component is likely to be small relative to the magnitude of 'real' variability in the fluxes in question. So, overall, it is likely that a substantial portion of the relationship identified between NEE and P_g is real. Moreover, the regression coefficients for the relationship found (table 4.3.1.3) show that NEE becomes more negative as P_g becomes more negative, which is in line with expectations.

Examining figure 4.3.1.5, it appears that, on average, only lawn grass and Sphagnum were net sinks of CO_2. Cotton grass appeared to be neutral and all other vegetation types were net sources. The sink identified in the lawn grass dataset may be somewhat deceptive. This is because the lawn grass was sown in areas of extensive erosion, which has left old catotelm peat exposed (i.e. the soil substrate is comparable to the bare peat on the Bleaklow Summit sites) and active measures have been undertaken to raise the water table. As such, many of the largest sources of respiratory activity (e.g. young acrotelm peat, an extensive rhizosphere, litter deposits etc.) were not present on plots where lawn grass was sown. This would limit the potential magnitude of R_{eco} allowing for net sinks to occur more commonly than would be the case if lawn grass was found in more intact peatland ecosystems. This is good news from the perspective of restoration of bare peat in the Peak District; however, it is unlikely that these results would be repeated (with respect to lawn grass NEE), if this species were sown in areas without exposed bare catotelm peat. As such, lawn grass can be said to be apparently successful in maintaining a CO_2 sink (relative to areas of bare peat) but it is unlikely that land management for this vegetation type in more intact peatlands would result in the same net sink of CO_2 being achieved. Therefore, only Sphagnum has been found to be a net sink of CO_2 in areas of peatland comparable to the majority of blanket peatland in the Peak District. This finding implies that management for Sphagnum in the uplands has the potential to increase the size of the carbon sink found in these environments. However, it is essential to increase water tables in order to increase Sphagnum abundance and maximise productivity (e.g. Bragazza and Gerdol, 1996; McNeill and Waddington, 2003). In fact, it could be argued that the main issue affecting the blanket peatlands of the Peak District, from a CO_2 flux perspective, is not necessarily the presence of vegetation types that are bad for CO_2 storage but the deep water table depths these vegetation types indicate. Indeed, Couwenberg et al. (2011) recommend the use of vegetation as a proxy for CO_2 flux as vegetation reflects “long-term water level” within a given peatland environment Underlining this point in the context of this study, increasing water tables through closure of drainage gullies, has created the ‘wet heath’ in the sub-locality known as Ravenslow and it was in this area only that Sphagnum spp. was found in great abundance in the areas investigated in Peak District region.

It is known that water table level will, to some extent, influence the vegetation found on a peatland (e.g. Bragazza and Gerdol, 1996; Couwenberg et al., 2011) and that therefore some magnitude of the effects of vegetation on carbon cycling could be related to the long-term water table position, for which, vegetation is acting as a proxy. To examine this idea a figure (figure 4.4.1.1) has been created showing the relationship between mean R_{eco}, NEE and DOC versus mean water table depth. This figure shows that (not withstanding areas of bare peat or bare peat revegetation, which have been excluded as they are not properly vegetated) mean NEE increases with increasing depths to the mean water table. This relationship is effectively linear for cotton grass, heather, non-Sphagnum moss and Sphagnum. Bilberry and Molinia are offset relative to the trend formed by the other groups. The fit (R^2) of the trend line is nearly 40%; however, given the small number of data points (n = 6) the trend is insignificant (p = 0.125). The fact that both Molinia and bilberry lie so far from the line reinforces the notion that vegetation specific effects are also important. For example, it could be argued that the reason Molinia plots where it does is that it allows O_2 to enter the rhizosphere through its lacunae (Thomas et al., 1996) and thus the rhizosphere has more molecular O_2 than would be expected at an equivalent water level dominated by non-lacunal vegetation (e.g. dicots, bryophytes), leading to a greater amount of net CO_2 flux out of the peat than would be predicted by the trendline. However, while a relationship between long-term water level and vegetation type is to be expected, the data in figure 4.4.1.1 are very limited in their ability to demonstrate whether it is vegetation or average water level that is controlling average NEE, or indeed a combination of both. Thus, this figure was provided to aid discussion rather than present a firm conclusion. The relationship with mean water level was examined for mean R_{eco} by vegetation type also, with no relationship being apparent (R^2 = 0.02%, p = 0.977, n = 6). This may imply that long term (i.e. average) water level is effective on productivity and its ratio to respiration, rather than being effective on respiration itself.

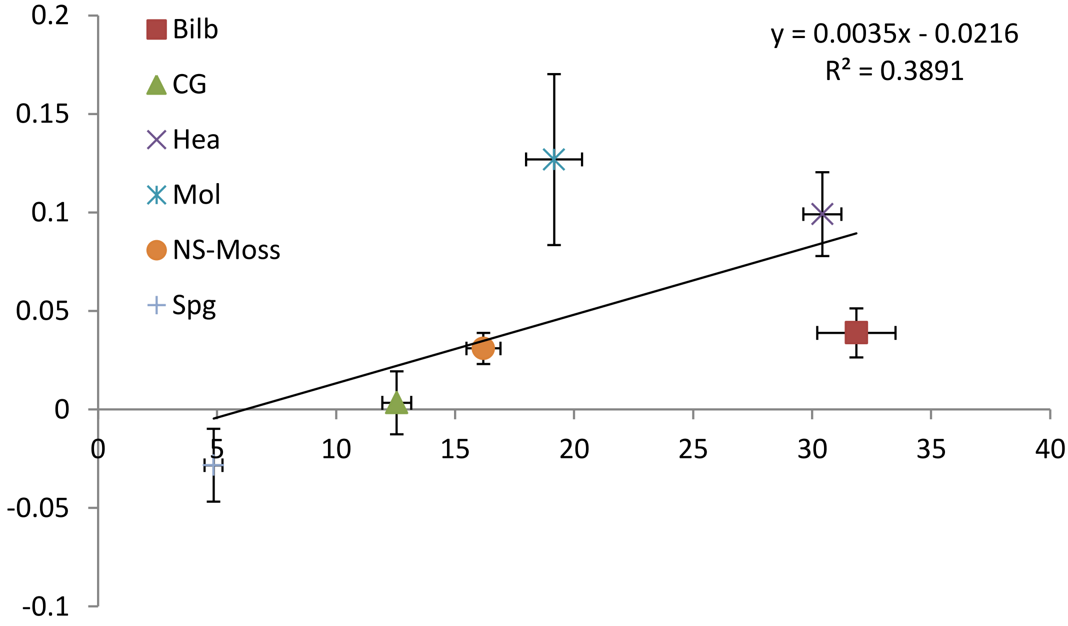


Figure 4.4.1.1 – Scatter plot showing the relationship between mean NEE (y-axis, g CO_2 m^{-2} h^{-1}) versus mean water table depth (x-axis, cm below soil surface). Bare peat and lawn grass were excluded from this analysis due to them not representing properly vegetated sites. The trendline is insignificant ($p > 0.05$). The trend-line is based on the mean data. The error bars represent one standard error of the mean.

The seasonal pattern of soil pore water DOC concentration (figure 4.3.1.8) shows a general increase in DOC concentrations during the autumn and early winter, representing the 'autumn flush' of DOC seen in similar blanket peat environments (e.g. Worrall et al., 2002; Dawson et al., 2011). The 'autumn flush' is thought to represent removal of DOC, created but not transported due to low rainfall, during the growing season months. Concentrations of DOC between vegetation groups tend to be closely clustered, taking into account error bar magnitudes, with bilberry showing generally higher concentrations than the other groups. Interestingly, *Molinia* has lower DOC concentrations than those under bare peat during several months across the year. The results of ANCOVA demonstrated that a large amount of variance in the DOC datasets was unexplained by the predictors. Vegetation was, however, the most important significant predictor of DOC concentration, explaining 10% of dataset variation. The main effect and *post hoc* results (figure 4.3.1.9) indicated that DOC concentrations between vegetation types are roughly distributed in three overlapping groups. The highest concentration group contains only bilberry, the middle group contains the bryophytes, cotton grass and heather and the final group contains bare/revegetated peat and *Molinia*. The fact these groups overlap demonstrates the fact that the differences between the groups are not large relative to the differences observed in the R_{eco} dataset.

The pattern of results for bare peat and lawn grass are unsurprising as these areas are either still bare or are only just re-establishing a functioning vegetative layer, and thus DOC production would be expected to be lower when compared to areas with long standing vegetative layers. This is because litter and root exudates are known to be sources of DOC (e.g. Fenner et al., 2004; 2007) and their absence or partial re-establishment would be expected to reduce DOC production (and thus concentration) relative to areas of long standing vegetation. However, spatial differences in water table levels may complicate this relationship. The very large magnitude CO_2 fluxes from *Molinia* contrast to its relatively low soil pore water DOC concentrations; this could be due to a relatively enhanced rate of microbial respiration of root exudates, possibly stimulated by transport of O_2 to the rhizosphere via lacunae (e.g. Thomas et al., 1996). As root exudates are a component of DOC (e.g. Kuzyakov, 2002) this may explain the relatively low concentrations of DOC observed beneath *Molinia.* Alternatively, it could be due to a greater ratio of plant biomass production: root exudation, when compared with the other vegetation types considered. Research into the effects of rain quality on DOC concentrations (Strand et al., 2002) found that, irrespective of rain quality, DOC concentrations were higher under heather lysimeters than moor grass lysimeters (i.e. *Molinia*).

A plot of mean water level versus mean DOC conentration by vegetation type (excluding the bare and lawn grass sites due to their relatively unvegetated nature) was created (figure 4.4.1.2). It can be seen that mean soil pore water DOC concentrations increase with mean water table depth. The trend line fitted to the data has an R^2 of 40.41%; however, it was insignificant ($p = 0.175$) due to the small number of data points. Nonetheless, this pattern of results mirrors figure 4.4.1.1 where peatland carbon loss (as net CO_2 emission) also increased with increasing mean water table depth. The trend identified, while not significant, is in agreement with Clark et al. (2009) which demonstrates that water table drawdown stimulates DOC production. However, Clark et al. (2009) note that the redox conditions and subsquent transformations of sulphur species within the peat will control the solubility of DOC and thus periodic rewetting and anoxia were needed to stimulate the release of DOC after draw-down events.

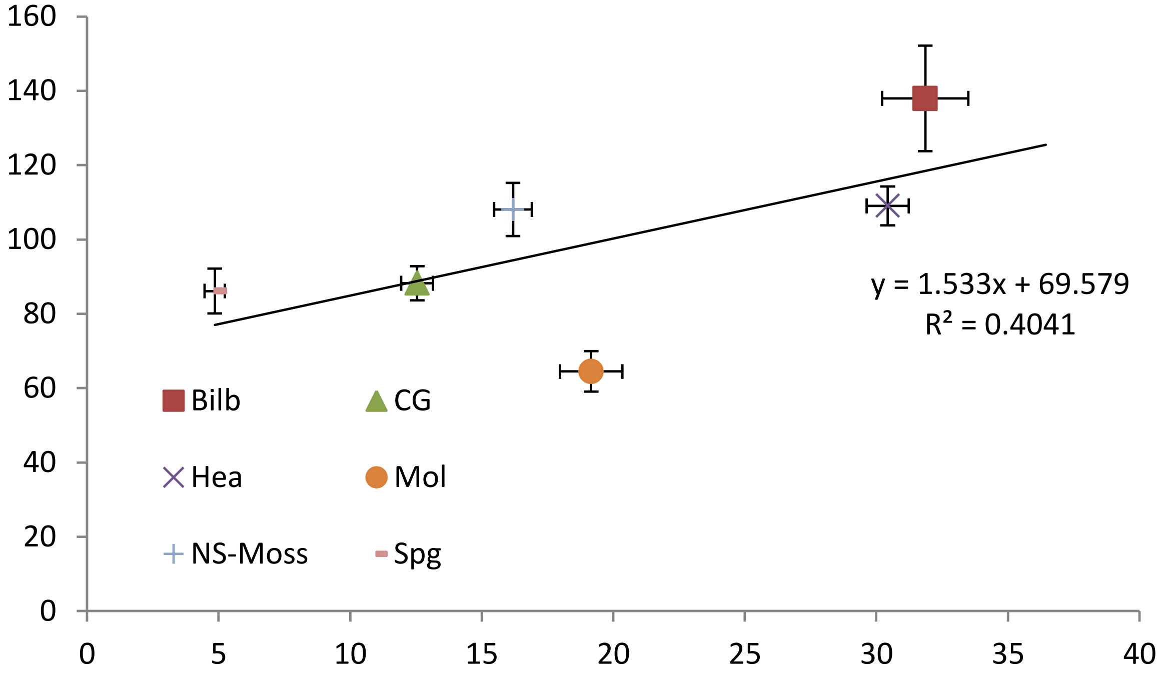


Figure 4.4.1.2 – Scatter plot showing the relationship between mean DOC (y-axis, mg C l^{-1}) versus mean water table depth (x-axis, cm below soil surface). Bare peat and lawn grass were excluded from this analysis due to them not representing properly vegetated sites. The trendline is insignificant ($p > 0.05$). The trend-line is based on the mean data. The error bars represent one standard error of the mean.

The apparent increase in methane during September (figure 4.3.1.6), relative to the January data, is to be expected given the fact that methane flux from organic soils is known to be controlled by temperature (Chapman and Thurlow, 1996). The groups which most frequently have the largest fluxes of methane are cotton grass, Molinia and non-Sphagnum moss. This result is not surprising for cotton grass, as its lacunal system is known to provide a conduit for emission of CH_4 to the atmosphere (Thomas et al., 1996). That emissions of CH_4 from Sphagnum appear to be relatively low is likely related to the fact that Sphagnum mosses are known to support large communities of methantrophic bacteria (Chen and Murrell, 2010). Heather is usually found in close proximity to collars containing non-Sphagnum moss however it has a uniformly smaller flux of methane than non-Sphagnum moss. This may well be related to heather supporting large communities of methantrophic micro-organisms, which are known to decrease in areas where heather has been removed (Chen et al., 2008). Bilberry appears to have the smallest flux of methane of the groups studied, with it only having a (relatively small) measurable flux in one of three campaigns (January 2009).

4.4.2 – Canopy Height Study

It was evident in figure 4.3.2.1 that the differences between canopy heights in terms of R_{eco} are not large relative to overall dataset variability. Indeed, the ANCOVA results supported this suggestion, with canopy height explaining between only 3.12-6.01% of dataset variation depending on whether P_g was used as a predictor or not. The main effects and *post hoc* results (figure 4.3.2.2) suggested, in fact, that canopy height becomes important when the heather canopy increases to a level greater than 30 cm. At this point ecosystem respiration appears to increase significantly, relative to all other canopy heights. Heather with a canopy height in excess of 30 cm on the sites in this study appeared to be in the degenerate phase of the heather life cycle (i.e. broken/breaking canopy, large amount of dead branches – e.g. Gimingham, 1972, pp 127). This means that the stand is older than the other canopy heights. Older heather has been shown to have larger litter and root matter deposits than younger heather (Chapman et al., 1975) and thus, perhaps, older/degenerate heather could be expected to respire more than younger heather due, at least in part, to these factors.

The importance of canopy height was even less for NEE (ω^2 = 2.03-1.71%), nonetheless the pattern of differences between canopy heights was much clearer (figure 4.3.2.4). It appeared that only canopy heights between 0-30 cm exhibited net sinks of CO_2 in any month, with the 0-20 cm canopy heights being the most likely to exhibit sink behaviour. Heather in excess of 30 cm tall was uniformly a CO_2 source; with a seasonal pattern mimicking that of R_{eco}. The results of the ANCOVA and subsequent *post hoc* testing of main effects demonstrated that canopy heights between 0-20 cm were significantly different to 30-40 cm, whereas the 20-30 cm canopy height range was not different to any other range. This pattern of results supports the visual interpretation of figure 4.3.2.4 given above. Use of P_g as a covariate in the model changed the pattern somewhat with all canopy heights between 0-30 cm being significantly lower than 30-40 cm. This would imply that the 30-40 cm canopy height range has a significantly lower rate of P_g relative to R_{eco} than the other canopy heights, assuming that the NEE-P_g relationship is real. This idea is supported by figure 4.4.1.3, which shows box plots of the ratio of P_g to R_{eco} and demonstrates that the majority of the data in the 0-20 cm categories have a ratio of greater than 1 (i.e. more P_g than R_{eco}) whereas the majority of the data for 20-30 cm are less than 1 (i.e. less P_g than R_{eco}). This pattern of results agrees with the observations of Wallèn (1987), who showed that the amount of assimilating biomass, as a percentage of total biomass, decreases with increasing shoot age. The net effect of these changes over time eventually appears to result in the plant becoming a perpetual net source of CO_2 to the atmosphere, due a decreasing ratio of assimilating to respiring biomass.

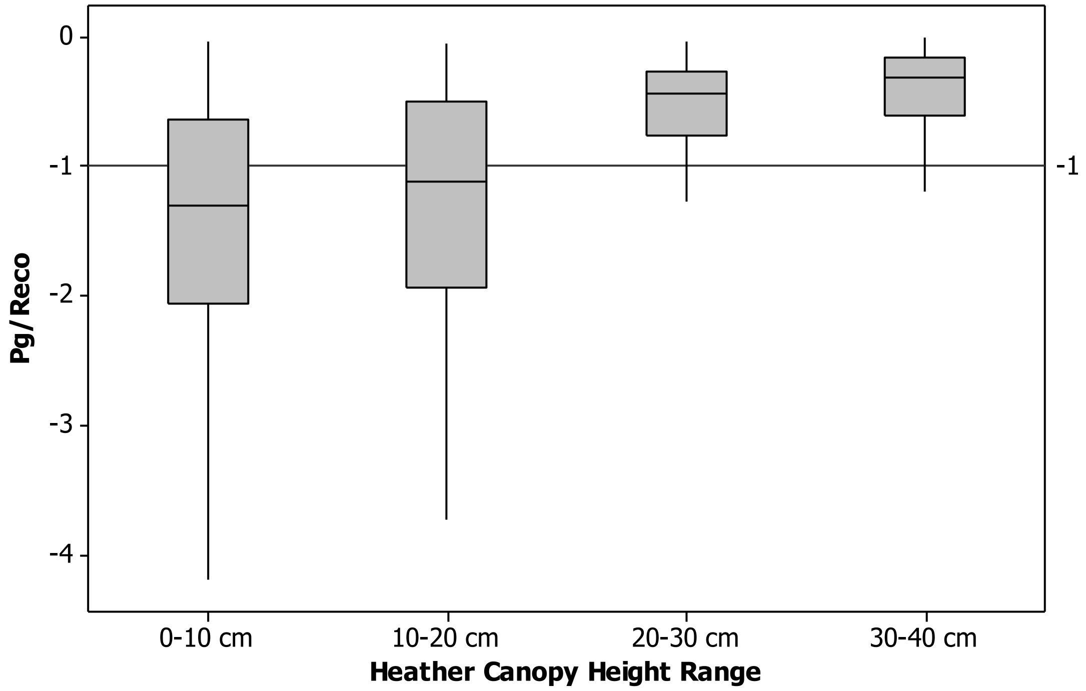


Figure 4.4.1.3 **–** Boxplots of the ration of P_g/R_{eco} for each heather canopy height range. The reference line a -1 represents the transition from more P_g to R_{eco} (anything < -1) to less P_g to R_{eco} (anything > -1).

Soil pore water DOC production, in general, follows a seasonal pattern that is out of phase with the CO_2 flux patterns: it peaks in spring and autumn/winter with a relative depression of DOC production in the mid to late summer months. The post summer peak could represent the 'autumn flush' of growing season DOC from the soil due to increased rainfall (e.g. Worrall et al., 2002; Dawson et al., 2011). However, the variability within the data suggests caution should be taken interpreting patterns in the data by eye. ANCOVA of the DOC concentration dataset has shown that, as for CO_2 flux, heather canopy height does exert a significant influence on DOC production. This effect, however, is not very important with canopy height explaining only 2.85% of dataset variation. Post hoc results (figure 4.3.2.8) for DOC show that canopy height becomes effective once the canopy exceeds 30 cm. Heather stands with a canopy height greater than 30 cm appear to have soil pore water DOC concentrations greater than those of the other canopy heights. This may, again, be related to the increased amount of rhizospheric deposits and litter accumulation in old/degenerate heather than in younger heather (Chapman et al., 1975).

Overall, while canopy height is not the most important predictor of dataset variance, it does exert a consistent and statistically significant effect on the carbon species studied. In terms of CO_2 and DOC it was apparent that, once heather makes the transition from 20-30 to 30-40 cm canopy height the amount of carbon lost to the environment, both in a net and gross sense for CO_2, increases significantly. The implication of these results from a management perspective is that it would appear that burning (or cutting) heather before it reaches 30 cm canopy height is to be preferred from a carbon storage perspective. Historically, management by burning (or cutting) has been planned on a temporally rotating basis with the heather being burnt when it reaches a given stand age/life cycle interval (e.g. Mowforth and Sydes, 1989), with the burning rotation differing between localities based on the local conditions and heather growth rates. However, Burch (2008) has demonstrated, on the North York Moors, that stand age/life cycle interval is not a useful indicator of heathland bryophyte regeneration after burning. Instead, Burch (2008) proposed that canopy height was to be preferred as an objective predictor of bryophyte regeneration. The results implied that in wetter moorland areas (i.e. those most akin to blanket bogs) that burning was most appropriate between 25-30 cm canopy heights. This was because the abundance of pleurocarpous mosses, which store water efficiently when compared with other bryophytes, was maximised at this level. By burning at this stage it was felt that the burn would be cooler, due to the moist conditions in the bryophyte layer and thus subsequent damage to the field- and bryophyte-layer vegetation would be minimised. This would prevent damage to the soil and allow for quicker re-establishment of a favourable bryophyte community. Moreover, Wood-Gee (1996) argues that burning at 20-30 cm canopy height is preferable because regeneration from buds at the bases of stems would be favoured and the amount of fuel would be relatively low ensuring a cooler (i.e. less damaging to the field-layer/soil surface) burn. Furthermore, the UK government’s moorland and grassland burning codes, which are voluntary best-practice guidelines for land managers, also recommend burning at a canopy height of 30 cm (DEFRA, 2007). As such, it can be seen that the results of this study from a CO_2 and DOC stand point are in agreement with recommendations from both policy makers and ecologists and add to a growing consensus that management plans for heather can be outcomes based (i.e. minimal effects on the field-layer ecology/carbon cycle) on the basis of objective research which may represent an improvement on traditional methods.

4.4.3 – Modelling Carbon Cycling

The presence of photosynthesis, implied by the difference between NEE and R_{eco}, on bare peat surfaces may suggest the presence of surficial algae communities. Given the negative effects of algae on peat forming *Sphagnum* mosses (e.g. Hulme, 1986), the presence of algae may be of concern from a peatland restoration and carbon storage perspective. However, the results of the bare peat revegetation are encouraging as they suggest that areas revegetated with lawn grass are relatively insensitive to changes in temperature (figure 4.3.3.6) and P_g (figure 4.3.3.7). Also, revegetated areas were shown to be the largest net daytime CO_2 sinks; however, as discussed previously this may be a result of the recalcitrance of the exposed catotelm peat substrates and a lack of a litter layer supressing R_{eco} rather than lawn grass being especially productive.

The results for bilberry suggest that it is relatively insensitive to changes in temperature a proposition supported by figure 4.3.3.6. R_{eco} from bilberry collars also seems to be relatively insensitive to variations in the rate of P_g as attested by figure 4.3.3.7. Taken together, these facts imply that bilberry heathland may be less sensitive to the effects of climate change than some of the other groups studied.

Figures 4.3.3.5 - 4.3.3.7 show that cotton grass is the third most sensitive group studied to temperature and the most sensitive group to P_g. Trinder et al. (2008) demonstrated that carbon turnover in cotton grass is relatively high compared with shrubs like heather. In addition Breeuwer

(2008) demonstrated that cotton grass litter is relatively decomposable when compared with that of peat forming *Sphagnum* mosses. As such it seems that cotton grass may not be efficient at storing carbon on long time scales and that it may also be more sensitive to climate change than most of the other groups analysed. This view is endorsed by Kivimaki et al. (2008) who suggested that a *Sphagnum*/cotton grass mix was better than cotton grass alone from a carbon storage perspective due to cotton grasses' rapid turnover of carbon with respect to *Sphagnum*. Moreover, the internal lacunal system within cotton grass is known to facilitate transport of CO_2 and CH_4 from the rhizosphere to the atmosphere (Thomas et al., 1996).

Despite having a below-average Q_{10}, figure 4.3.3.6 suggests that heather is, in fact, the second most sensitive vegetation type to temperature when this is modelled by the Lloyd and Taylor (1994) method. Moreover, figure 4.3.3.7 implies that heather R_{eco} is also the second most sensitive to changes in the rate of photosynthesis as modelled by the Larsen et al. (2007) approach. This agrees with Verburg et al. (1998) who, noted that increased levels of CO_2 tend to increase the rate of photosynthesis in heather which in turn increases the rate of root exudation. As such increasing atmospheric CO_2 concentrations and increasing air and soil temperatures are likely to lead to increasing rates of R_{eco} from heather. In addition, heather litter is highly decomposable when compared to that of cotton grass or *Sphagnum* (Breeuwer et al, (2008); Trinder et al., (2008)). These facts imply that heather may not be an ideal species for promoting carbon storage in the uplands with respect to climate change.

The results suggest that *Molinia* R_{eco} is very sensitive to changes in temperature and by implication climate change. In fact, this interpretation is supported by figure 4.3.3.6. This plot shows *Molinia* varying much more rapidly with temperature than the other vegetation types, when estimated by the Lloyd and Taylor (1994) model. That said *Molinia* R_{eco} is least sensitive to changes in the rate of P_g (figure 4.3.3.7) when modelled using the approach of Larsen et al (2007). However, the litter produced by *Molinia* is known to be highly decomposable in comparison to woody ericaceous plants like *Erica tetralix* (e.g. Berendse, 1998). Moreover, *Molinia* is known to have a system of internal lacunae that transport CO_2 and CH_4 from the rhizosphere to the atmosphere, this coupled with its temperature sensitivity may mean it is poorly suited for climate change mitigation.

The findings of the bryophyte analyses showed that the two groups studied non-*Sphagnum* and *Sphagnum* spp. mosses behaved differently. Non-*Sphagnum* mosses R_{eco} fluxes were shown to be relatively insensitive to temperature while *Sphagnum* spp. were shown to be relatively sensitive to temperature. Moreo,ver once variations in P_g were included in the models, *Sphagnum* mosses were shown to be sensitive to water table variations whereas non-*Sphagnum* mosses were shown to be insensitive to water table variations. These findings are worrying as *Sphagna* are the principal peat-forming mosses and, if they are likely to sink less CO_2 with increasing temperature and decreasing water tables, then the uplands will lose part of their most effective carbon sink. Moreover, Fenner et al. (2007) demonstrated that with elevated CO_2 concentrations *Sphagnum* moss cover declined 39% over three years and that the species that took over increased soil pore water DOC concentrations by 66%.

Overall, the obvious statement that can be made about the modelling results is that R_{eco} (mean and median R^2 range = 27.78-58.79% and 20.50-62.02% respectively) is more accurately modelled than NEE (mean and median R^2 range = 5.35-45.13% and 7.27-48.33% respectively). This pattern of results was also evident in chapter 3. It may be that, as NEE is a vector dataset (R_{eco} being scalar by comparison) interactions between the predictive variables (not formally considered in any model applied) represent a large and unaccounted for source of variation. This view is demonstrated in the work of Adkinson et al. (2011), who demonstrate that it is the interactions between water table and air temperature that drive seasonal and inter-annual variation in NEE fluxes from two trophically distinct boreal peatlands. It was notable that the NEE model of Nykanen et al. (2003) had uniformly poor model fits. The model parameter K (the half-saturation parameter) for the Nykanen et al. (2003) model, which had originally been estimated from a linear regression with PAR, was recalculated, by multiple non-linear regression (i.e. independently of PAR). However, the values of the newly fitted parameter K were all in excess of 1,500 µmol m^{-2} s^{-1}, for each vegetation type. Such a large values of K is ecologically unfeasible as photosynthesis in most plants becomes light saturated and thus carboxylation limited somewhere between 500-1000 µmol m^{-2} s^{-1} (Taiz and Zeiger, 2002, pp 178-179). As such only the values based on ecologically realistic parameters are presented here (i.e. the first set of model outputs).

Models including P_g as a predictor were better fitting than those without. As discussed on several occasions in this thesis there is a growing body of research that suggests photosynthesis is an important predictor of temporal variation in both ecosystem and soil respiration (e.g. Hogberg et al., 2001; Bhupinderpal-Singh et al., 2003; Tang et al., 2005; Larsen et al., 2007; Bahn et al., 2009; Migliavacca et al., 2011) on diurnal and seasonal timescales. However, again as mentioned previously, the data gathered in this dataset may be subject to self-correlation as a result of the method used to obtain the P_g data. Nevertheless, the fact that P_g generally improves the fit of NEE models more than it improves R_{eco} models makes sense as P_g is a component flux of NEE and thus would be expected to account for a larger fraction of variation within NEE than R_{eco}. Furthermore obvious and expected seasonal trends and expected relationships with other fully independent predictors (i.e. air temperature) were identified. This suggests that the magnitude of random error is low in comparison to the variation due to 'real' effects. This being the case it is justifiable to presume that at least some of the magnitude of the correlation observed between R_{eco}/NEE and P_g is real.

4.5 – Conclusions

Vegetation was shown to be a significant predictor of variability in R_{eco}, NEE and DOC datasets for all ANCOVA methods used. Of the carbon pathways studied, it was found that R_{eco} was most affected by vegetation type, followed by DOC with NEE being least affected. The use of covariates and other significant factors did not explain the effects of vegetation and as such these differences between vegetation types should be taken into account within carbon budget models (e.g. the Durham Carbon Model) in order to improve model accuracy.

Molinia was found most frequently to have large differences relative to some/all of the other vegetation types, with it being a significant source of CO_2 while having generally lower DOC concentrations. Bare peat had uniformly low fluxes of CO_2 and DOC, while areas revegetated with lawn grass were shown to have relatively low DOC concentrations at the same time as being an apparent net sink of CO_2. This finding is important as it suggests that revegetation of peatlands with lawn grass has the potential to return a net CO_2 sink without releasing large amounts of DOC. More research looking in much more depth at the role of land management is currently ongoing within the research group, which should be able to significantly expand on this conclusion. Of the vegetation types found in conditions more typical of blanket peat in the UK uplands, *Sphagnum* mosses were found to be the only likely net daytime sink of CO_2. Furthermore, there was a suggestion that the vegetation present on a given site may be a proxy for the long term (i.e. average) water table depth. Indeed, it appeared that net fluxes of CO_2 to the atmosphere and concentrations of DOC in the soil pore water increased with increasing depth to long term (i.e. average) water table. The implication of these findings from a management perspective is that, if carbon emissions from blanket peatlands are to be minimised, then the water tables need to be raised to a level where *Sphagnum* mosses are able to establish themselves and thrive.

Management of heather by burning and cutting is being examined in detail with respect to CO_2 and DOC in another study within the research group. Here, visual inspection of the ANCOVA residuals suggested that there were no large differences between management types after ANCOVA. This implied that the interpretations of the inter-vegetation type results were not biased by management. However, it was found that heather canopy height was a consistent and significant predictor of CO_2 flux and DOC concentrations. In all datasets analysed it was apparent that loss of carbon to the environment was significantly greater under heather canopy heights in excess of 30 cm. The management implication of this finding is that to avoid/minimise losses of peatland carbon, through enhanced CO_2 emission and DOC production, managers should aim to burn or cut heather before it exceeds a height of 30 cm. This recommendation is in concert with other ecological and policy based recommendations.

ANCOVA, MLR analysis and fitting of literature process-based models all demonstrated that temperature and the rate of photosynthetic CO_2 sequestration are fundamental drivers of blanket peat carbon cycling. However, additional controls on carbon cycling were found in some vegetation types. For instance cotton grass and *Sphagnum* were sensitive to water table depth variation with respect to ecosystem respiration. Moreover, a number of groups had seasonality measures as significant predictors of R_{eco} and/or NEE. These functions, while entirely empirical in basis, are repeating functions over an annual cycle and are intended to capture residual seasonal dataset variation not accounted for by the other predictors. The fact that one or both of these predictors were significant in some MLR models implies that there are ongoing processes, that vary seasonally, that have not been measured in this analysis but which exert a significant control on carbon cycling for these groups.

The idea that peatland ecosystem respiration is partly controlled by photosynthesis on a seasonal time scale has potential implications for the estimation of the diurnal CO_2 budget of a blanket peat. As this relationship has been found on seasonal and diurnal time scales (see references in section 4.4) in other ecosystems, it is important to determine whether or not it is present on diurnal time scales in peatlands. Moreover, if this relationship is present on diurnal time scales, how does it manifest itself? What are the main controls on CO_2 exchange at night? If it is the supply of recent photosynthate to the rhizosphere that controls the relationship between P_g and R_{eco}, as has been suggested elsewhere, then on what time scale are these substrates respired? Would there be a surplus in the rhizosphere after P_g has stopped thus resulting in a lag period between darkness and R_{eco} decreasing to its overnight minima? These questions are the main focus of chapter 5, which deals with diurnal flux of CO_2 on an *E. vaginatum* dominated blanket bog (site code: Pen) on Bleaklow Plateau.

An important outcome of the modelling component of this chapter is that comparison between the process-based and empirical (i.e. MLR) models have shown that in general the empirical models are the best fitting. This result is apparent even when fitting the MLR models to the validation data (i.e. data not used when the model was being created). For R_{eco} the MLR model without P_g was shown to fit the data relatively poorly but not as poorly as the model of Lloyd and Taylor (1994) (also lacking P_g). Larsen et al. (2007) fitted better than any model without P_g but not as well as the MLR (with P_g) model. This supports Larsen et al. (2007) and Migliavacca et al. (2011) who suggest that P_g is needed to explain the temporal dynamics of R_{eco}; however the potential for self-correlation in this relationship should be borne in mind when evaluating this interpretation. For NEE, the Nykänen et al. (2003), Bubier et al. (1998) and MLR (without P_g) models were poorly fitting when compared to the MLR (with P_g) model. Thus the overall conclusion that can be drawn from the modelling is that empirical models of CO_2, can be as effective, if not more so, than process-based models, even when using randomly selected validation data. Thus, there is no evidence in this chapter to dismiss the use of MLR modelling of CO_2 fluxes from peatlands in comparison to other process-based approaches. Moreover, MLR models without P_g were still better fitting than the process-based alternatives tested, and as such even if P_g cannot be used as a predictor the MLR approach would still be justifiable.

5 – The Role of Diurnal Processes

5.1 – Introduction

Thus far, the research presented in this thesis has dealt with fluxes of CO_2 on a monthly time scale. However, a proper understanding of the overall dynamics of CO_2 flux on the peat bogs of the Peak District requires an understanding of the dynamics of CO_2 flux on diurnal time scales. A principal reason for this is that the data gathered in the monthly campaigns for chapters 3 and 4 of this thesis were all gathered in the daytime, usually in the late morning or early afternoon, meaning the fluxes measured will be indicative of daylight hours CO_2 flux only. However, if the data gathered for this thesis are to be used to estimate the CO_2 balance of a given site on an annual basis, then some understanding of the overnight dynamics of CO_2 flux is necessary.

Before detailing the aims and objectives of this chapter, it is useful to consider the pathways and controls on CO_2 flux from soils. Firstly, CO_2 is sequestered from the atmosphere by plants through photosynthesis, the gross flux of which is thought to be circa -104-120 Pg C/y globally (Field et al., 1998; Schlesinger, 1997, pp 358-359). The total amount of CO_2 fixed by plants (i.e. the net primary production – NPP) is determined by the amount of plant respiration subtracting the amount of gross photosynthesis (P_g). As the magnitude of global terrestrial plant resipration is estimated at ~60 Pg C/y, the NPP is thus around ~60 Pg C/y (Schlesinger, 1997, pp 358-359). However, this figure does not take into account the impact of plants on soil carbon fluxes. As such, the CO_2 balance of a given ecosystem is quantified by the net ecosystem exchange of CO_2 (NEE). This is measured as the difference between P_g and total ecosystem respiration (i.e. plant and soil respiration: R_{eco}). Global R_{eco} is thought to be slightly smaller in magnitude than global P_g resulting in a relatively small (when compared to the gross fluxes) global sink of CO_2 estimated to be 2.3 ± 1.3 Pg C/y (Grace, 2004).

These overall gross fluxes, however, are themselves the sum of other smaller component fluxes, underlining the complexity of carbon cycling within the terrestrial environment. For example,

R_{eco} can be described in terms of autotrophic (i.e. plant metabolic) and heterotrophic (i.e. microbial) respiration. On the other hand, it can also be described in terms of above- (i.e. plant and litter) and below-ground (i.e. soil and roots) respiration. As such, it is important to understand which components of the ecosystem are changing if overall patterns of CO_2 flux are to be accurately modelled and understood.

An important area of uncertainty in carbon cycling science relates to the interaction between the various gross CO_2 fluxes and their components. It is known, for instance, that there is a relationship between P_g and R_{eco} (e.g. Hogberg et al., 2001) and that this effect is apparent at diurnal time scales in forested ecosystems (Tang et al., 2005). Moreover, the fit of first-order exponential models of R_{eco} with temperature (e.g. Lloyd and Taylor, 1994) were shown to be improved by the incorporation of a P_g term in a temperate heathland (Larsen et al., 2007). However, uncertainty remains concerning exactly what effect photosynthesis has on the component fluxes of R_{eco}, i.e. autotrophic and heterotrophic respiration. In forested soils, Ryan et al. (2004) demonstrated that 64-77% of annual P_g is given to autotrophic respiration. Moreover, Bond-Lamberty et al. (2004) demonstrate, again for forested soils, that there is a correlation between the rate of autotrophic and heterotrophic respiration. They postulate that this relationship is global in nature and represents stimulation of heterotrophic respiration by the provision of labile substrates from plant root exudation.

Plant root exudates are organic compounds, sometimes partially composed of recently photosynthetically sequestered C (e.g. Fenner et al., 2004), that are exuded by plant roots into the soil and subsequently dissolve into the soil pore water solution. Thus, they can be defined as a component of DOC. Exudates are usually composed of relatively labile materials (e.g. sugars, amino acids; Rovira, 1969) and therefore provide an easily metabolised substrate for soil microorganisms. As root respiration (e.g. Hansen, 1977; Kuzyakov and Cheng, 2001) and root exudation (e.g. Kuzyakov et al., 2003) are both known to be controlled by the rate of photosynthesis, it is thought that this shared control explains the global relationship between autotrophic and heterotrophic respiration described by Bond-Lamberty et al. (2004).

Studies of the effects of root exudates on ecosystem respiration suggest that 50-60% of soil respiration is made up of heterotrophic respiration of root exudates and other rhizosphere substrates (e.g. Kuzyakov, 2002). In addition, Hogberg et al. (2001) showed, in a tree girdling experiment (i.e. cutting off the supply of recent photosynthate from the leaves to the roots), that soil respiration decreased after girdling by up to 37% but only after five days had elapsed. In addition, Bhupinderpal-Singh et al. (2003) showed that *Pinus sylvestris* stored starches and other carbohydrates in its roots which explained why heterotrophic respiration did not decrease immediately after girdling, as expected. This storage of carbohydrates was inferred by the authors and others (e.g. Ryan and Law, 2005) to be a capacitor which served to temporally decouple photosynthesis from respiration (i.e. it introduced a lag between peak photosynthesis and peak respiration). A lag of approximately one day was observed between photosynthesis and an associated rise in soil CO_2 concentration, [CO_2], in a peat soil (Panikov et al., 2007). This was attributed, by the authors, to a delay in transport of recent photosynthate to the roots of the vascular plants present. However, Panikov et al. (2007) cite a study (Dilkes et al., 2004) that suggests transport of photosynthate to roots takes place in minutes in vascular plants. It could be that this photosynthate is subsequently stored as carbohydrate in the roots, as noted in other environments (e.g. Bhupinderpal-Singh et al., 2003), explaining the observed lag.

Aside from photosynthesis and associated respiration, there are a number of other important controls on diurnal CO_2 flux from soils. Firstly, soil (e.g. Riveros-Iregui et al., 2007; Zhao et al., 2006) and air temperature (e.g. Parkin and Kaspar, 2003) are known to control soil CO_2 fluxes on diurnal timescales. Additionally, Riveros-Iregui et al. (2007) demonstrated that diurnal hysteresis in the relationship between the soil [CO_2] and soil temperature is controlled by soil moisture. Underlining the importance of soil moisture on diurnal timescales, Zhao et al. (2006) reported that both R_{eco} and NEE are affected by the timing of rainfall events, rather than the total amount of precipitation (i.e. the length of the growing season was affected by the onset of rain). Moreover, they observed short duration (< diurnal scale) pulses of R_{eco} immediately affect rainfall events.

Many studies sampling full annual cycles, across multiple ecosystems, including this thesis, show that the growing season is the period of time where variations in CO_2 fluxes are greatest (e.g. Epron et al., 2001; Zhao et al., 2006) as this is when the plants are most active. It is common in the ecological literature to study only growing season fluxes of CO_2 in order to make more general comments about the dynamics of CO_2 flux (e.g. Bubier et al., 1998; Marinier et al., 2004; Oberbauer et al.,1996; Otieno et al., 2009; Risch and Frank, 2010; Wu Hu et al., 2008). As such this chapter employs a growing season sampling strategy in order to assess the diurnal controls on CO_2 flux.

5.1.1– Aims and Objectives

The data generated in previous chapters of this thesis were gathered only during daylight hours. In order to determine whether these data can be used to estimate nightly fluxes (and thus temporally upscale the measurements), it is important to understand what controls CO_2 flux from blanket peat on diurnal timescales. The aim of this chapter is to identify these controls by sampling four diurnal cycles across the growing season (June to September). The objectives of this chapter are then:

- To determine whether daytime rates of R_{eco} are equivalent to night time rates of R_{eco}, i.e. whether their controls are the same. This information is to be used to then determine whether daytime measurements of CO_2 flux can be used to estimate the whole diurnal cycle.
- To identify whether the link between P_g and R_{eco} identified in the other chapters of this thesis is solely instantaneous or whether there is a lag that may represent the delay between photosynthesis and enhancement of autotrophic and/or heterotrophic respiration

due to the time taken to transport the photosynthate to the roots for subsequent exudation/respiration.

5.2 – Experimental Design

All datasets used in this chapter were gathered at the Penguins fieldsite on Bleaklow Plateau in the Peak District (see chapter 2). Data were obtained in four campaigns sampling diurnal cycles across four months, during the early/mid growing season (June – September). In order to trace the course of diurnal ecosystem fluxes of CO_2, the dynamic closed chamber IRGA method, described in chapter 2, was employed following the standard protocols therein.

While the data gathered for this study were not gathered during the monthly field campaigns the same measurement and sampling protocols used in the monthly campaigns (chapter 2) were followed nonetheless. Alongside CO_2 flux, soil pore water DOC, water table depth, chamber air temperature and PAR were recorded. In addition, meteorological data (i.e. air temperature, total solar radiation, rainfall, wind speed) and soil temperature (at 5 and 10 cm depth) were recorded at a permanently fixed weather station located near to Penguins field site on the Bleaklow Plateau (SK 10864 93922).

On each monthly campaign CO_2 flux readings were taken hourly, starting at 09:00, on each replicate plot on the site. Water table depth readings and the environmental readings associated with the CO_2 flux measurements were also recorded. Soil pore water samples were only taken every four hours in order to prevent excessive, artificial draw down of the water table. Readings were taken from 09:00 until 08:00 the following day. During the September campaign, overnight roadwork prevented data gathering past 00:00 and as such the September dataset is shorter than the preceding cycles sampled. This chapter employs a factorial approach to studying diurnal variations in CO_2 flux as each collar is sampled every hour for a complete diurnal cycle. Moreover, four diurnal cycles were sampled, from June to September. This means that the effects of month in the growing season, time of day and plot can be considered as fully-factorial fixed-factors in an ANOVA model.

There were a number of analytical techniques employed in this chapter. Firstly, in order to characterise what processes and factors control CO_2 flux on a diurnal time scale ANCOVA analysis was undertaken for both the individual monthly datasets and the all-month dataset. Following this MLR analysis of the CO_2 datasets for all data (i.e. day and night) and split into daytime and night time fluxes (night time is defined as the period where PAR = 0) was performed in order to see how the controls on CO_2 flux vary between month and day and night. Finally a set of monthly ANCOVA models on the light/dark data were also produced for comparison with the MLR models.

To test for any lag effects in the relationship between P_g and R_{eco} cross correlation analysis was employed. Cross-correlation analysis involved lagging the P_g dataset by a number of hours (between 0 – 10) relative to R_{eco} and then calculating the coefficient of determination between the datasets with the lag in place. A lagged response of R_{eco} to P_g was detected when the coefficient of determination was greater when lagged than the original (zero lag) correlation. Both raw and residual R_{eco} datasets were analysed by cross-correlation. The residual cross-correlation analysis was performed on the R_{eco} datasets with the effects of the significant predictors from the full cycle (i.e. day and night) MLR analysis removed. Cross correlation requires that there are no data gaps in the data sets being compared. As such, any missing data, due to machine error etc. were estimated by linear interpolation between surrounding data points prior to cross correlation analysis.

5.3 – Results

5.3.1 – All Months

The meteorological conditions on the site during the measurement campaigns are summarised below (table 5.3.1.1 and figure 5.3.1.1). It can be seen that the mean ambient air temperature across each diurnal cycle, recorded at the Upper North Grain meteorological station, varied between 15.7 and 10.8^{o}C, with a cooling trend from June to September. Soil temperature at both 5 and 10 cm depth was always within 2^{o}C of measured air temperature with soil temperature at 5 cm being slightly greater than at 10 cm. Air temperature in June and September was higher than the soil temperature, however; this pattern was reversed in July and August. Rainfall was initially zero on the cycle sampled in June, peaking at 18.0 mm in July with the August and September cycles having rainfall totals of 3.2 and 1.6 mm respectively. Total solar radiation decreased exponentially from a high of 7820 W m^{2} in June to a low of 429 W m^{2} in September.

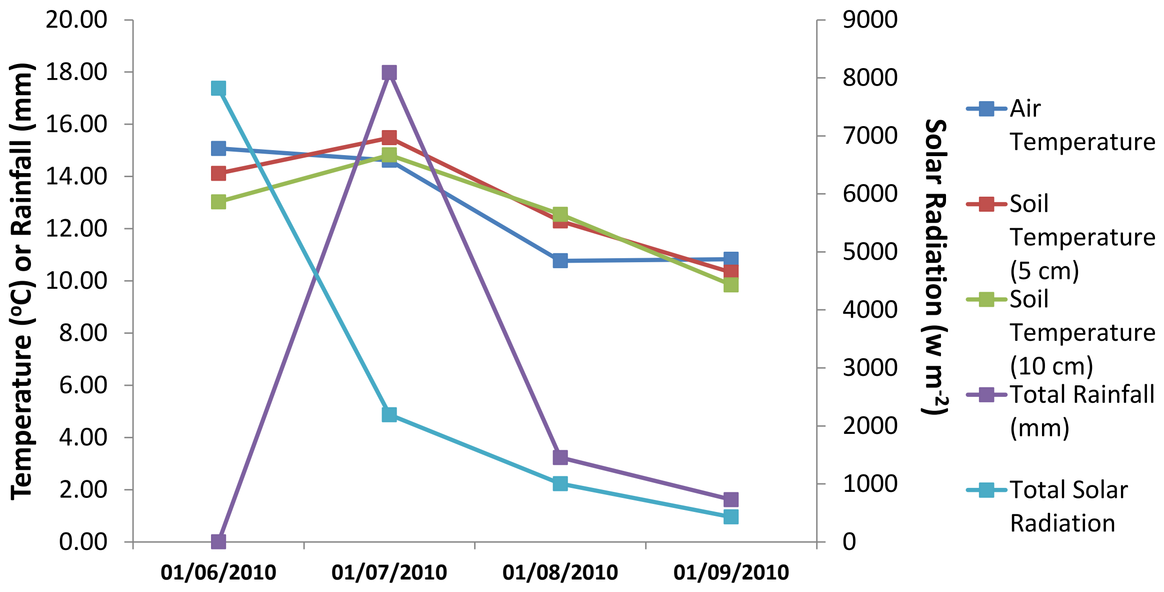


Figure 5.3.1.1 **–** Overview of the meteorological conditions recorded at the Upper North Grain weather station during diurnal sampling. Air and soil temperatures are the mean values for the time interval sampled. Rainfall and total radiation are the sum of the values during the time interval sampled.

Table 5.3.1.1 – Meteorological Data – Upper North Grain Station

Weather Station Data - Upper North Grain

Date	**Air Temperature** (°C)	**Soil Temperature (50 mm)** (°C)	**Soil Temperature (100 mm)** (°C)	**Total Rainfall** (mm)	**Total Solar Radiation** (W/m^2)
21/06/2010	15.1	14.1	13.0	0.0	7820.0
20/07/2010	14.6	15.5	14.8	18.0	2191.9
17/08/2010	10.8	12.3	12.5	3.2	1004.3
28/09/2010	10.8	10.3	9.8	1.6	429.7

Diurnal variation in ambient and chamber air temperature is shown below (figure 5.3.1.2). It is evident that during daylight hours on all months there is some greenhouse warming within the chamber relative to the external air temperature. This effect is greatest in June with a maximum difference in temperature of 20.2°C when solar radiation and ambient temperature were highest. The magnitude of the greenhouse effect decreases rapidly by about half in July with a maximum difference of 11.2°C followed by 13.1°C in August. The effect decreases again in September with a maximum difference of 3.6°C. In most months the maximum difference between air and chamber temperature occurred at 14:00 hours apart from September when the maximum difference occurred at 13:00. During the hours of darkness it is apparent that the difference between air and chamber temperatures approaches zero, with some periods showing cooler chamber temperatures than the ambient conditions.

An overview of the hourly R_{eco} and NEE fluxes from each measurement sortie is given in figures 5.3.1.3 and 5.3.1.4. It can be seen that for both R_{eco} and NEE flux variation was greatest in June, with a generally decreasing trend for the remaining months.

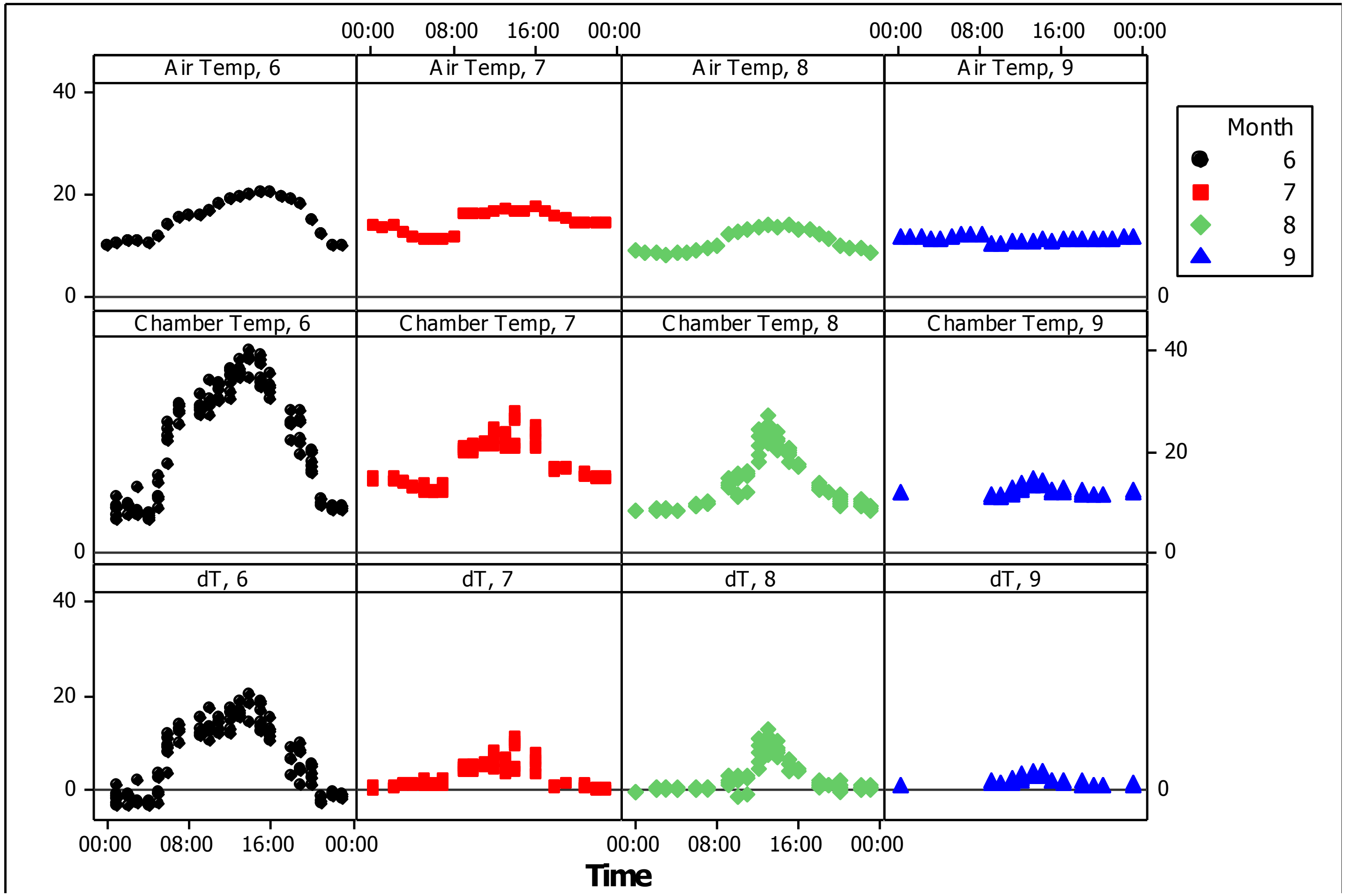


Figure 5.3.1.2 **–** Graphs showing the diurnal variation in ambient and chamber air temperatures for each month sampled. The plots of dT show the difference between chamber and ambient air temperatures across each diurnal cycle.

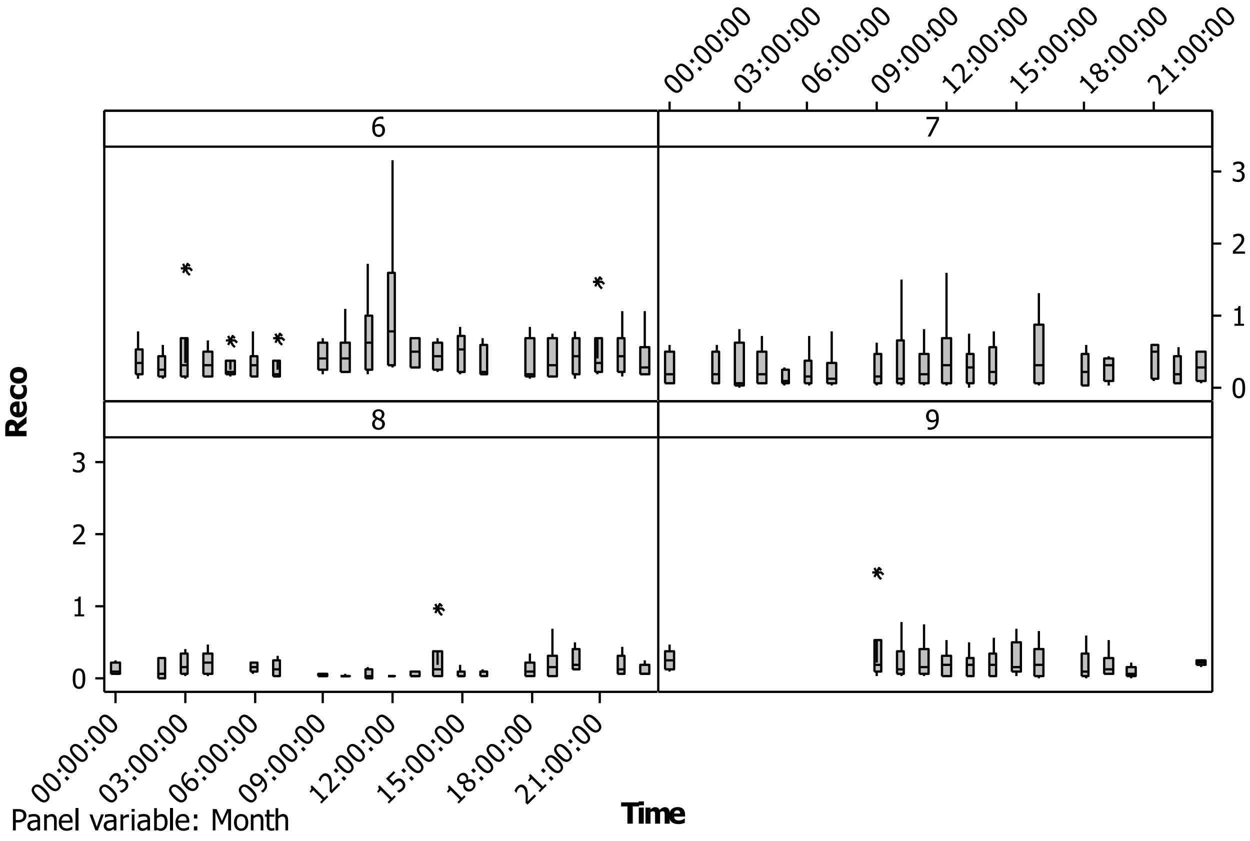


Figure 5.3.1.3 – Boxplots of hourly Reco from each month (denoted by month number). The data from all collars on the site have been aggregated to form the dataset each box represents. Statistical outliers are represented by an asterisk. R_{eco} is in units of g CO_2 m^{-2} h^{-1}.

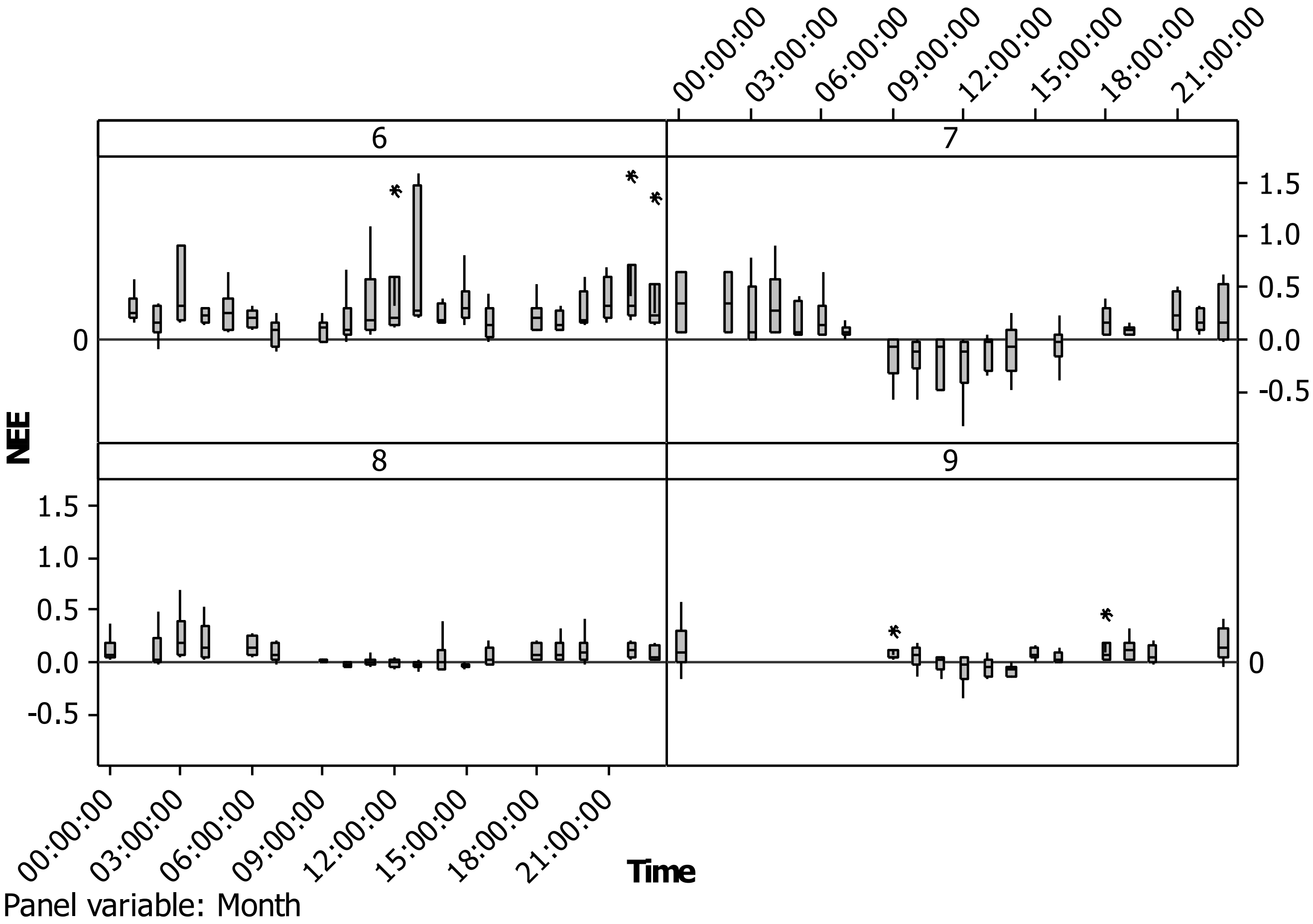


Figure 5.3.1.4 **–** Boxplots of hourly NEE from each month (denoted by month number). The data from all collars on the site have been aggregated to form the dataset each box represents. Statistical outliers are represented by an asterisk. NEE is in units of g CO_2 m^{-2} h^{-1}.

ANCOVA results from the all month datasets are summarised in tables 5.3.1.2 and 5.3.1.3. These indicate that P_g is the most important control on diurnal R_{eco} explaining 57.7% of dataset variation. The next most important factor was 'month', which accounted for 12.23% of dataset variation. Both 'collar' and 'time' were also significant, accounting for about 4.5% of dataset variation each. Tukey testing revealed that all months were statistically different from each other apart from July and September. The ANCOVA results for NEE showed that while all the factors and covariates present in the R_{eco} model were significant in the NEE model, P_g is no longer than most important predictor. The most important predictor is now 'collar', accounting for 21.19% of dataset variation. Following collar the covariate water table depth is next most important control predicting 11.51% of dataset variation. 'Month' and 'time' factors both account for 5.5 and 5.6% of dataset variation respectively, with P_g accounting for 8.56% and chamber air temperature a further 0.05%. *Post hoc* Tukey testing shows that June is different to all other months, August and September differ and July is not different to August or September.

Table 5.3.1.2 *– All Data R_{eco} ANCOVA Results*

	ln Reco		
All data	n	249	
Coding	Source	p	ω^2
Cov	ln GPP	<0.0001	57.71%
FF	Collar	<0.0001	4.53%
FF	Time	<0.0001	4.53%
FF	Month	<0.0001	12.23%
R-Sq	81.26%		
Tukey: Month: 6 -7,8,9; 7 -8; 8 -9			

Coding: Cov = covariate, FF = fixed factor

Table 5.3.1.3 *– All Data NEE ANCOVA Results*

NEE			
All data	n	249	
Coding	Source	p	ω^2
Cov	WTD	<0.0001	11.51%
Cov	Pg	<0.0001	8.56%
Cov	Air Temp	0.023	0.05%
FF	Collar	<0.0001	21.19%
FF	Time	0.003	5.62%
FF	Month	<0.0001	5.55%
R-Sq	57.20%		
Tukey: Month: 6 -7,8,9; 8 -9			

Coding: Cov = covariate, FF = fixed factor

5.3.2 – Monthly Comparison

A summary of the mean values of the data measured across the diurnal cycles sampled is given in table 5.3.2.1. These data show that the site was a net source of carbon (i.e. NEE > 0) on all cycles sampled. Moreover, it indicates that the gross flux R_{eco} was highest in June, when the water table was much lower than the following months. Air temperature and PAR were both substantially lower on subsequent cycles.

Table 5.3.2.1 – All collar mean data for each cycle sampled

Mean All Collar Data

Date	**WTD** (mm)	± Error	**PAR** (μmol s^{-1} m^{-2})	± Error	**Air Temperature** (^{o}C)	± Error	**R_{eco}** (gCO_2 m^{-2} h^{-1})	± Error	**NEE** (gCO_2 m^{-2} h^{-1})	± Error
21-22/06/2010	372.6	95.3	567.3	55.0	21.8	1.0	0.4519	0.0361	0.2859	0.0285
20-21/07/2010	17.6	4.2	220.6	26.9	17.3	0.4	0.2863	0.0289	0.0763	0.0271
17-18/08/2010	16.0	5.1	65.3	11.9	13.4	0.5	0.1321	0.0156	0.0828	0.0123
28-29/09/2010	20.4	6.1	96.1	10.6	11.8	0.1	0.218	0.0275	0.0586	0.0158

ANCOVA revealed that natural log models generally fit the diurnal R_{eco} data better than models produced on the untransformed data, with the exception of the cycle sampled in August. It can be seen from the ANCOVA results (table 5.3.2.2) that the most important predictor of R_{eco}, in all sampling months is P_g, with ω^2 statistics ranging between 72.47% and 45.78%. 'Time' (i.e. hour of the day) is also significant in every cycle sampled, with an ω^2 statistic ranging between 10.98% and 4.79%. There are, however, a number of other predictors which are not significant in every month. In June 'collar' is the second most important predictor (ω^2 = 21.66%) with water table depth as the least important predictor (ω^2 = 4.58%). In July and September 'collar' is again the second most important predictor (ω^2 = 22.45 and 9.90% respectively).

Table 5.3.2.2 – ANCOVA R_{eco} results for each cycle sampled

Ln R_{eco}			
June	n	70	
Coding	Source	P	ω^2
Cov	ln WTD	0.048	4.58%
Cov	ln Pg	< 0.0001	48.07%
FF	Collar	< 0.0001	21.66%
FF	Time	< 0.0001	10.98%
R-Sq	89.68%		

Ln R_{eco}			
July	n	67	
Coding	Source	P	ω^2
Cov	ln Pg	< 0.0001	64.36%
FF	Collar	< 0.0001	22.45%
FF	Time	< 0.0001	5.42%
R-Sq	94.62%		

R_{eco}			
August	n	47	
Coding	Source	P	ω^2
Cov	Pg	0	66.93%
FF	Time	0.019	8.75%
R-Sq	83.53%		

Ln R_{eco}			
September	n	63	
Coding	Source	P	ω^2
Cov	ln Pg	< 0.0001	72.47%
FF	Collar	< 0.0001	9.90%
FF	Time	0.004	4.79%
R-Sq	91.01%		

Coding: Cov = covariate, FF = fixed factor

ANCOVA modelling of NEE shows a similar pattern of results (table 5.3.2.3) with P_g (ω^2 between 64.25 and 0.84%) and 'time' (ω^2 between 20.17 and 7.37%) the most frequently identified significant predictors, alongside 'collar' (ω^2 between 36.35 and 12.61%). However, no single predictor was found to be significant across all cycles analysed. In June 'collar' (ω^2 = 36.35%) was significant alongside 'time'. In July, P_g and 'time' were significant alongside 'collar' (ω^2 = 12.61%) and water table depth (ω^2 = 0.30%). In September, P_g is significant alongside 'collar' (ω^2 = 14.67%) and PAR (30.55%). It should be noted that as the September sampling was cut short the fact PAR is significant only in this month may relate to the fact that very few dark (i.e. PAR = 0) hours were sampled.

Table 5.3.2.3 – ANCOVA NEE results for each cycle sampled

NEE			
June	n	122	
Coding	Source	P	ω^2
FF	Collar	< 0.0001	36.35%
FF	Time	0.003	11.86%
R-Sq	59.00%		

NEE			
July	n	97	
Coding	Source	P	ω^2
Cov	WTD	0.001	0.30%
Cov	Pg	< 0.0001	64.25%
FF	Collar	< 0.0001	12.61%
FF	Time	< 0.0001	7.37%
R-Sq	88.75%		

NEE			
August	n	54	
Coding	Source	P	ω^2
Cov	Pg	< 0.0001	27.89%
FF	Time	0.011	20.17%
R-Sq	56.88%		

NEE			
September	n	62	
Coding	Source	P	ω^2
Cov	PAR	< 0.0001	30.55%
Cov	Pg	< 0.0001	0.84%
FF	Collar	0.002	14.67%
R-Sq	53.45%		

Coding: Cov = covariate, FF = fixed factor

5.3.3 – Day/Night Comparison

In order to identify whether differences in the controls on CO_2 flux exist between the hours of darkness and light, the datasets for each cycle were split into hours of light and dark. A dark dataset was defined as having been recorded when PAR = 0, with light datasets being recorded when PAR > 0. Table 5.3.3.1 summarises the mean light and dark data from each cycle sampled. It can be seen that average night time R_{eco} and soil pore water DOC concentration are within errors of daytime R_{eco} and soil pore water DOC concentration on all cycles sampled (table and figures 5.3.3.1 and 5.3.3.2). Average NEE in the dark is greater (outside of errors) than NEE in the light (table 5.3.3.1 and figure 5.3.3.3); however, NEE and R_{eco} in the dark are within errors of each other (figure 5.3.3.4), which is expected and demonstrates dataset reliability. It is interesting to note that when NEE is split into light and dark subsets that on only one occasion (the cycle sampled in July) was the site a net daylight hours sink of CO_2 (table 5.3.3.1). However, this daylight sink was cancelled out by night-time respiration resulting in no cycle recording a daily net sink of CO_2.

Table 5.3.3.1 – Carbon data split into light and dark means for each cycle sampled

Light/Dark Mean Comparison

Date	**R_{eco} - Dark** (gCO_2 m^{-2} h^{-1})	± Error	**R_{eco} - Light** (gCO_2 m^{-2} h^{-1})	± Error
21-22/06/2010	0.4122	0.0539	0.4724	0.0472
20-21/07/2010	0.2674	0.0412	0.2939	0.0372
17-18/08/2010	0.1597	0.023	0.1189	0.0201
28-29/09/2010	-	-	0.218	0.0275
	NEE - Dark (gCO_2 m^{-2} h^{-1})	± Error	**NEE - Light** (gCO_2 m^{-2} h^{-1})	± Error
21-22/06/2010	0.3466	0.0515	0.2563	0.0338
20-21/07/2010	0.2786	0.0473	-0.0119	0.0278
17-18/08/2010	0.1498	0.0264	0.0515	0.0117
28-29/09/2010	-	-	0.0586	0.0158
	DOC - Dark (mg L^{-1})	± Error	**DOC - Light** (mg L^{-1})	± Error
All Dates	93.2	13.9	101.4	10.6

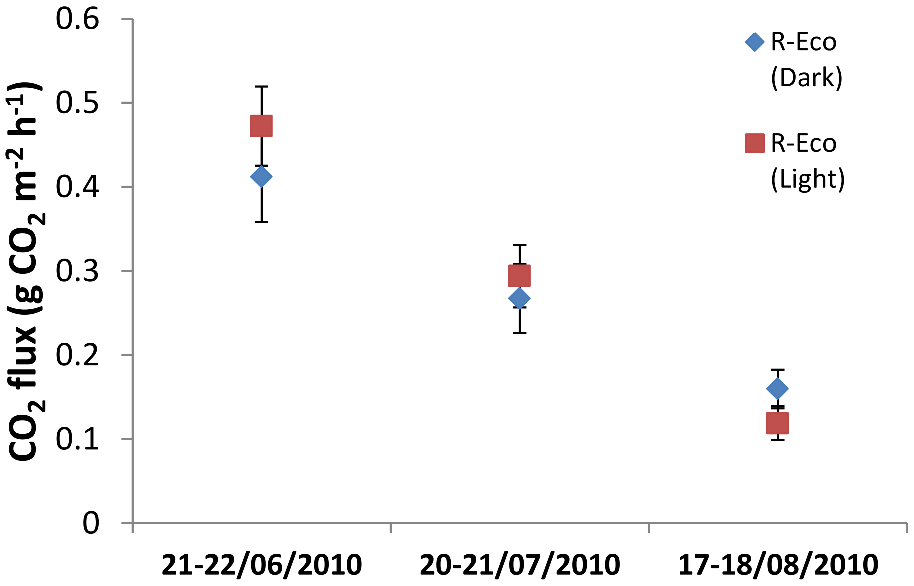


***Figure 5.3.3.1* –** Comparison of the mean dark and light values for R_{eco} across the cycles with full night time datasets. Error bars represent ± one standard error of the mean

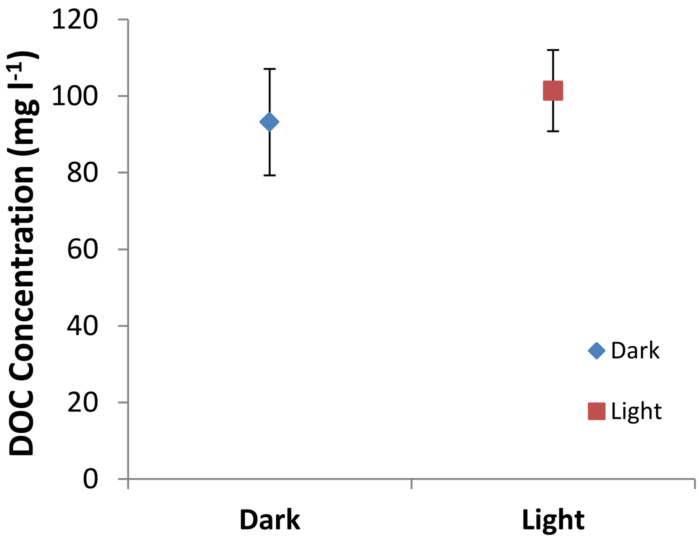


***Figure 5.3.3.2* –** Comparison of the mean dark and light values for soil pore water DOC concentration from all cycles sampled. Error bars represent ± one standard error

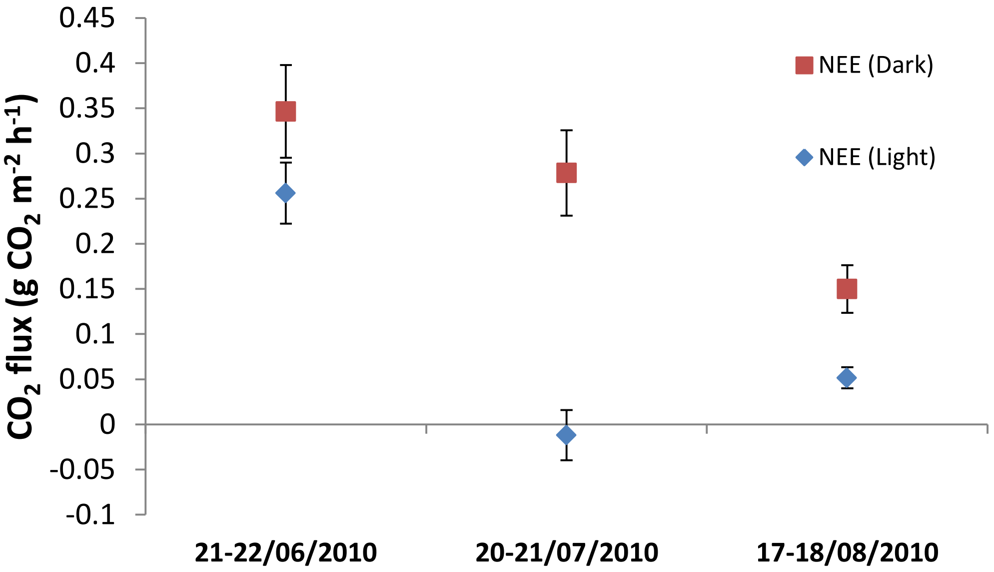


***Figure 5.3.3.3* –** Comparison of mean NEE value in the hours of darkness and light across the diurnal cycles with full night-time datasets. Error bar represent ± one standard error

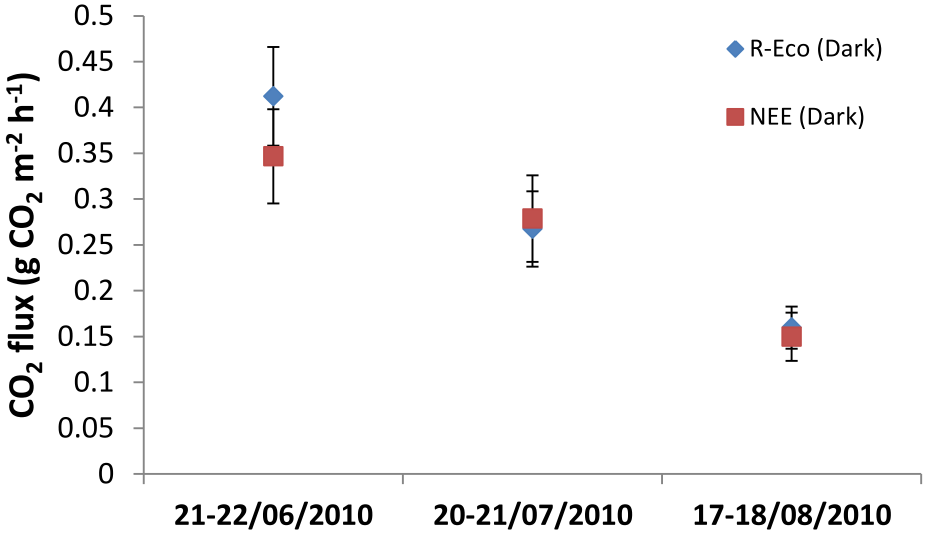


***Figure 5.3.3.4* –** Comparison of the mean dark R_{eco} compared to mean dark NEE for the diurnal cycles sampled with complete night time datasets. Error bars represent ± one standard error of the mean.

The ANCOVA results from section 5.3.2 demonstrate that there are significant differences between collars. These differences are to be expected and reflect the heterogeneity of peatland environments. As such, using statistics like the mean to estimate the overall patterns on the site as a whole is reasonable. This is because the collars should be considered to be a sample of the population of all possible peatland surface positions, on that site. However, it is important to show where these differences lie. Therefore, boxplots of the R_{eco} and NEE datasets have been created showing the dataset distributions by collar, light/dark hours and month, figure 5.3.3.5-5.3.3.6 for R_{eco} and NEE respectively. These plots show, as confirmed by the *post hoc* results of the ANCOVA models in section 5.3.2, that it is collar 6 that appears to have the most distinct differences to the rest of the collars. This point is also demonstrated in figure 5.3.3.7.

Multiple linear regression analysis of the light and dark R_{eco} datasets (table 5.3.3.2) shows that P_g (a plant-mediated process) is the most important daylight predictor across all diurnal cycles sampled (i.e. P_g appears most frequently). In July both air temperature and soil temperature at 5 cm depth alongside water table depth were significant predictors of R_{eco} in daylight hours. Air temperature continued to be a significant predictor of R_{eco} during daytime in the August and September cycles. Water table depth was significant during daylight once again in September. Night time R_{eco} during June had no significant predictors in the MLR analysis. This lack of predictors may be explained by the fact that the within-collar hour to hour variation was small (figure 5.3.3.7) with the exception of collar six which showed a pronounced decrease in R_{eco} through the hours of darkness. In both the July and August cycles water table depth was found as the only significant predictor of night-time R_{eco} with model R^{2}'s of 52% and 50.7% respectively. Multiple linear regression analysis of the NEE datasets split into light and dark groups showed a very similar pattern of results to R_{eco} (Table 5.3.3.3). The main difference between the two fluxes, in terms of their light/dark MLR results is the addition of PAR into the September NEE model.

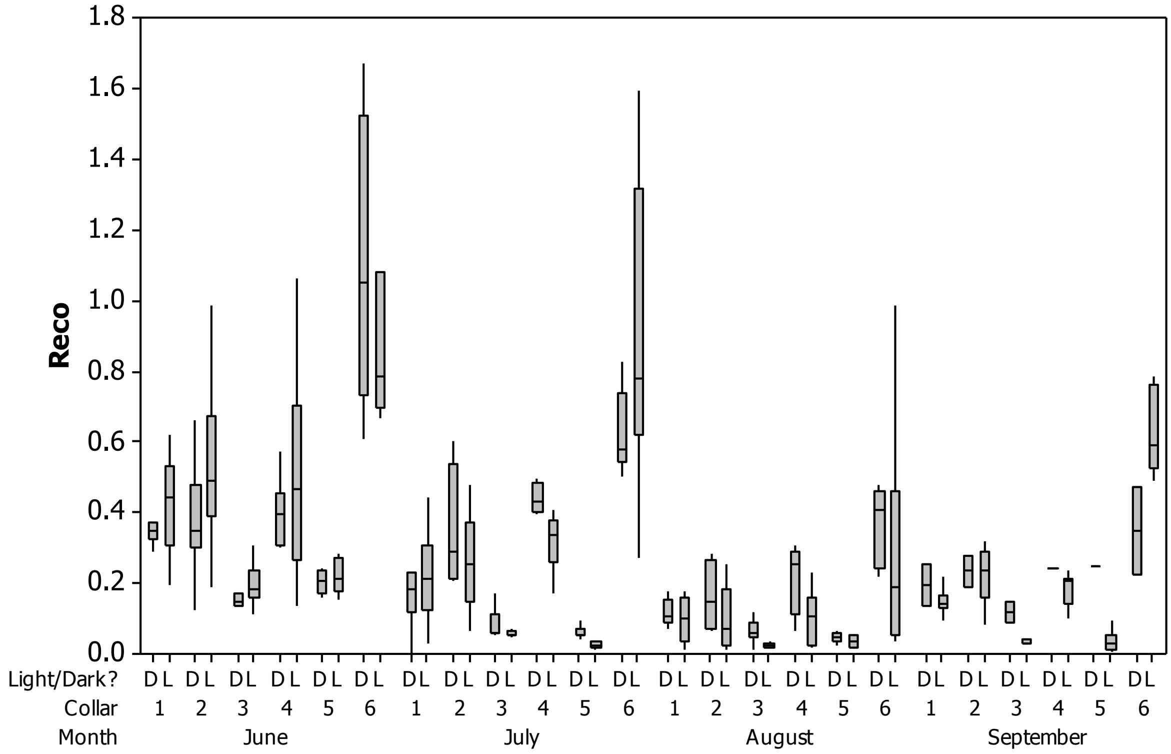


***Figure 5.3.3.5* –** Boxplot of the entire Reco (units = g CO_2 m^{-2} h^{-1}) dataset by month, collar and dark/light (D/L).

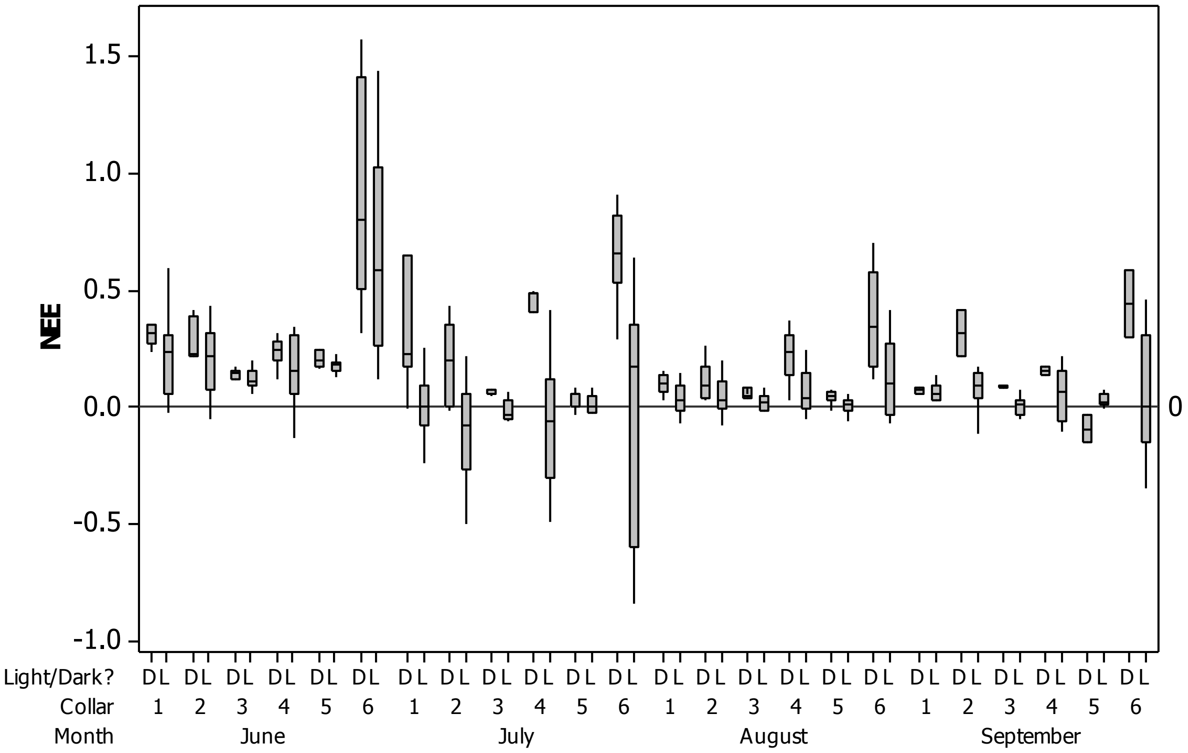


Figure 5.3.3.6 **-** Boxplot of the entire NEE (units = g CO_2 m^{-2} h^{-1}) dataset by month, collar and dark/light (D/L).

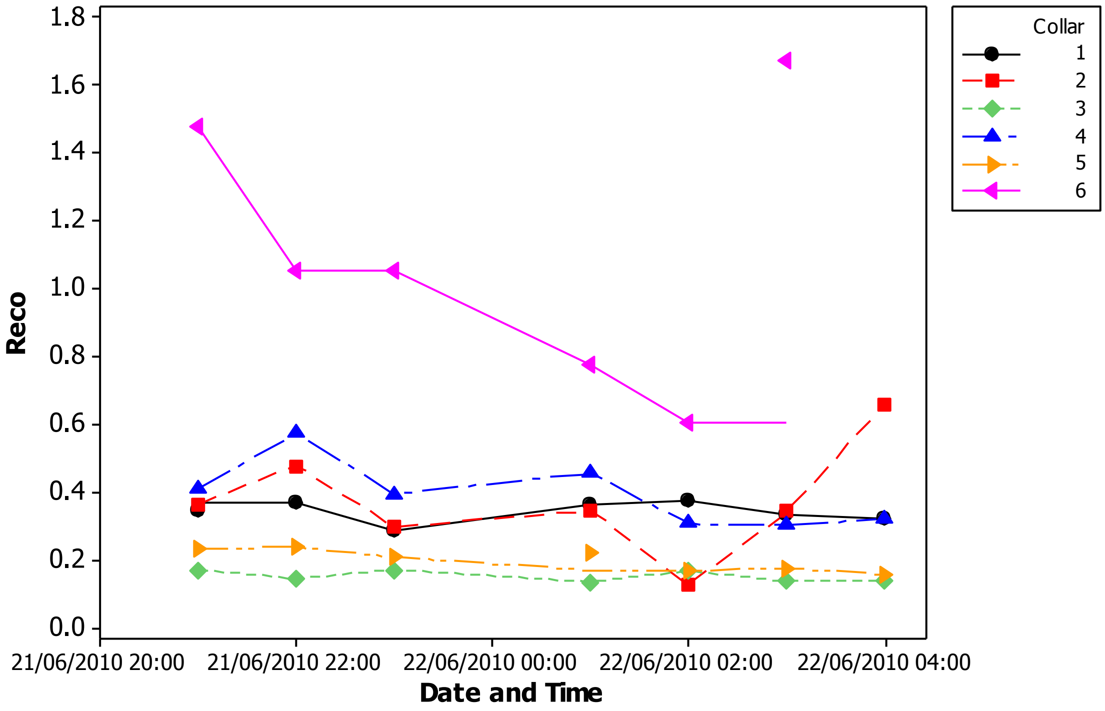


Figure 5.3.3.7 – Measured dark (i.e. night-time) R_{eco} values during the June sampling sortie by collar. R_{eco} is measured in units of g CO_2 m^{-2} h^{-1}

Table 5.3.3.2 – MLR R_{eco} results for light and dark during all cycles sampled

R_{eco} - Light				
June		n	71	
Predictor	Coef	SE	T	P
C	0.12111	0.03746	3.23	0.002
Pg	-1.35907	0.09718	-13.99	0
R-Sq	73.90%			

R_{eco} - Dark				
June				
Predictor	Coef	SE	T	P
n/a				

R_{eco} - Light				
July		n	64	
Predictor	Coef	SE	T	P
C	-0.2743	0.2137	-1.28	0.204
WTD	0.02828	0.004329	6.53	0
AT	-0.02711	0.005596	-4.84	0
Pg	-0.53049	0.04513	-11.57	0
ST-5	0.05465	0.01766	3.09	0.003
R-Sq	89.20%			

R_{eco} - Dark				
July		n	31	
Predictor	Coef	SE	T	P
C	0.24985	0.02918	8.56	0
WTD	0.040843	0.00729	5.6	0
R-Sq	52%			

R_{eco} - Light				
August		n	47	
Predictor	Coef	SE	T	P
C	0.18808	0.03689	5.1	0
AT	-0.01193	0.002236	-5.33	0
Pg	-1.6344	0.122	-13.39	0
R-Sq	81.00%			

R_{eco} - Dark				
August		n	31	
Predictor	Coef	SE	T	P
C	0.13092	0.01727	7.58	0
WTD	0.014279	0.02616	5.46	0
R-Sq	50.70%			

R_{eco} - Light				
September		n	61	
Predictor	Coef	SE	T	P
C	0.7348	0.162	4.54	0
WTD	0.011322	0.003491	3.24	0.002
AT	-0.05625	0.01371	-4.1	0
Pg	-0.75583	0.0642	-11.77	0
R-Sq	85.90%			

R_{eco} - Dark				
Predictor	Coef	SE	T	P
no data				

C - Intercept, WTD - Water table depth , AT - Air Temperature, ST-5 - Soil Temperature (5 cm)

Table 5.3.3.3 – MLR NEE results for light and dark during all cycles sampled

NEE - Light				
June	n		71	
Predictor	Coef	SE	T	P
C	0.12111	0.03746	3.23	0.002
Pg	-0.35908	0.09718	-3.69	0
R-Sq	16.50%			

NEE - Dark				
June				
Predictor	Coef	SE	T	P
n/a				

NEE - Light				
July	n		64	
Predictor	Coef	SE	T	P
C	-0.2739	0.2138	-1.28	0.205
WTD	0.028271	0.004333	6.52	0
AT	-0.02712	0.005601	-4.84	0
Pg	0.46966	0.04517	10.4	0
ST-5	0.05467	0.01768	3.09	0.003
R-Sq	80.10%			

NEE - Dark				
July	n		34	
Predictor	Coef	SE	T	P
C	0.25166	0.03664	6.87	0
WTD	0.046578	0.009455	4.93	0
R-Sq	43.10%			

NEE - Light				
August	n		54	
Predictor	Coef	SE	T	P
C	0.17207	0.03387	5.08	0
AT	-0.6149	0.1099	-5.59	0
Pg	-0.0108	0.002007	-5.38	0
R-Sq	50.80%			

NEE - Dark				
August	n		36	
Predictor	Coef	SE	T	P
C	0.11542	0.02169	5.32	0
WTD	0.015846	0.00324	4.89	0
R-Sq	41.30%			

NEE - Light				
September	n		62	
Predictor	Coef	SE	T	P
C	0.12257	0.01895	6.47	0
WTD	0.011592	0.003434	3.39	0.001
PAR	-0.00063	0.000137	-4.6	0
Pg	0.21034	0.06506	3.23	0.002
R-Sq	44.90%			

NEE- Dark				
September				
Predictor	Coef	SE	T	P
no data				

C - Intercept, WTD - Water table depth , AT - Air Temperature, ST-5 - Soil Temperature (5 cm)

The main limitation of the MLR analyses above (tables 5.3.3.2-5.3.3.3) is that they do not take into account significant differences between factor levels, like collars, identified in the previous ANCOVA analyses. As such, additional ANCOVA models for R_{eco} and NEE were produced for the hours of light and darkness. The results of these analyses are summarised in tables 5.3.3.4-5.3.3.5 for R_{eco}

and NEE respectively. For R_{eco} it can be seen that, in general, the significant covariates in the models reflect those identified in the MLR analyses. Moreover, during daylight hours the fit of ANOVA models is generally only slightly greater than the original MLR (with the exception of June). That said, there are differences between ANCOVA and MLR with the factor 'time', appearing to account for variation attributed to temperature in the MLR models for both July and September during daylight hours. Moreover, during the hours of darkness in August the effects of water table depth in the MLR model appear to be explained by inter-collar variation in the ANCOVA model (i.e. the variable is no longer significant at the same time as the factor). Furthermore, for the hours of darkness in June it can be seen that a weak relationship between R_{eco} and air temperature has been identified. This implies that, as seen in previous chapters, removing the effects of more important predictors (in this case the factor 'collar') allows for the identification of weaker relationships that would otherwise be masked by the larger magnitude effects.

For NEE ANCOVA models have been produced only for daylight hours as in the hours of darkness NEE = R_{eco}. Once again the predictors in the MLR models are generally reflected in the covariates in the ANCOVA models. Moreover, the fits of the MLR models were only slightly lower than the ANCOVA models (with the exception of June). However, the factor 'time' appears to account for the variation ascribed to temperature in July, temperature and P_g in August and PAR in September. These results are unsurprising as temperature, PAR and P_g are known to follow diurnal cycles and thus it is to be expected that a factor accounting for time (as hours) would account for variation induced by these predictors.

Table 5.3.3.4 – R_{eco} ANCOVA results for light and dark hours for each month

Ln R_{eco}

June	Light	n	71
Coding	Source	P	ω^2
Cov	Pg	< 0.0001	61.73%
FF	Collar	< 0.0001	17.44%
FF	Time	< 0.0001	7.89%
R-Sq	90.69%		

Ln R_{eco}

June	Dark	n	40
Coding	Source	P	ω^2
Cov	Air Temperature	0.017	3.12%
FF	Collar	< 0.0001	74.67%
R-Sq	81.57%		

R_{eco}

July	Light	n	65
Coding	Source	P	ω^2
Cov	WTD	< 0.0001	64.46%
Cov	Pg	< 0.0001	20.55%
FF	Collar	0.001	2.21%
FF	Time	< 0.0001	6.01%
R-Sq	90.69%		

R_{eco}

July	Dark	n	31
Coding	Source	P	ω^2
Cov	WTD	< 0.0001	51.75%
FF	Collar	< 0.0001	43.50%
R-Sq	90.69%		

R_{eco}

August	Light	n	47
Coding	Source	P	ω^2
Cov	Pg	< 0.0001	67.80%
FF	Time	0.019	8.86%
R-Sq	83.53%		

R_{eco}

August	Dark	n	31
Coding	Source	P	ω^2
FF	Collar	< 0.0001	70.86%
R-Sq	70.86%		

R_{eco}

September	Light	n	47
Coding	Source	P	ω^2
Cov	WTD	0.017	41.81%
Cov	Pg	0.002	38.76%
FF	Collar	0.026	2.42%
R-Sq	85.10%		

R_{eco}

September	Dark	n	
Coding	Source	P	ω^2
no data			
R-Sq			

Coding: Cov = covariate, FF = fixed factor

***Table 5.3.3.5* –** NEE ANCOVA results for light hours by month (for dark hours see R_{eco} results)

	NEE		
June	Light	n	71
Coding	Source	P	ω^2
Cov	Pg	0.034	15.61%
FF	Collar	< 0.0001	28.82%
R-Sq	49.51%		
	NEE		
July	Light	n	65
Coding	Source	P	ω^2
Cov	WTD	< 0.0001	0.20%
Cov	Pg	< 0.0001	71.62%
FF	Collar	0.001	4.23%
FF	Time	< 0.0001	11.44%
R-Sq	91.27%		
	NEE		
August	Light	n	77
Coding	Source	P	ω^2
FF	Collar	0.005	11.16859
FF	Time	0.001	23.97913
R-Sq	49.89%		
	NEE		
September	Light	n	64
Coding	Source	P	ω^2
Cov	WTD	0.04	0.34232
Cov	Pg	0.013	17.07124
FF	Time	0.024	15.68323
R-Sq	47.70%		

Coding: Cov = covariate, FF = fixed factor

5.3.4 – Cross Correlation Analysis

An important part of this chapter was to test for the presence of a lag between photosynthetic uptake of CO_2 and subsequent enhancement of respiration. Cross correlation analysis was used to test for this effect. Figure 5.3.4.1 summarises the results of this analysis. It can be seen that there are large differences between collars, which appear to vary month by month. In general the best fit between R_{eco} and P_g is found with a lag of zero hours. However, in June in both the raw and residual dataset it appears that, on average, a significant lag of about 3 hours (for some collars at least) appears to be present. However, this pattern of results does not recur in the subsequent months, with the mean R^2 only being significant at a lag of zero hours. The number of data missing (due to machine error and data quality control procedures) and hence estimated by linear interpolation in this analysis is given in table 5.3.4.1. Note a large

Table 5.3.4.1 – Data estimated by linear interpolat5ion

	Potential Data	Data Used	% Interpolated
R_{eco}	396	300	24.24
P_g	240	194	19.17

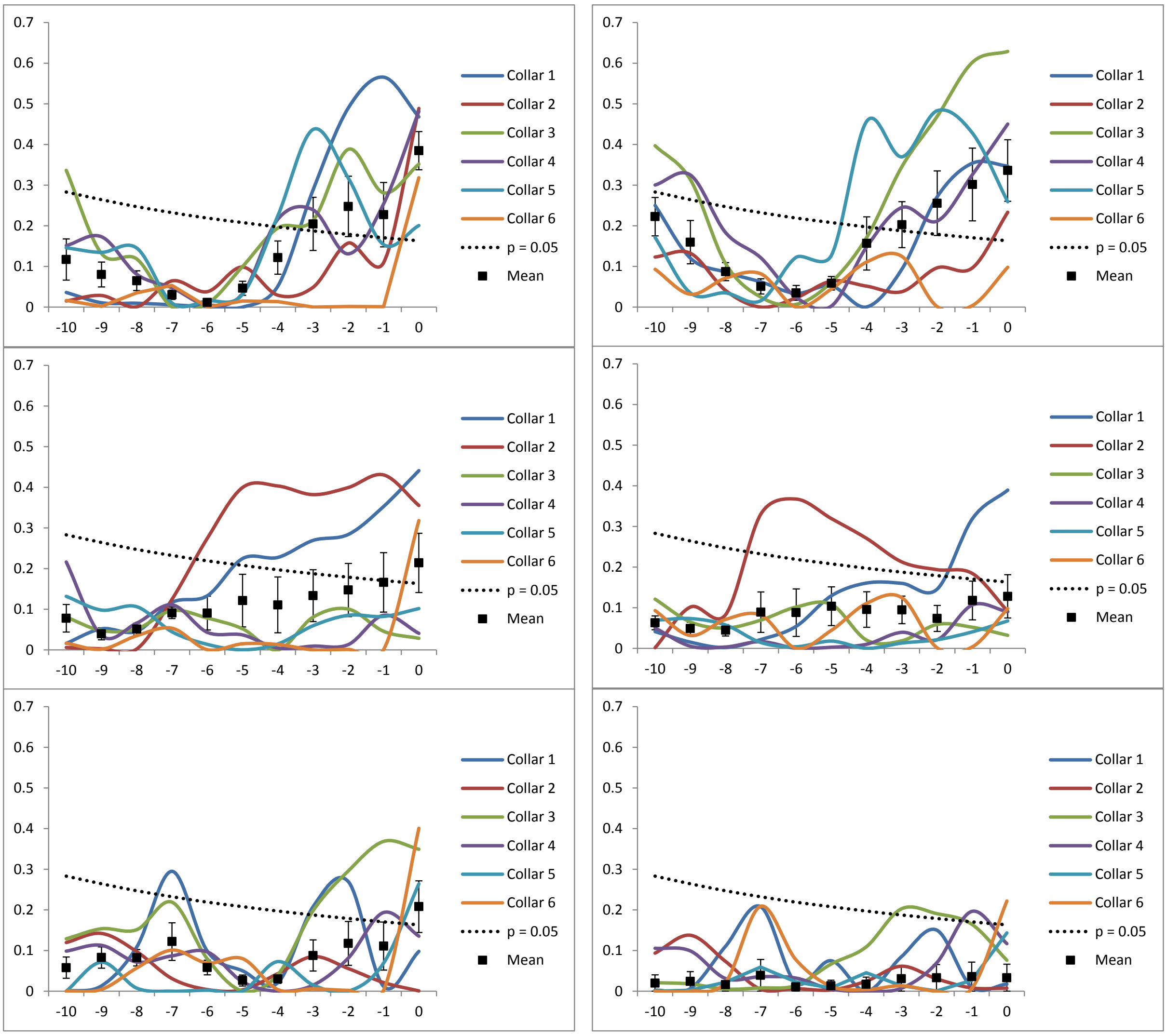


Figure 5.3.4.1 – Plots summarising the results of the cross correlation analyses. The left column shows the ‘raw’ dataset results and the right column shows the ‘residual’ dataset results. The rows from top to bottom show the monthly results for June, July and August. On each panel the y-axis represents the R^2 of the collection between R_{eco} and P_g and the x-axis represents the number of hours that P_g has been lagged relative to R_{eco}. The error bars represent one standard error of the mean. The dotted line represents the point at which the critical t-statistic of the correlation between R_{eco} and P_g is significant to at least of level of 95%.

5.3.5 – Modelling and Estimating Daily Ecosystem Respiration

The total amount of CO_2 respired at the site during each full diurnal cycle sampled was 10.97 ±0.75, 7.11 + 0.61 and 3.01 ± 0.27 g CO_2 m^{-2} d^{-1} for June, July and August respectively. Estimated values for the same diurnal cycles produced using Lloyd and Taylor (1994)'s model and the light/dark MLR models from this study are given in table 5.3.5.1.

It can be seen from this table and the comparison chart (figure 5.3.4.1) that the modelled values of daily R_{eco} in June and July underestimated the actual value of R_{eco}. For the Lloyd and Taylor (1994) model the percentage underestimation between modelled and observed was 20.69 and 19.97% in June and July respectively with a 33.12% overestimation in August. For the light/dark MLR models produced in section 5.3.3, the percentage magnitude of underestimation was 29.84, 21.62 and 1.36% for June, July and August respectively. It can be seen from figure 5.3.5.2 that the degree of correspondence between model and observed data is much greater for the light/dark MLR models produced in this chapter than for the Lloyd and Taylor (1994) model. The R^2 of the models versus observed data was 9.82 and 52.19% for Lloyd and Taylor (1994) and MLR respectively. Moreover, figure 5.3.5.2 shows that in general the fit of the MLR models produced in this study are biased mainly by large underestimations of a relatively small number of outlying data points with the bulk of the data lying much closer to the 1:1 line than is the case for the Lloyd and Taylor (1994) model.

Table 5.3.5.1 – Total daily R_{eco} model output comparison

	R_{eco} (g CO_2 m^{-2} d^{-1})			
	Lloyd and Taylor, 1994	± Error	**This Study**	± Error
June	8.70	0.09	8.37	0.54
July	5.69	0.04	5.89	0.44
August	4.00	0.04	2.95	0.22

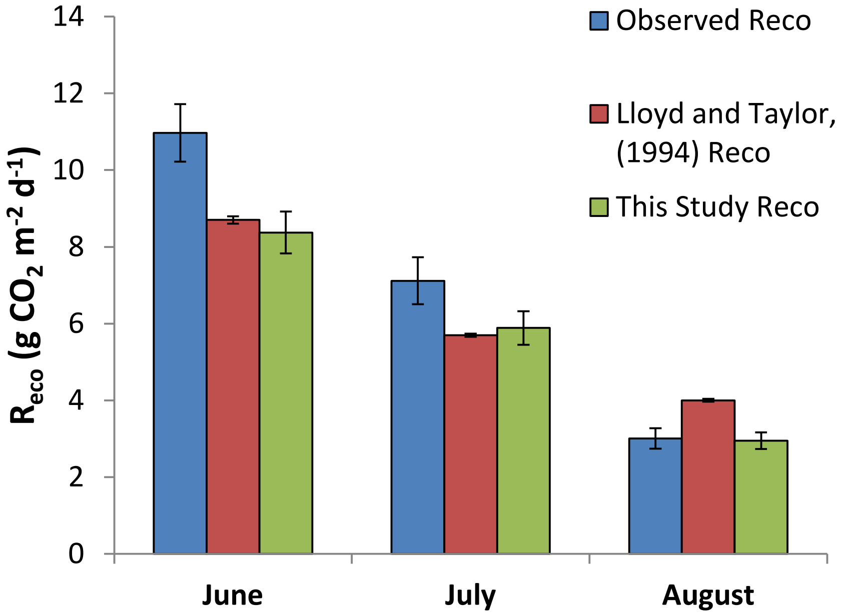


***Figure 5.3.5.1* –** Comparison of total R_{eco} over each diurnal cycle sampled. The blue dataset shows the observed values measured, the red dataset shows the modelled values using the Lloyd and Taylor (1994) model and the green dataset shows the modelled values using the light/dark MLR models produced in this study.

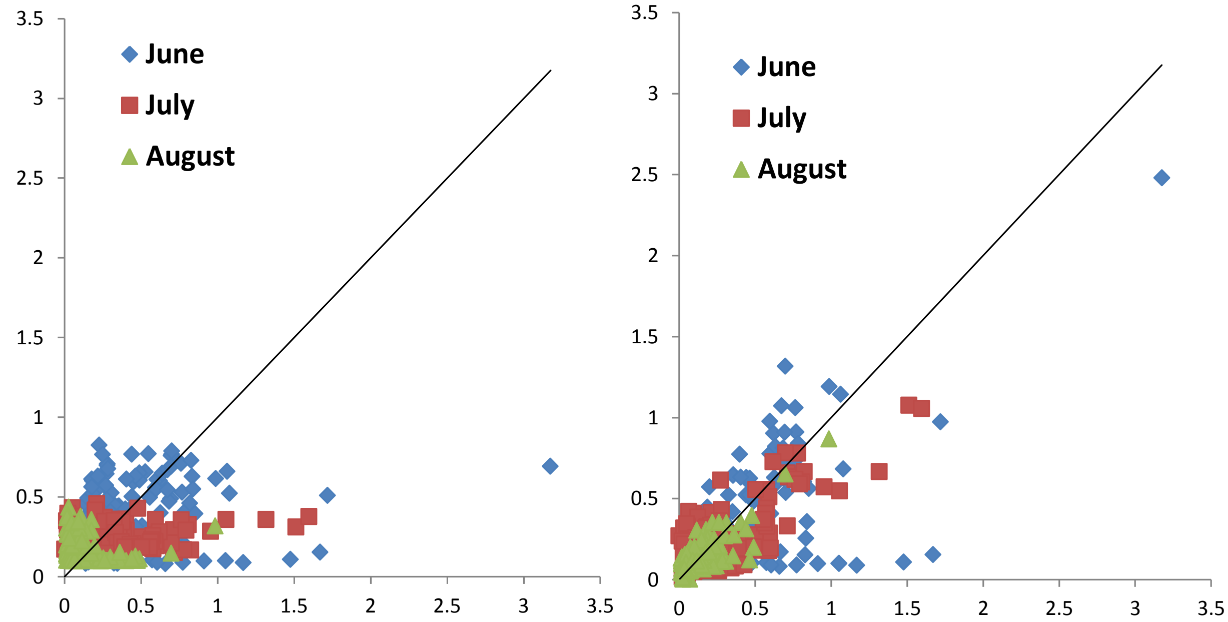


Figure 5.3.5.2 **–** Comparison of the performance of the Lloyd and Taylor (1994) (left panel, y-axis) and MLR (right panel, y-axis) R_{eco} models to the observed data (x-axis). All units are in g CO_2 m^{-2} h^{-1}. The blue lines represent the 1;1 (i.e. [perfect fit) lines.

Plots of the fits (figure 5.3.5.3) and residuals (figure 5.3.5.4) of the daylight hours R_{eco} MLR models (table 5.3.3.3) for June showed that the model residuals (as a % of the observed R_{eco}) are greatest during the hours of darkness. The model is seen to under-predict observed night time R_{eco}. The addition of a lagged P_g term into the MLR model showed a statistically significant relationship between R_{eco} and P_g lagged by -3 hours. The magnitude of the lag used in the MLR model was determined by an iterative process until a best fit model was determined. This method differs from the cross-correlation analysis in that it also considers the other significant variables in the MLR model at the same time as the R_{eco} – P_g relationship rather than simply looking at the bivariate relationship between R_{eco} and P_g. This relationship improved model R^2 for the whole diurnal cycle from 40.1% to 44.4%. Examination of the lagged model fits and residuals (also figures 5.3.5.3 and 5.3.5.4) shows that the night time underestimation is reduced somewhat compared to the original model. However, this improvement in night time model fit is at the expense of over estimating daylight hours R_{eco}. Examination of the original and lagged models for July and August (figures 5.3.5.5 to 5.3.5.9) indicate that lagged P_g terms do improve overall model fit R^2 from 81.5% to 85.8% in July (-7 hour lag) and 58.9% to 64.2% in August (-3 hour lag). However, inspection of the residual and fits suggest that night time was not greatly underestimated during these cycles and as such model fits during the hours of darkness were not as obviously improved as was the case in June The identification of a significant lag using the MLR method may imply that in July and August the lagged effect of P_g on R_{eco} is more subtle than in June. Thus, removal of variance due to more important effects in the MLR approach allowed for more subtle this effect to become apparent. This would explain why there were no significant lags identified in the bivariate (i.e. not MLR) cross-correlation analysis.

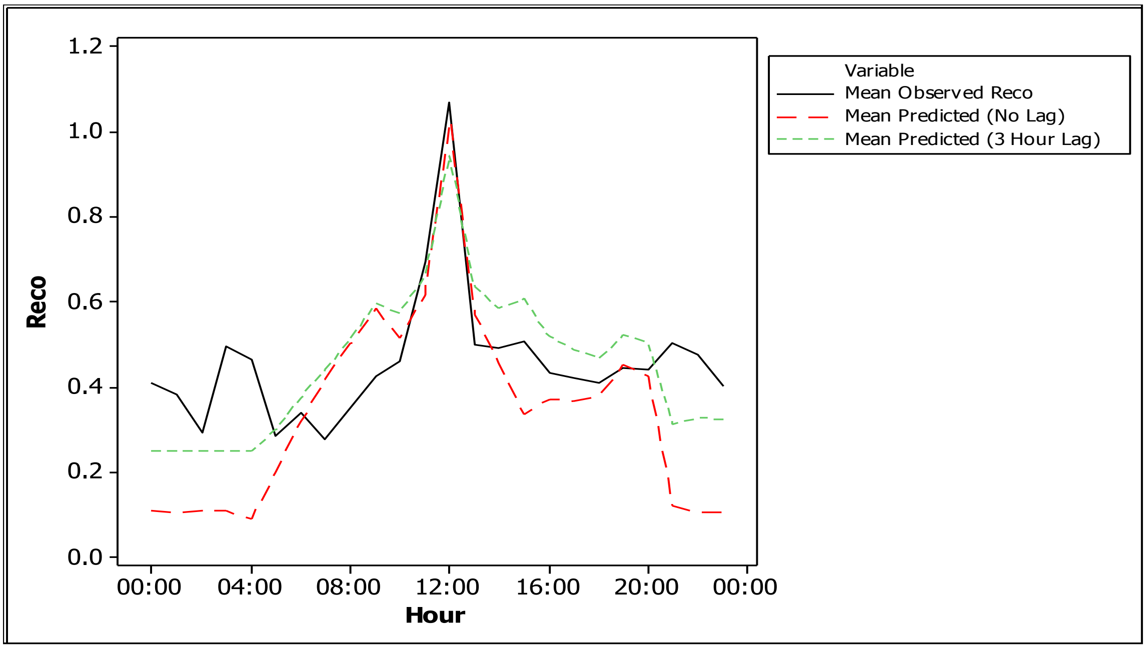


Figure 5.3.5.3 **–** Plot of the mean temporal pattern of R_{eco} (observed and modelled) during the June cycle. The units of Reco are in g CO_2 m^{-2} h^{-1}.

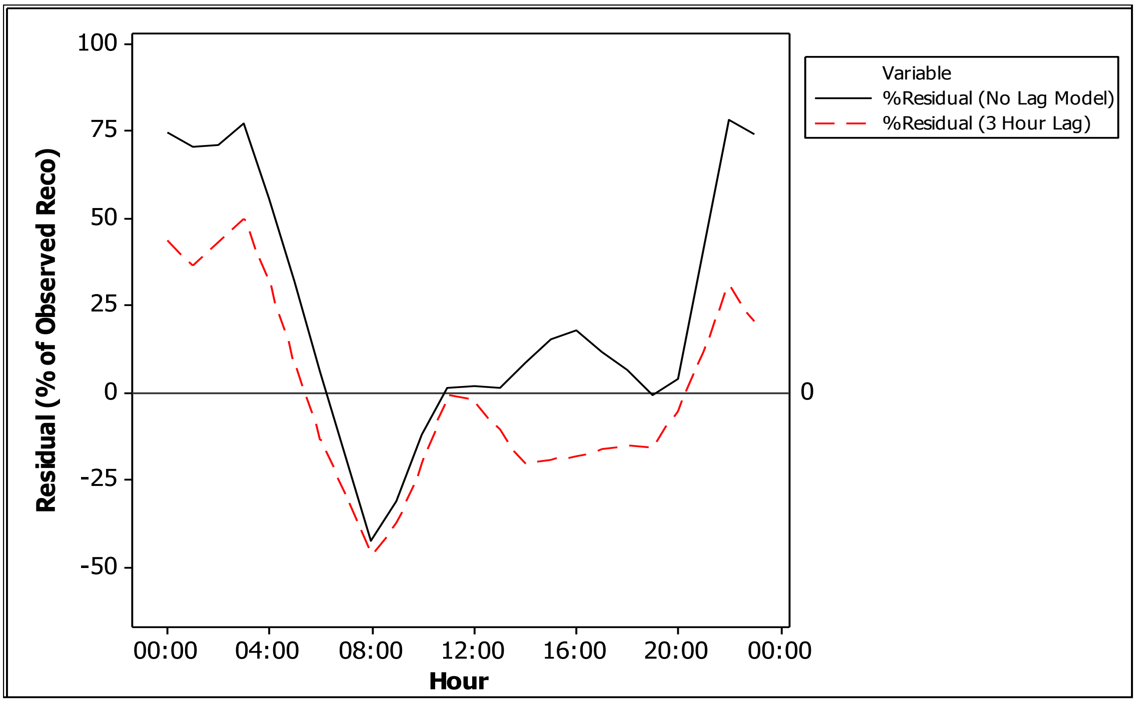


Figure 5.3.5.4 **–** Plot of the residual R_{eco} variation, expressed as a % of the observed Reco after MLR modelling (with and without lags) during the June cycle.

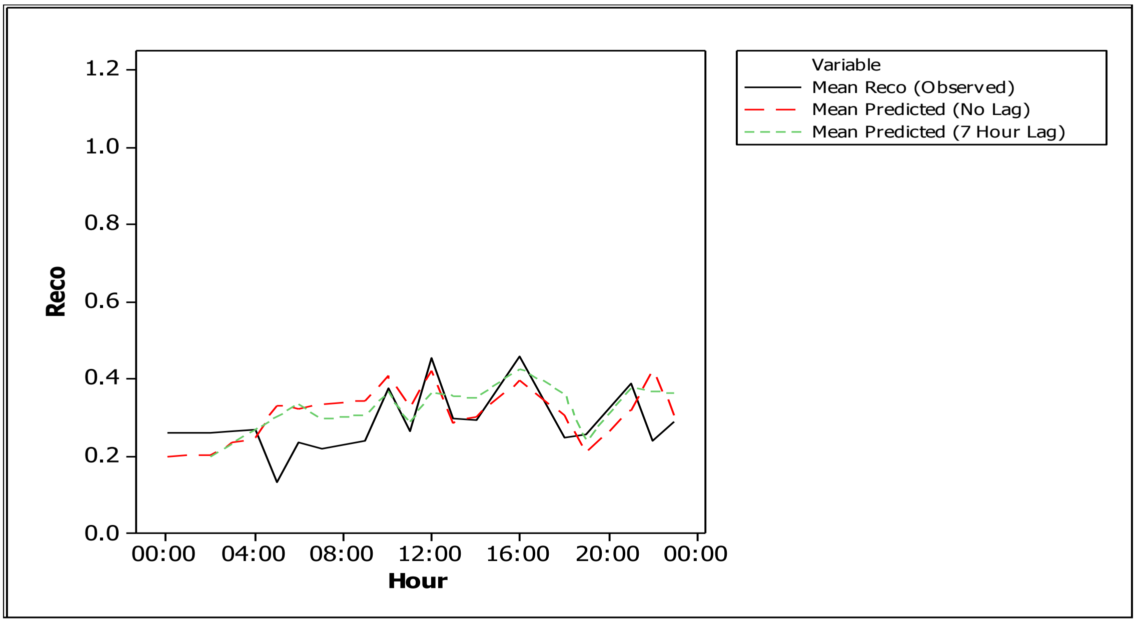


Figure 5.3.5.5 **–** Plot of the mean temporal pattern of Reco (observed and modelled) during the July cycle. The units of R_{eco} are in g CO_2 m^{-2} h^{-1}.

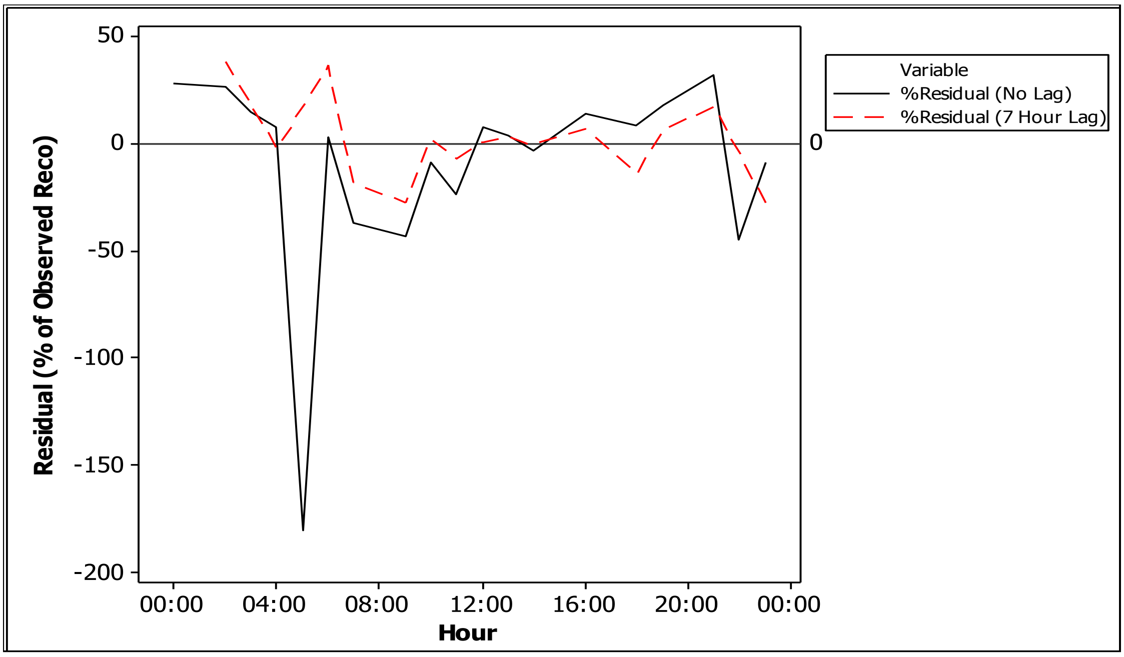


Figure 5.3.5.6 **–** Plot of the residual Reco variation, expressed as a % of the observed Reco after MLR modelling (with and without lags) during the July cycle.

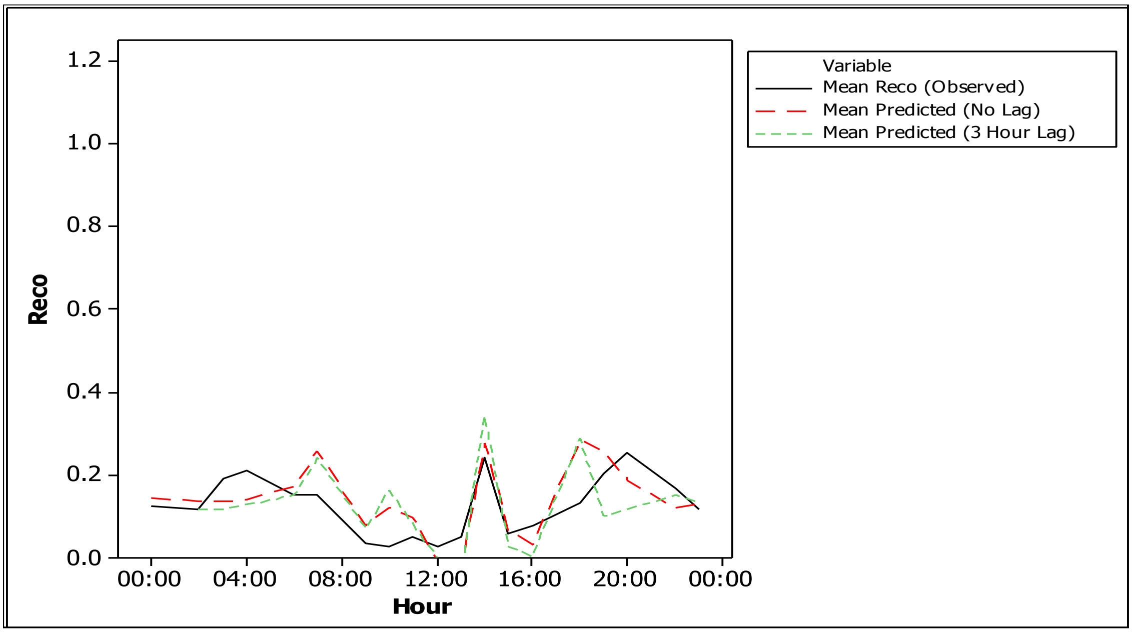


***Figure 5.3.5.7* –** Plot of the mean temporal pattern of R_{eco} (observed and modelled) during the August cycle. The units of Reco are in g CO_2 m^{-2} h^{-1}.

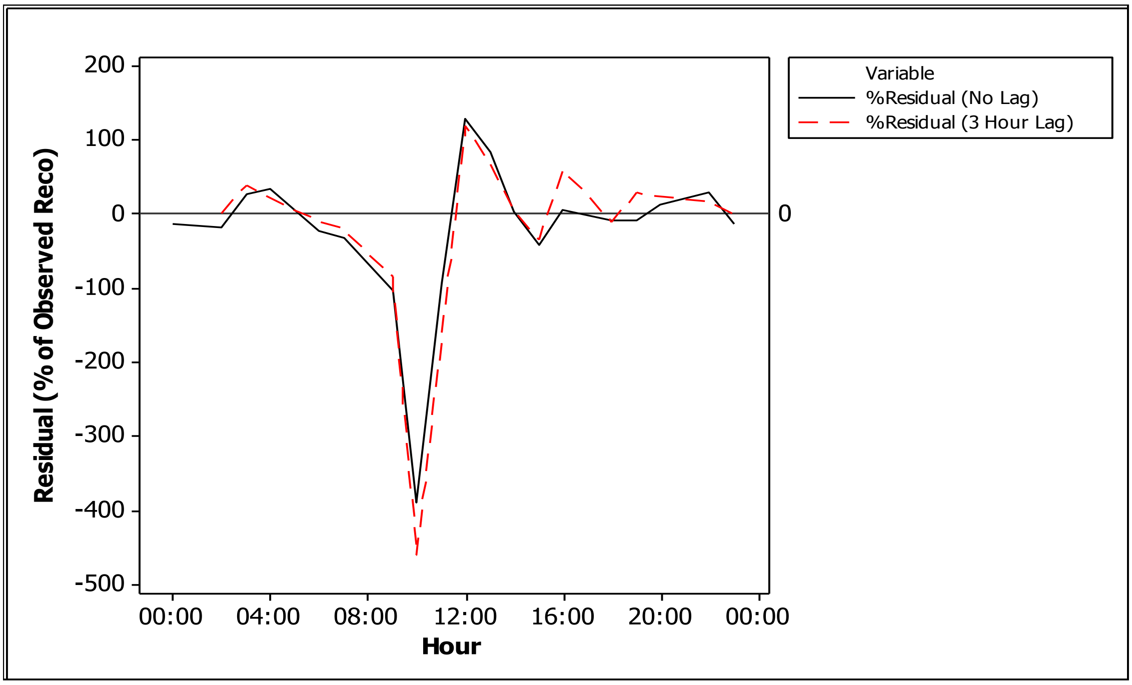


***Figure 5.3.5.9* –** Plot of the residual R_{eco} variation, expressed as a % of the observed Reco after MLR modelling (with and without lags) during the August cycle.

5.4 – Discussion

5.4.1 – Cross-Correlation Analysis of Diurnal CO_2 Flux

The results of the cross-correlation analysis implied that, in June, a lag of about three hours was present between P_g and R_{eco}, in addition to the instantaneous (i.e. zero lag) relationship. The magnitude of the average effect appeared to decrease with time in a roughly linear fashion, dropping below the significance threshold after three hours in both the raw and residual datasets. The existence of such a lag between R_{eco} and P_g is supported by Kuzyakov (2002) who suggests that 50-60% of soil respiration (i.e. not considering above ground vegetative effects) is made up from microbial degradation of “root exudates and other rhizodeposits”, with the remainder being direct root respiration/mychorrizal respiration. The substrates to fuel these fluxes will take time to reach the rhizosphere, thus explaining why a lag would be observed. Delayed transport (lag of a few minutes in vascular plants, Dilkes et al., 2004), exudation (lag of up to four hours under *Sphagnum spp.*, Fenner et al., 2004) and soil zone mineralisation to CO_2 (lag of about one day in forested ecosystems, Panikov et al., 2007) of recently sequestered carbon have been observed elsewhere. As such, it is at least feasible to argue that the lag observed in the June data represents a real process of below ground allocation of recently derived photosynthates.

This pattern is not repeated in any of the July or August datasets, raw or residual. This lack of reproducibility may cast doubt on the validity of the lagged relationship observed. However it is important to bear in mind that this was a field experiment and thus a large number of potentially confounding factors were uncontrolled. Most important, in the context of this discussion, is the fact that the meteorological conditions varied widely between months. The cycle sampled in June was much hotter and sunnier with rainfall being completely absent than the other months. Indeed, there was rainfall during at least five of the hours in the cycles sampled in July, August and September. Rainfall can instantaneously supress the efflux of CO_2 from soils (e.g. Zhao et al., 2006) by blocking pores, diluting rhizospheric substrates in solution, temporarily inverting the soil-atmosphere pressure gradient and reducing the diffusivity of CO_2 (as CO_2 diffuses 10,000 times more slowly in water than air, e.g. Evans and von Caemmerer, 1996). Thus the effects of a lagged below ground enhancement in CO_2 flux may have been obscured by suppression of soil respiration by rainfall in these months. Furthermore, the reduced levels of PAR due to raincloud cover may have been sub-optimal for photosynthesis (e.g. Limbach et al., 1982; Robertson and Woolhouse, 1984) thus reducing the amount of photosynthate available for below-ground transfer. As such, while the lag observed in June was not repeated in subsequent months, it may be reasonable to suppose that confounding effects like rainfall and cloud cover could account for this discrepancy. More evidence however, either laboratory or field based, is required before this issue can be definitively settled.

Nonetheless, weight was added to existence of a lagged relationship between R_{eco} and P_g by the results of MLR analysis which revealed that adding a lagged P_g term improved MLR model fits in June, July and August. Examination of the temporal pattern of the model fits and residuals showed, in June, that night time R_{eco} was better explained with lower underestimation. The MLR model fits and residuals in July and August however did not as clearly show model fit improvement during the hours of darkness. This would tend to agree with the results of the cross-correlation analysis which did not demonstrate significant lags in the bivariate relationship between R_{eco} and P_g.

5.4.2 – Controls on Daily CO_2 Flux

Analysis of covariance revealed, for the 'all months' and individual months datasets, that P_g was, generally, the most important predictor of R_{eco}. This result is to be expected, and agrees with results found in the monthly datasets in this thesis and in studies of other peatlands (e.g. Larsen et al., 2007) and other ecosystems (e.g. Hogberg et al., 2001; Tang et al., 2005). The next most important predictor of R_{eco} in the 'all months' dataset was the factor 'month', which explained 12.23% of dataset variation. June, had the greatest average CO_2 fluxes, with diurnal fluxes generally decreasing on a monthly basis. This emphasises the importance of seasonality in the context of CO_2 flux.

Also significant in 'all months' were 'time' and 'collar'. When *post hoc* testing was carried out on the 'collar' factor, the results showed that the only difference found was between collars three and five and collar six. The plot of the night-time R_{eco} data for June (figure 5.3.3.7) is a good demonstration of the differences in flux magnitudes between the collars in all months, with collar 6 being greater in magnitude than the rest. This pattern of results suggests that collar six is an outlier with respect to some of the rest; however, this will have been taken into account by the ANCOVA. Visual inspection (not systematically recorded) of the vegetation densities in the collars suggested that variations in vegetation density may explain the differences noted. This variation is because collars three and five were almost bare of vegetation while collar six had a much denser canopy during all study months.

Post hoc Tukey testing revealed that for 'all months' (and some individual months) R_{eco} datasets the factor 'time' had significant differences hours in the late morning/early afternoon (09:00-13:00) with 21:00. An explanation for this pattern is that, when considered across all cycles sampled, there was a distinct pulse of rainfall occurring between the hours of 18:00-20:00, mainly (generated in June), which resulted in the pulse of R_{eco} seen at 21:00 (figure 5.4.2.1). This pattern is also appears to be present in the individual monthly datasets on occasions when it rained (see figure 5.4.2.2). It can be seen that, in July and August particularly, rainfall apparently to suppresses R_{eco}, with spikes and higher rates of R_{eco} occurring after periods of rainfall, this has also been observed elsewhere (e.g. Jensen et al., 1996; McNeil and Waddington, 2003; Zhao et al., 2006). The suppression of R_{eco} by rainfall in July appears to have allowed a NEE to become less positive (i.e. a smaller net source), when compared to June, despite the fact that PAR and air temperature (two variables which should reduce productivity) were lower in July than June. Another contributing factor to this is that the soil temperature at 5 cm depth increased between June and July and this was found to be a significant predictor of NEE in daylight hours in July. This increase may have offset the decrease in air temperature.

ANCOVA revealed that NEE is also controlled by the same predictors and factors as R_{eco}, but with the addition of water table depth and air temperature. Moreover, the relative importance of the factors and covariates in the model differs with respect to R_{eco}. For instance, instead of P_g, 'collar' was found to be the most important factor, accounting for 21.19% of dataset variation. Second most important was water table depth (11.5%) followed by P_g (8.56%). Despite this difference in the 'all months' analysis, NEE appeared to share many of the same controlling factors and covariates as R_{eco} on a month to month basis. This agrees with the results of chapters 3 and 4 and is explained by the fact that R_{eco} is a constituent flux of NEE (i.e. the would be expected to share some controls).

The plot of daytime and night time mean R_{eco} across the months showed no differences (figure 5.3.3.1) which suggests that daytime variability in R_{eco} was not great enough to make the average daylight hours mean R_{eco} discernibly greater than night time fluxes. Indeed, even in June, when it did not rain, only the hours of 11:00-12:00 were much greater than some of the rest. This implies that average daytime fluxes of CO_2 can be used to estimate overall daily (i.e. full diurnal cycle) fluxes of CO_2. However, this specific result should only be extrapolated to areas dominated by *Eriophorum* spp.

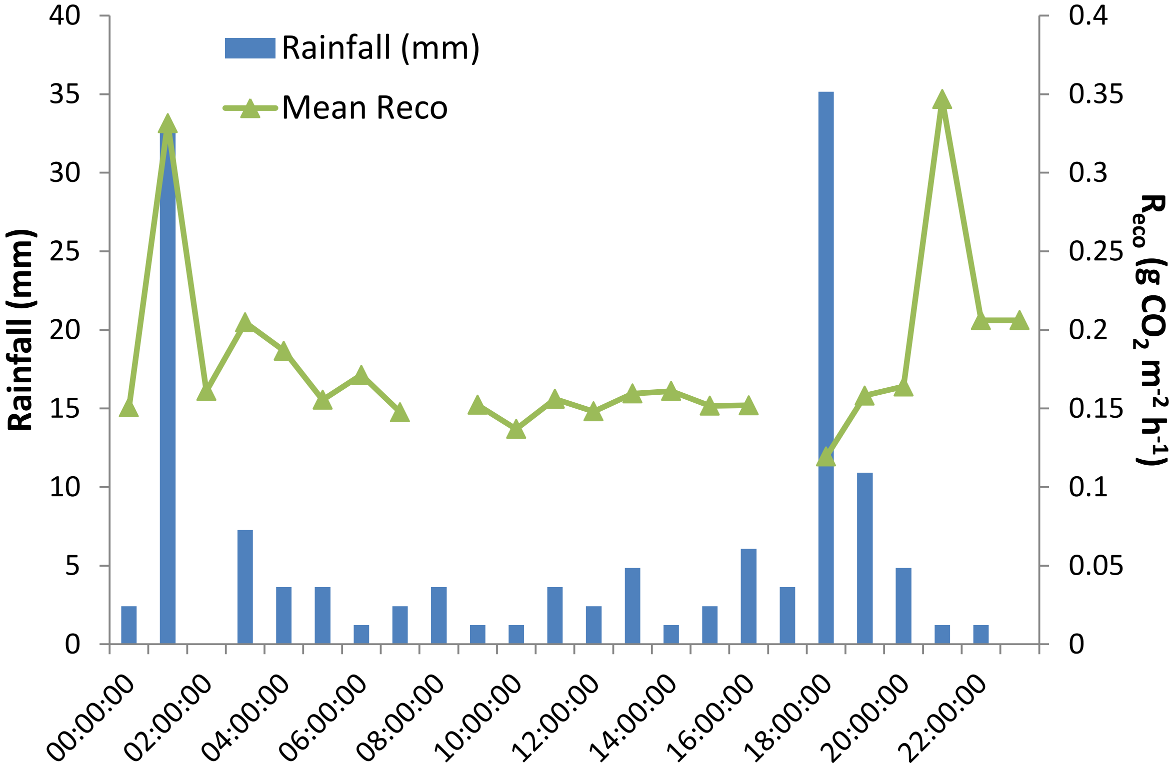


***Figure 5.4.2.1* –** The total amount of rainfall in each hour (summed for every diurnal cycle sampled) alongside the mean R_{eco} for each hour (averaged for every diurnal cycle sampled)

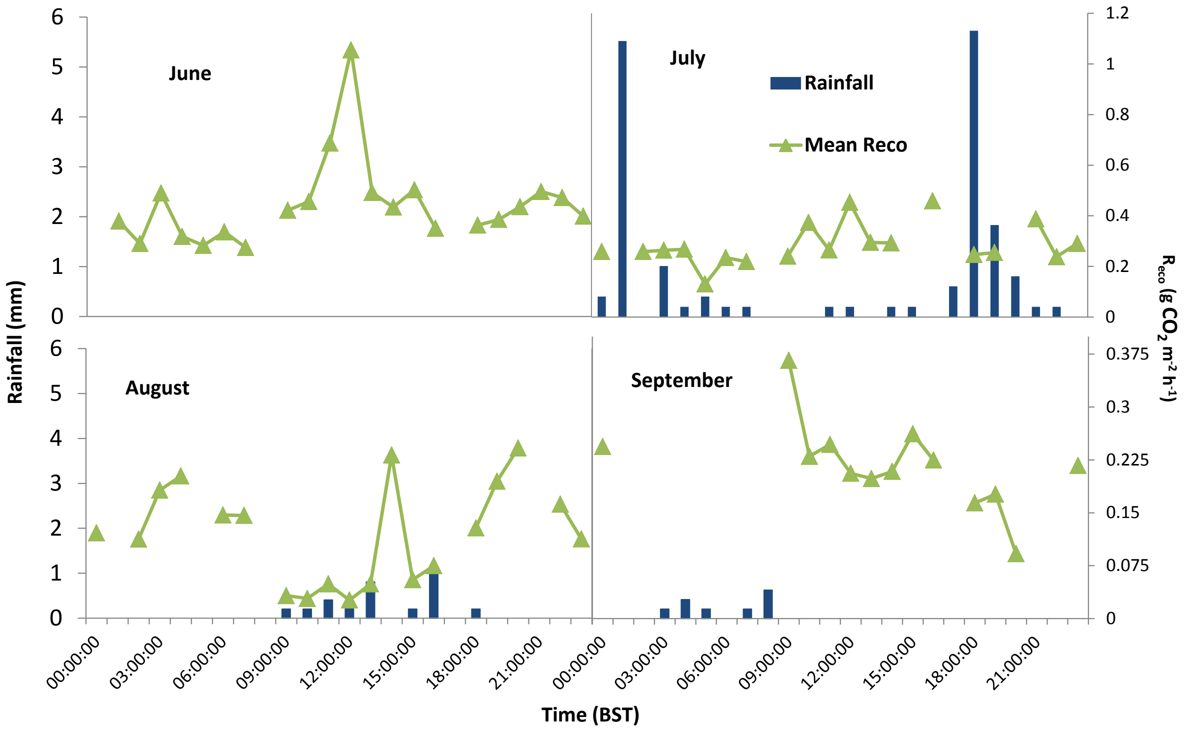


Figure 5.4.2.2 – Plots of mean hourly R_{eco} and rainfall versus time, split into separate panels by month

In order to investigate how the controls on CO_2 flux differ between day and night the datasets were split into the hours of light and dark (as defined by PAR) and modelled with MLR and ANCOVA. The results of these analyses for both R_{eco} and NEE showed a similar pattern of results. They showed that during daylight and night time hours the predictors of both fluxes were similar. This is not unexpected as NEE is simply the balance between P_g and R_{eco} and is thus likely to share the same controls as both. The interesting observation about these results is that for June when no rain fell, air temperature was the only (weak) predictor of R_{eco}/NEE identified at night. In July and August when it rained, water table depth variation was identified as the only significant predictor of both fluxes and in September there was no night time data. The fact that air temperature was only weakly related to R_{eco} at night on the June cycle reflects the fact that night-time environmental conditions were stable (in comparison to daylight hours) and as such the rate of R_{eco} was also relatively stable.

5.4.3 – Comparison to Other Studies

It is important to consider how the results of this chapter compare to those of other studies from other peatland and similar ecosystems. The average hourly fluxes (across for each monthly diurnal cycle) from this study were compared to those reported in a number of other studies. For R_{eco} the comparison chart (figure 5.4.3.1) clearly shows that the results from this study are generally lower than those reported in other ecosystems, with the difference between this study's results and the average of all the studies considered being -0.224, -0.412, -0.522, -0.206 g CO_2 m^{-2} h^{-1} for June to September respectively. It should be noted that the September value for this chapter was based on an incomplete dataset (as mentioned earlier) and as such may be greater than in reality due to many of the hours of darkness being missing.

Comparison of R_{eco} between the other ombrotrophic bogs (i.e. Lafleur et al., 2003, 2005; Oberbauer et al., 1996) shows that this study measured similar magnitude fluxes; however, the seasonal pattern was different. In this study R_{eco} was highest in June, decreasing to August and then increasing again in September. The other ombrotrophic bog studies instead show an increase from June to August with a decrease to September. This difference can be explained by two limitations; firstly, that the monthly averages in this study are based on one single diurnal cycle per month rather than a multiply-sampled monthly dataset as in the literature studies and, secondly that there will be inter-annual and latitudinal differences between all of the studies cited. In the case of this study, rainfall during the July, August and September sampling runs was shown to have suppressed the fluxes, as seen in Zhao et al. (2006), which may further explain the different seasonal pattern of results observed. These limitations should be noted when considering the comparisons being made between this study and others. However, despite these limitations the overall flux magnitudes from all of the ombrotrophic bogs are comparable.

The studies with the greatest differences in R_{eco} fluxes (i.e. Otieno et al., 2009) to this study come from other ecosystems. In the case of Otieno et al. (2009) this may be explained by the fact that it was based on a fen-type peatland in Germany, that was less acidic and more sulphur and iron-rich than is the case in a bog. These conditions will have enhanced the rate of carbon turnover, as observed along a fen-bog gradient in Leppälä et al. (2008) relative to the rate observed in this and other bog studies. Upland grasslands and tundra (e.g. Oberbauer et al., 1996; Risch and Frank et al., 2010; Wu Hu et al., 2008; Zhao et al., 2006) had generally greater magnitude R_{eco} fluxes than the bog studies. This demonstrates the fact that bogs have relatively low carbon turnover rates (e.g. Bubier et al., 1998; Leppälä et al., 2008) and thus make good long-term sinks of carbon (i.e. Gorham, 1991).

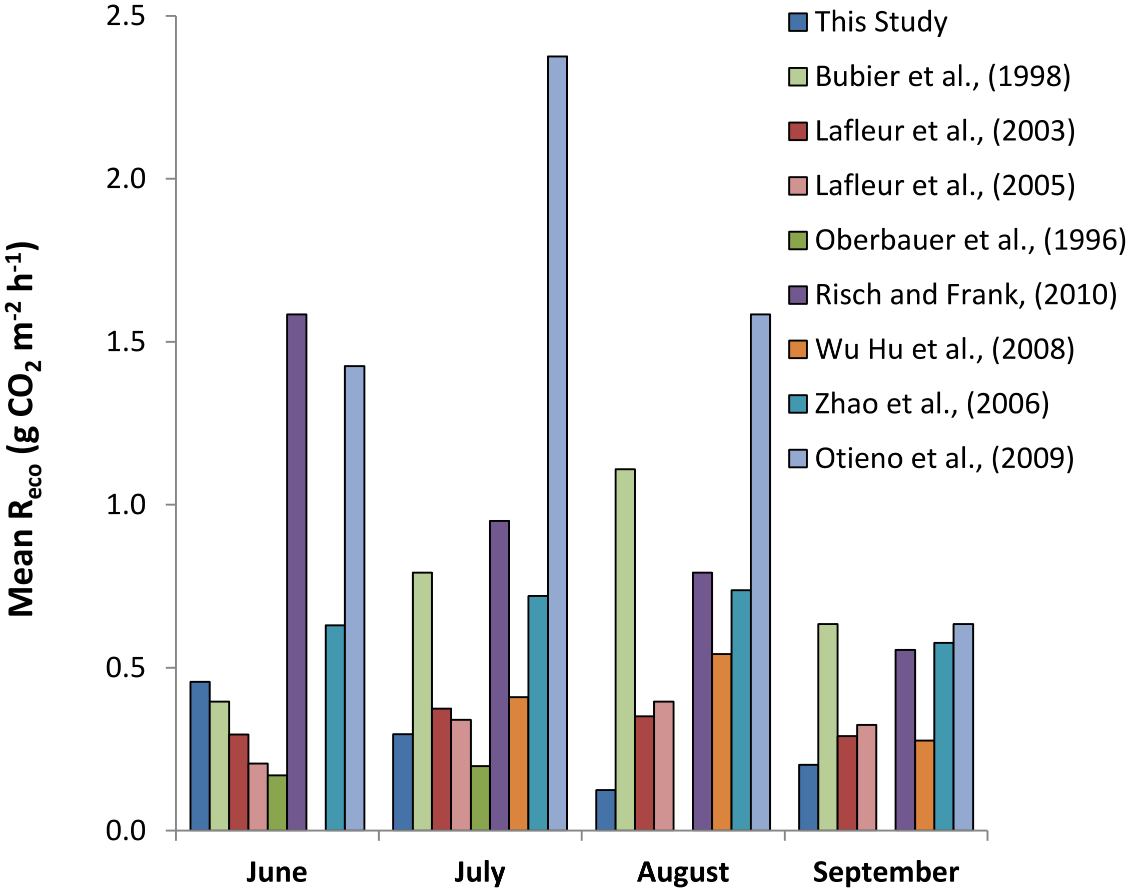


Figure 5.4.3.1 – Comparison between average daily R_{eco} values from a number of studies of similar (high latitude) ecosystems. Ecosystems studied include: Boreal Mire Complex (Fen-Bog) (Bubier et al., 1998), Temperate Bog (Lafleur et al., 2003,2005), Upland Tundra (Oberbauer et al., 1996), Mountain Fen (Otieno et al., 2009) and Upland and Temperate Grassland (Risch and Frank, 2010; Wu Hu et al., 2008; Zhao et al., 2006).

Fewer studies were found reporting daily NEE rates; however, the pattern of results (figure 5.4.3.2) is interesting. For all months of this study there was a, relatively small, net daily source of CO_2 recorded, taking into account night-time respiration. The size of this source was greatest in June, decreasing to July and remaining relatively stable for the remaining months. This was not the case for the other studies considered. In the same manner as R_{eco} the study with the greatest similarity in flux magnitude and direction to this came from a bog-type ecosystem (Nieveen et al., 1998), the seasonal pattern, however, was different with NEE negative in June to August but becoming positive, like this study, in September. The next closest study was the temperate grassland study of Risch and Frank, (2010), which was a source in June, but a sink for the remaining months, peaking in August. The fen-bog complex (Bubier et al., 1998) and mountain fen (Otieno et al., 2009) studies were most different to this being relatively large net sinks of CO_2 during all months analysed. This likely reflects the richer nutrient conditions in fens relative to bogs.

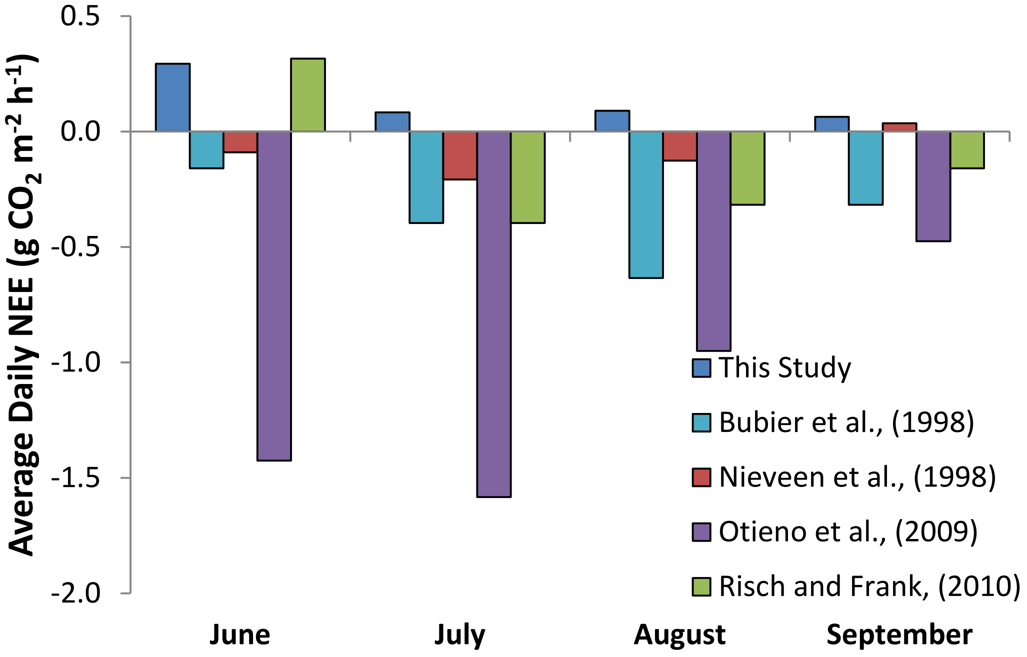


Figure 5.4.3.2 **–** Comparison between average daily NEE values from a number of studies of similar (high latitude) ecosystems. Ecosystems studied include: Boreal Mire Complex (Fen-Bog) (Bubier et al., 1998), Mountain Fen (Otieno et al., 2009), Raised Bog (Nieveen et al., 1998) and Temperate Grassland (Risch and Frank, 2010).

When modelling R_{eco} it was found that the monthly day/night MLR models produced in this chapter fit the data better (R^2 = 52.19% versus 9.82%) than a simple exponential temperature dependent model (Lloyd and Taylor, 1994). The largest model residuals were observed in June. Despite this both models underestimated R_{eco} in June and July. In August, however, the MLR models became very close (within errors) of the observed data. Indeed, figure 5.3.5.2 shows that the MLR models produced in this chapter generally fit the data well. The exceptions to this are underestimated outlying data points on the warmer months. This implies that the MLR models fit well in 'average' conditions but do not fit well during infrequently high flux periods (i.e. midday on the warmest/driest month). Overall, these results confirm that temperature alone is not the only important predictor of R_{eco} on diurnal time-scales, they also agree with modelling results obtained in earlier chapters of this thesis on annual and monthly time scales.

5.5 – Conclusions

This chapter had two research aims, with the objective of characterising diurnal CO_2 fluxes on upland blanket peat. Firstly, this chapter aimed to determine whether daytime and night-time rates of R_{eco} were equivalent and whether they are controlled by the same processes. Examination of the data gathered showed the night time and daytime R_{eco} fluxes were within errors of each other on all cycles where enough data had been collected to make a comparison possible. However, in order to be able to use day time data to estimate night time R_{eco} CO_2 flux would have to either be sampled during the early morning and late afternoon/evening to avoid biases imposed by the statistically significant enhancement of R_{eco} observed in the middle of the day. Moreover, subsequent MLR and ANCOVA of the data indicated that, in general, different processes control R_{eco} flux during daylight compared with the hours of darkness. This change in controls relates principally to the relatively stable night-time environmental conditions in comparison to those during daylight hours for the cycles sampled.

Predictors identified in the daytime MLR models were variable between cycles (with the exception of P_g) and were thought to relate to the meteorological conditions during the sampling hours. As such, a model based on daytime data alone is unlikely to fit night time data well. However, the addition of a lagged P_g term was found to improve the fit of all night-time MLR models and in

June, when rainfall did not occur, it noticeably improved the fit of the model in the hours of darkness. The number environmental of predictors (as identified by ANCOVA and MLR) of night time CO_2 flux was generally less than in the day-time. This finding seemed to be explained by the relatively stable night-time environmental conditions, on the cycles sampled, when compared to day-time conditions.

The second primary aim of this chapter was to identify whether any lag exists in the widely observed relationship between R_{eco} and P_g. Cross correlation analysis gave support to this hypothetical lag in June, where an apparent lag of three hours was identified. This lag, moreover, was present in both the raw and residual datasets. The lag, however, was not observed in any of the subsequent cycles sampled. A plausible explanation for this discrepancy was that rainfall in the months of July and August obscured the lagged relationship. As such, more evidence is required in order to properly characterise the lag effect and its relation to the other environmental drivers.

Manipulation Trials

6.1 – Introduction

This thesis has examined a number of physical, biological and environmental factors that exert control on the carbon cycle of upland blanket peat. Very often structural, linear empirical (or log-linear) regression models of R_{eco} have been found to fit the datasets better than process-based models (e.g. chapter 4). These MLR models often contain differing combinations of terms (e.g. photosynthesis, air temperature etc.) specific to the site/factor/vegetation type being modelled. Despite having different combinations of terms, all of the models produced follow the general form of the MLR equation given in chapter 2.

The MLR models are described as 'structural' because the model is composed of elements that are themselves thought to be physically-interpretable (i.e. representative of physical, chemical or biological processes in the system). In addition, the model terms can be split into two categories: terms that are thought to describe process drivers (e.g. air temperature), and terms that are thought to describe process modifiers (e.g. water table depth). As the model terms are thought to be physically interpretable, it follows that hypotheses can be established to test whether these process related terms behave as expected when the system is experimentally manipulated.

A feature of almost all of the models, where P_g was included, is that they find a significant positive relationship between P_g and R_{eco}. This relationship is recognised elsewhere (e.g. Hogberg et al., 2001) and has been modelled in peatlands (e.g. Larsen et al., 2007). The relationship is thought to be due to enhancement of ecosystem respiration of recent photosynthate both above-ground and in the soil zone (e.g. Bond-Lamberty et al., 2004; Ryan et al., 2004). However, evidence from chapter 5 implies that this process could be lagged to some extent (~ 3 hours). The fact that the R_{eco}-P_g relationship is frequently identified and is one of the most important predictors in the MLR models makes it a good term to target with experimental manipulations. The aim of these experiments is to determine whether the mechanisms controlling the relationship between P_g and R_{eco} can be manipulated in a way that will produce a predictable change in the modelled coefficient of the predictor in question. As has been discussed in previous chapters it is likely that self-correlation will affect the relationship between R_{eco} and P_g in this dataset. However, it has also been argued in this thesis that this effect is minimised by the standardised procedures and quality control techniques used to collect the data. As such, it is likely that the magnitude of the 'self-correlation' will be small with respect to the real correlation that is expected (e.g. Larsen et al., 2007; Migliavacca et al., 2011) to be observed in the data. Given that this chapter aims to manipulate the relationship between R_{eco} and P_g it is necessary to assume that any correlations observed in the datasets gathered here are real and not an artefact of the experimental design.

In the MLR models the coefficient between R_{eco} and P_g is interpreted as the proportion of photosynthesis that is instantly respired, a similar interpretation to that in the model of Larsen et al., (2007). There is uncertainty, however, about the relative importance of heterotrophic versus autotrophic respiration enhancement due to the R_{eco}-P_g relationship. As heterotrophs are substrate-limited experimental manipulation of the supply of labile substrates to the soil should reduce the sensitivity of R_{eco} to P_g, if the R_{eco}-P_g relationship were mainly due to stimulation of heterotrophs. This stimulation of heterotrophs via supply of substrate would reduce R_{eco} sensitivity to P_g because it represents a new, exogenous source of substrate meaning that the heterotrophs become less reliant on the plant root exudates as a substrate. However, if the R_{eco}-P_g relationship is due to the stimulation of autotrophic respiration (above or below ground) then the addition of substrates to the soil should not have a noticeable effect on the sensitivity of R_{eco} to P_g. That said, a reduction in the relative importance of the R_{eco}-P_g relationship in the model would be expected due to the increase in the magnitude of heterotrophic respiration that would be expected with the introduction of labile substrates to the root zone. As well as affecting the sensitivity of R_{eco} to P_g, manipulation of labile substrates should affect the sensitivity of the system to air temperature as increasing concentrations of labile substrates have been shown to increase the temperature sensitivities of several differing soil types (Gershenson et al., 2009; Larionova et al., 2007).

In the case that the relationship between R_{eco} and P_g is dominated by enhancement of autotrophic respiration, then addition of fertiliser to the system should enhance the sensitivity of R_{eco} to P_g. by increasing the plant productivity. Ombrotrophic peatlands are known to be nutrient limited ecosystems (e.g. Charman, 2002, pp 6-10) and fertilisation with N has been shown to increase plant productivity where the system is N limited (Aerts et al., 1995). Thus manipulating the nutrient supply to the ecosystem may add further insight into the dynamics of the R_{eco} – P_g relationship.

While it is possible to hypothesise about the impacts of experimental manipulation on the sensitivities of R_{eco} to the process-driving (i.e. P_g and air temperature) terms in the MLR models, it is difficult to make predictions about the effects on the process-modifying terms (e.g. water table depth). This is because the manipulations are designed to affect a driver of CO_2 cycling (i.e. photosynthesis). As the modifying terms do not directly drive the cycling of CO_2, R_{eco} sensitivity to these terms would *a priori* be expected to remain the same. However, this line of reasoning does not allow for interactions between the terms. For example, water table depth variations in peatlands can be ineffective on R_{eco} below certain threshold depths (e.g. Leppälä et al., 2008). However, the predicted changes in air temperature sensitivity may shift where this threshold level lies. Effects, like those just mentioned are difficult to predict in advance and as such unexpected effects observed in the modifying terms should not necessarily be interpreted as problems with the model the physical interpretability of the model.

6.1.1 – Aims, Objectives and Hypotheses

The primary aim of this chapter is to investigate the effects of manipulating the supply of labile substrates and nutrients on blanket peatland carbon cycling with the objective of inducing changes in the sensitivity of R_{eco} to P_g. These manipulations are intended to provide insights into the controls on the correlation between R_{eco} and P_g and will be identified by examining differences (relative to a control) in the sensitivity of R_{eco} to P_g by fitting MLR models to the data. As has been demonstrated in other chapters of this thesis, the carbon fluxes of upland peat vary on several time scales. As such this chapter is sub-divided into two trials, sampling on two different temporal scales. The first trial, known as the acute trial, focuses on the short-term (daily/weekly) impact of experimental manipulations. The second trial, known as the chronic trial, focuses on the impact of the experimental manipulations on a longer (monthly/annual) timescale.

In order to formalise the assessment of experimental effects, a set of hypotheses has been created for each treatment on each trial, which are to be judged relative to the control (table 6.1.1.1). Each hypothesis makes two predictions (‘a’ and ‘b’), the first regarding the presence of an effect and the second regarding the direction of the change in R_{eco} sensitivity to P_g. Below, the null (H_0) and working (H_1) hypotheses are given for each treatment of each trial. These hypotheses are broken into their two components (‘a’ and ‘b’) and tested separately later in the chapter, so it is possible to test to what extent the predictions of the hypotheses have been fulfilled. For the combined treatments it was not possible to make complete predictions of effects and the hypotheses below reflect this.

Table 6.1.1.1 – Hypotheses of R_{eco} for Acute and Chronic Trials

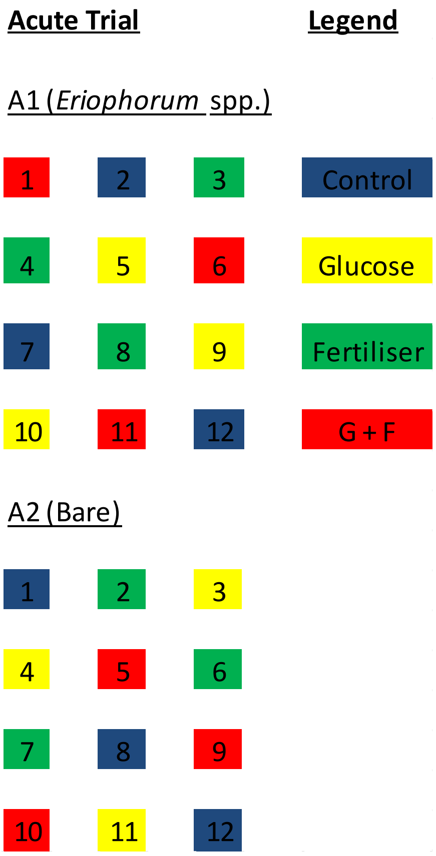
Acute Trial				
	H0a	H0b	H1a	H1b
Fertilised	No effect on magnitude	No effect on sensitivity to Pg	Increase in magnitude	Increase in sensitivity to Pg
Glucose	No effect on magnitude	No effect on sensitivity to Pg	Increase in magnitude	Decrease in sensitivity to Pg
Glucose & Fertilised	No effect on magnitude	No effect on sensitivity to Pg	Increase in magnitude	n/a

Chronic Trial				
	H0a	H0b	H1a	H1b
Fertilised	No effect on magnitude	No effect on sensitivity to Pg	Increase in magnitude	Increase in sensitivity to Pg
Litter Removed	No effect on magnitude	No effect on sensitivity to Pg	Decrease in magnitude	Increase in sensitivity to Pg
Litter Removed & Fertilised	No effect on magnitude	No effect on sensitivity to Pg	n/a	Increase in sensitivity to Pg

6.2 – Experimental Design

6.2.1 – Acute Trial

The acute trial employed a factorial design in order to test for differences between treatment levels. There were four treatments in this trial: a control treatment, a fertilised only treatment, a glucose (where glucose was used as the labile substrate) treatment and a combined glucose and fertilised treatment. Each treatment was applied to specially installed plots (i.e. plots not used as part of any study in the previous chapters) in triplicate. The plots were laid out in a grid spaced at, roughly, two meters from each other in all directions. Figure 6.2.1.1 shows the distribution of the plots and their respective treatments, the plots were laid out such that no treatment repeats in any row or column. There were two sites in the acute trial, with one site (site A1) installed into an *Eriophorum vaginatum* lawn within 10 metres of the Pengiuns (PEN) fieldsite (described in chapter 2 of this thesis). The second site (A2) was installed into entirely bare peat within 10 metres of the Trenches North (TN) fieldsite (Chapter 2).



Acute Trial **Legend**

A1 (*Eriophorum* spp.)

🟥 1	🟦 2	🟩 3	🟦 Control
🟩 4	🟨 5	🟥 6	🟨 Glucose
🟦 7	🟩 8	🟨 9	🟩 Fertiliser
🟨 10	🟥 11	🟦 12	🟥 G + F

A2 (Bare)

🟦 1	🟩 2	🟨 3
🟨 4	🟥 5	🟩 6
🟩 7	🟦 8	🟥 9
🟥 10	🟨 11	🟦 12

Figure 6.2.1.1 **–** Schematic plan of the distribution treatment levels on both sites of the acute trial. The abbreviation G+F in the legend stands for glucose plus fertiliser. The spacing between the plots is roughly two meters.

The acute trial was first instrumented in April 2010, with the primary sampling carried out between 17 – 28th May 2010. Each plot was instrumented in the fashion described in chapter 2 of this thesis. CO_2 flux and water samples were collected and analysed following the methods and protocols described in chapter 2. On 17th May 2010, CO_2 fluxes and soil pore water samples were collected prior to the application of the treatments to each plot. After this the treatments were applied to the plots, as described below. Carbon dioxide fluxes were then collected twice, from each plot, on each subsequent day stopping on 28th May 2010, with a two-day gap on the weekend of the 22-23rd May 2010. CO_2 was gathered twice daily in order to minimise the potential biases of sampling at only one time of day. Water samples were only collected once daily in order to minimise artificial water table draw down. Water samples and CO_2 flux data were collected on two subsequent days, 9th June 2010 and 14th July 2010 in order to identify any long lasting effects of the manipulation.

The treatments were applied evenly to the plots from 250 ml plastic bottles. The control treatment involved the application of 250 ml of deionised water to a 0.5 x 0.5 m square quadrat. This is equivalent to a 1 mm rain storm event and was not thought to be likely to noticeably affect the soil pore water composition or CO_2 fluxes on the time scale considered. The fertilised, and all other, treatments were also applied from 250 ml plastic bottles to 0.5 x 0.5 m quadrats.

Fertilised treatments had a single pulse application of ammonium nitrate and disodium phosphate. The dose rate of the fertiliser was calculated such that, if it was applied once every two weeks (rather than just once as in this study), it would be equivalent to an annual dose of 6 g N m^{-2} y^{-1}. This dosage was based upon a literature review of studies, on similar ecosystems (e.g. Gerdol et al., 2008; Pilkington et al., 2005; Williams and Silcock, 2000), where nutrient limitation removal was the objective and in those cases rates of application between 1 – 12 g N m^{-2} y^{-1} were considered, as such it seemed taking the middle of this range was appropriate. The dose of disodium phosphate was calculated so that it would produce a ratio of 16N:1P, this ratio in vegetation was found to be the dividing line between phosphate/nitrate limiting conditions in a number of terrestrial ecosystems (Koerselman and Meuleman, 1996).

The dose of the glucose treatment was intended to provide enough labile substrate to the plots to ensure that an excess of C, relative to baseline conditions, was applied. As such, the average amount of C released, via respiration, from the fieldsite PEN during the months of May, June and July 2009 was calculated, and a dose of glucose equivalent to this amount of C (i.e. 58.30 g glucose $quad^{-1}$) was applied to each glucose treatment on both sites.

The fertiliser only, fertiliser and glucose, and glucose only solutions were prepared within 24 hours of application to the plots. They were stored in sterile, 250 ml plastic bottles and were kept refrigerated between preparation and transport to the sites. These precautions were observed in order to minimise the potential for any significant mineralisation or utilisation of the active ingredients by biota in the bottles.

6.2.2 – Chronic Trial

In many respects the chronic trial is similar to the acute trial. It is factorial in nature, with four treatment levels, of three replicates a piece, set across two sites with an approximate spacing between plots of two metres. However, there are a number of important differences between the trials. Firstly the trial has been situated in differing stand ages of *C. vulgaris* (juvenile and degenerate) rather than bare peat and *Eriophorum* spp. The treatment levels were also somewhat different in this trial. There are control (deionised water only) and fertilised plots but instead of the addition of labile substrates (i.e. glucose), this trial removed potential labile substrates via the removal of surface litter. The most important distinction between the acute and chronic trials is that the chronic trial was conducted over twelve calendar months with two sets of readings taken each month: one set prior to treatment and the other set on the day after treatment.

The two sites of this trial were installed, in the Goyt Valley of the Peak District, in April 2010. The readings started in May 2010 and finished in April 2011. There were no data collected in December 2010 due to snow cover preventing access to the sites. The juvenile *C. vulgaris* site (C1) was within 10 metres of the Bottle South (BS) (Chapter 2) fieldsite and the degenerate *C. vulgaris* (C2) site was an extension of the former Lower A (LA) altitude transect (Chapter 3) fieldsite. The distribution of the plots by site is given in figure 6.2.2.1.

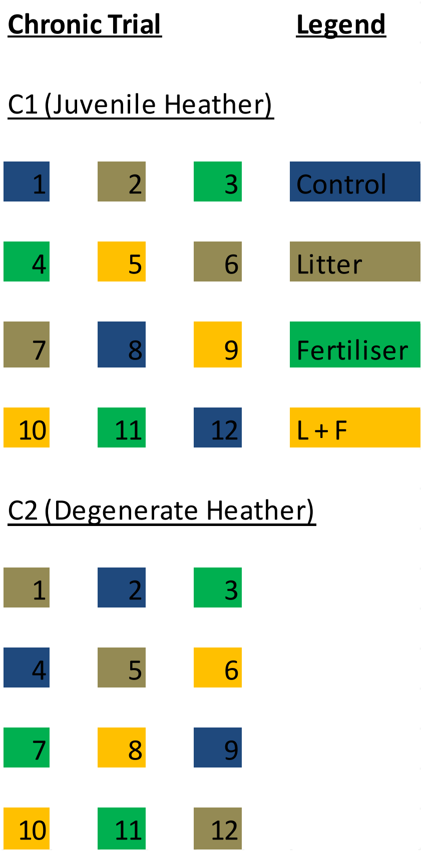


Figure 6.2.2.1 **–** Schematic plan of the distribution treatment levels on both sites of the chronic trial. The abbreviation L+F in the legend stands for litter removed plus fertiliser. The spacing between the plots is roughly two meters.

The treatments were applied from 250 ml plastic bottles to 0.5 x 0.5 m quadrats as in the acute trial. The control treatment was the same as the acute trial also. The fertilised treatment had the same annualised rate of N deposition (6 g N m^{-2} y^{-1}), this time divided equally between the months. Litter removal from the plots was done by hand in May 2010. All litter was removed within a 0.5 x 0.5 m quadrat, taking care not to cause too much damage to the field layer vegetation that used the litter as scaffolding. However, despite the care taken some damage was inevitably done to the plots where the field layer was densest (especially on C2). After the final set of gas flux readings *C. vulgaris* and peat (5 cm depth), samples were taken from all plots to determine whether the treatments had significantly affected the C:N ratios of the plots. All field, laboratory and statistical methods reported in this chapter follow the protocols established in chapter 2 of this thesis.

6.3 – Results

6.3.1 – Acute Trial

The meteorological conditions, at the nearby Upper North Grain weather station, during the period of the acute trial are summarised in figure 6.3.1.1. It is apparent that rainfall was infrequent and of low magnitude throughout the trial. Air temperature is greater than soil temperature at all depths until 24/05/2010 where this pattern reverses.

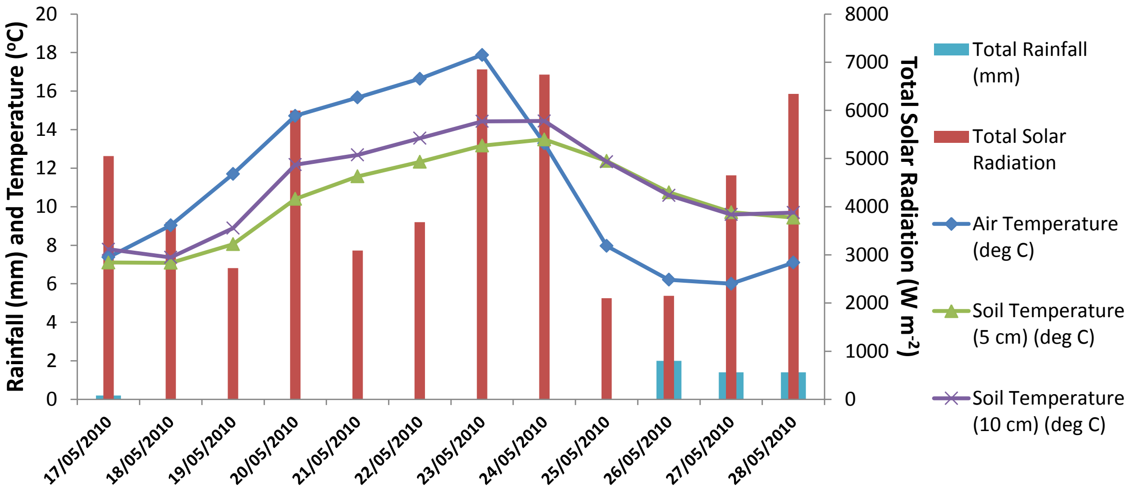


Figure 6.3.1.1 – This chart summarises the meteorological conditions (measured at Upper North Grain weather station) during the period of the acute trial. Total rainfall (mm) and all mean daily temperature measures (°C) are shown relative to the left hand axis while total solar radiation (W m^{-2}) is displayed on the right hand axis.

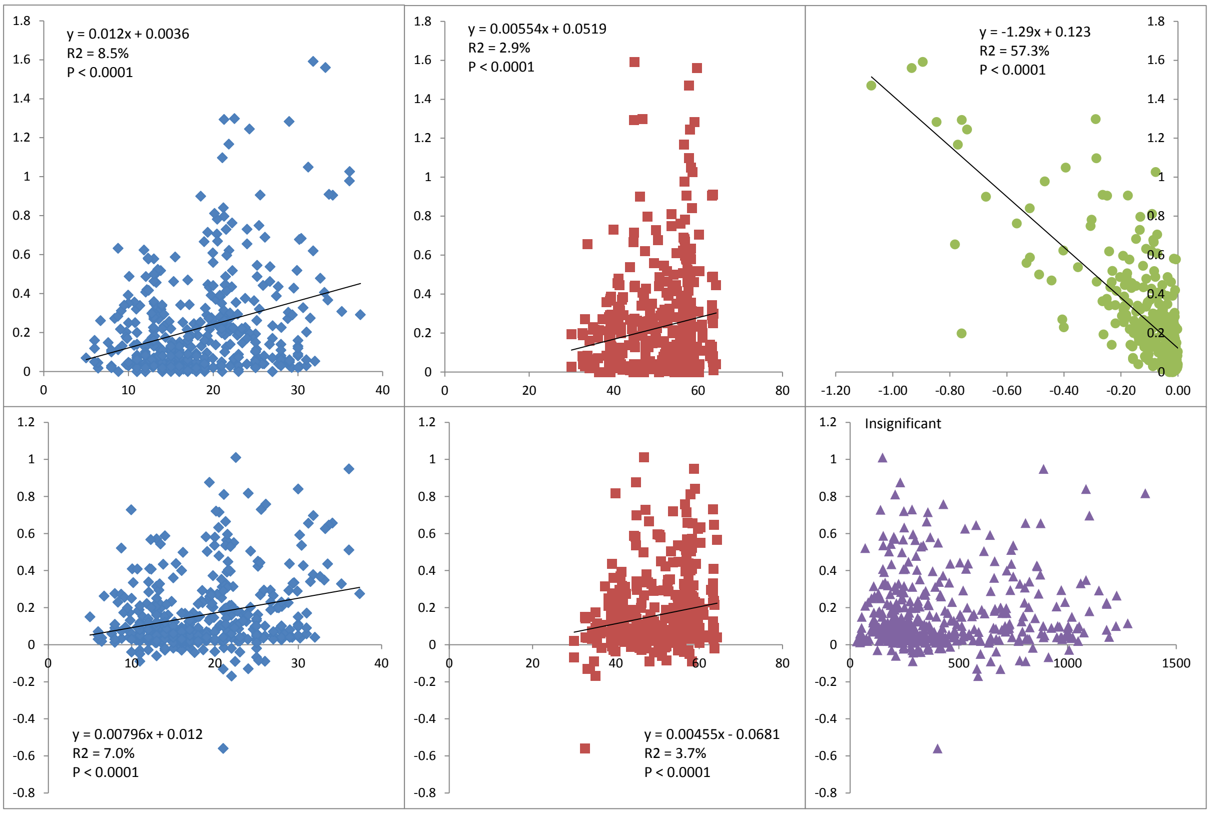


Figure 6.3.1.2 **–** Plots of R_{eco} (top row, g CO_2 m^{-2} h^{-1}) and NEE (bottom row, g CO_2 m^{-2} h^{-1}) (y-axis) versus air temperature (left column, ^{o}C), water table depth (middle column, cm below surface) and P_g (top row, g CO_2 m^{-2} h^{-1}))/PAR (bottom row, µmol s^{-1} m^{-2}) (x-axis) for the acute trial data. Linear regression lines, where significant, are shown.

Bivariate relationships between R_{eco}/NEE and important predictors are shown in figure 6.3.1.2. This figure suggests that air temperature, water table depth are significant predictors of both fluxes. Additionally, a relationship between R_{eco} and P_g was identified. These analyses however are only preliminary and are relatively unsophisticated; therefore, they should be thought of as indicative but not conclusive. Further, more sophisticated, ANOVA/ANCOVA results are summarised below. Mean daily R_{eco} for both sites is shown in figures 6.3.1.3 and 6.3.1.4. These plots suggest that R_{eco} is of generally greater magnitude on site A1 than A2. The pattern of resipration appears to roughly correspond to variations in air and soil temperature (figures 6.3.1.1 and 6.3.1.3 to 6.3.1.4), at least for the first week of the trial, but with noticeable differences in treatment levels. ANOVA and

ANCOVA on both raw and natural log transformed datasets revealed that R_{eco} was better predicted using a transformed dataset when both sites were considered simultaneously. When analysing the individual sites' datasets, the untransformed datasets had the greatest model fits (table 6.3.1.1). This implies that the difference in R_{eco} magnitudes between the sites is responsible for the better fitting logarithmic models, whereas in reality an untransformed model is best fitting on a site to site basis. This is confirmed by the fact that differences between sites explain most of the variation accounted for by the 'all sites' ANOVA model (i.e. without covariates) (table 6.3.1.1).

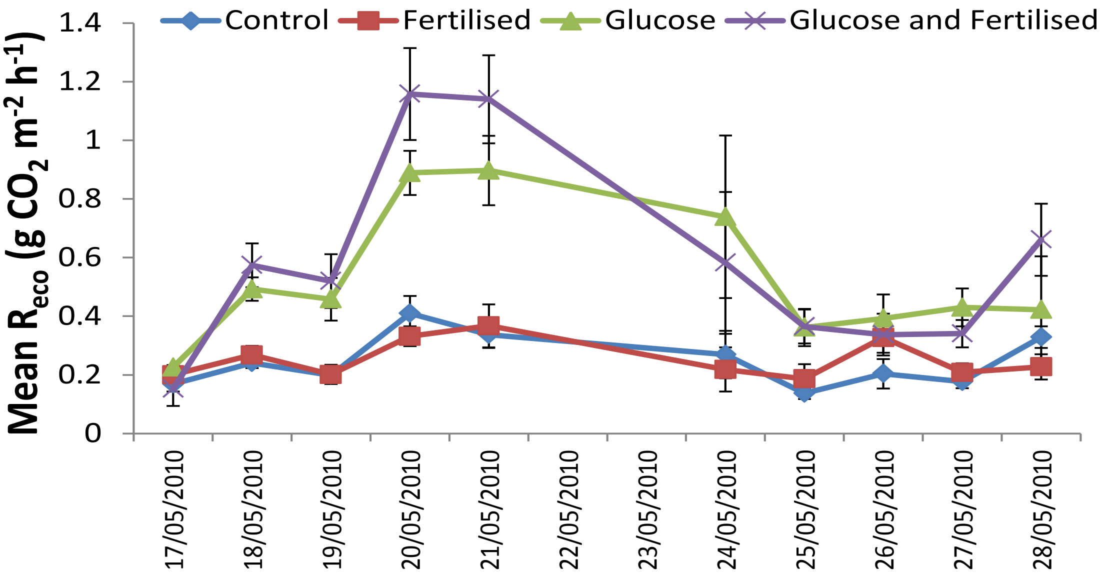


Figure 6.3.1.3 **–** Mean daily R_{eco} for all of the treatment levels of site A1. The error bars denote one standard error.

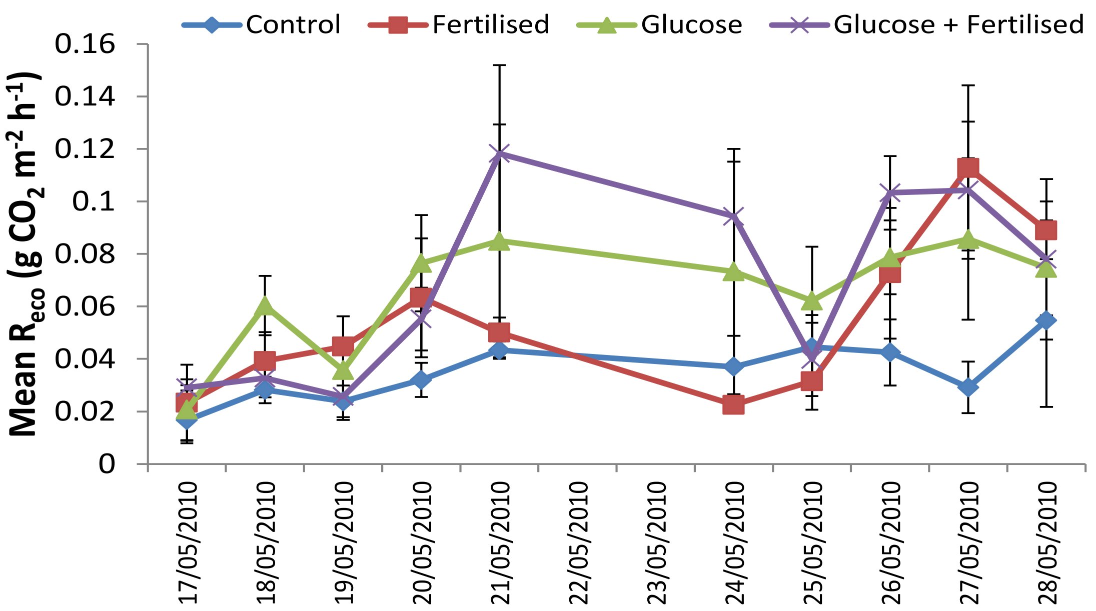


Figure 6.3.1.4 **–** Mean daily R_{eco} for all of the treatment levels of site A2. The error bars denote one standard error.

For the R_{eco} dataset ANOVA showed that regardless of site there were differences between the treatment levels. Moreover, these differences were not fully explained by any of the covariates tested in the ANCOVA models. The main differences observed on site A1, as revealed by Tukey's pairwise comparisons, were between the control and plots treated with glucose, with the glucose only plots being 1.66 times larger than the control on average. In addition, on site A1 there was only evidence of a fertilisation effect when in combination with glucose, this increased R_{eco} by an average factor of 2.01 relative to the control. On site A2 fertilisation appeared to increase R_{eco} by a similar (i.e. not significantly different) magnitude to glucose addition with a, statistically significant, average increase of all treatments relative to the control of 1.47. It is apparent on figure 6.3.1.3 that the temporal manifestation of the fertilisation effect was later than that for glucose peaking on fertilised plots after 10 days rather than after four days in the case of glucose. P_g was the most important predictor of R_{eco} on both sites with P_g being almost equally important in models from both sites.

The results for NEE (figures 6.3.1.5-6.3.1.6 and table 6.3.1.1) are similar to R_{eco}, which is unsurprising given the fact that R_{eco} is a constituent flux of NEE. NEE was less well modelled by ANOVA and ANCOVA than R_{eco}. The 'all sites' dataset showed that site to site differences in NEE were mainly explained by differences in conductivity and P_g. The results for site A1 showed that the addition of glucose caused a significant positive increase in NEE by an average factor of 2.68 relative to the control. In addition, the combination of glucose and fertiliser was found to increase NEE by an average factor of 3.46 relative to the control. The pattern of results on site A2 implied that the differences between treatments were explained by differences in the magnitude of the P_g- R_{eco} relationship, with no significant differences reported in treatment levels after the inclusion of P_g into the model. However, differences between treatment levels, as seen in the ANOVA model, indicated that there was no, statistically significant, fertilisation effect but that the addition of glucose caused an increase in R_{eco} by an average factor of 2.34.

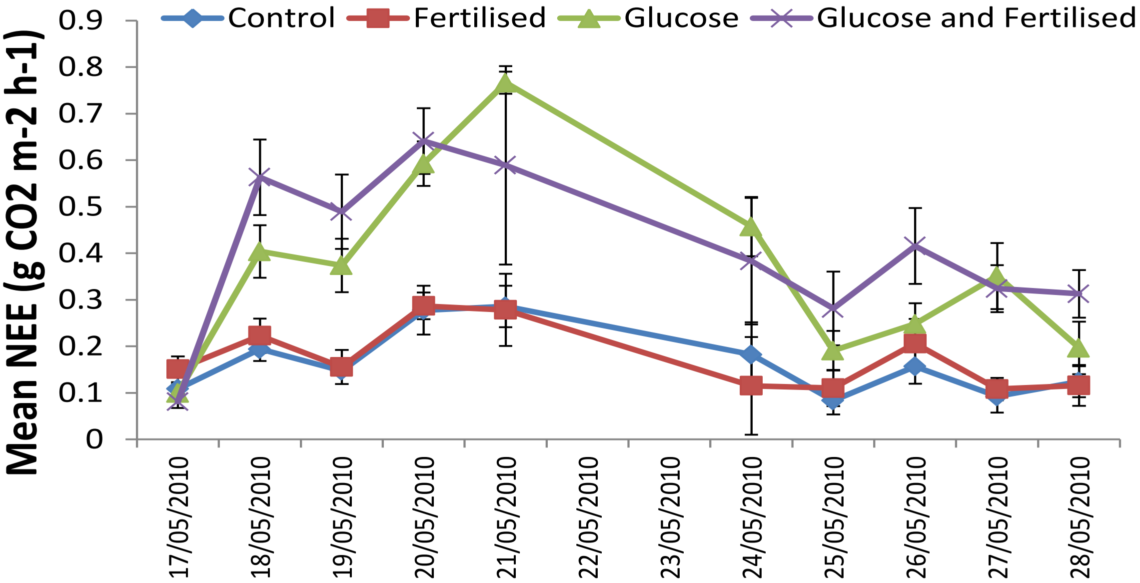


Figure 6.3.1.5 **–** Mean daily values for NEE by treatment on site A1. The error bars are one standard error.

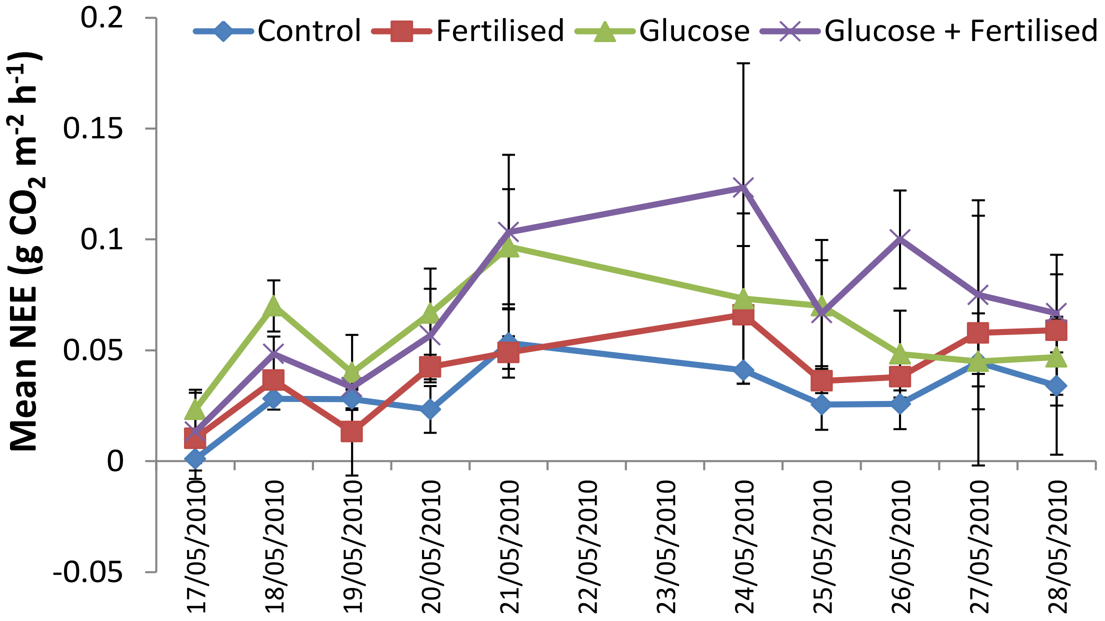


Figure 6.3.1.6 **–** Mean daily values for NEE by treatment on site A2. The error bars are one standard error.

Due to water table depths being greater than the base of the dipwells for many of the plots there were not enough DOC data to carry out an analysis for site A2. Looking at the pattern of results for site A1 (figure 6.3.1.7 and table 6.3.1.1), it can be seen that the inclusion of Abs_{400} into the models explains some of the magnitude of the effect of treatment on DOC. This effect may be due to the fact that plots under fertilised treatments appeared to have lower specific absorbance (i.e. Abs_{400}/DOC) values than the unfertilised plots (figure 6.3.1.8), while the plots with glucose had a higher total amount of DOC (figure 6.3.1.9). Overall, DOC seemed to increase by an average factor of 1.49 relative to the control on plots that were both fertilised and had glucose applied. There were no significant differences between the control and the fertilised or glucose alone treatments found in either the ANOVA or ANCOVA models.

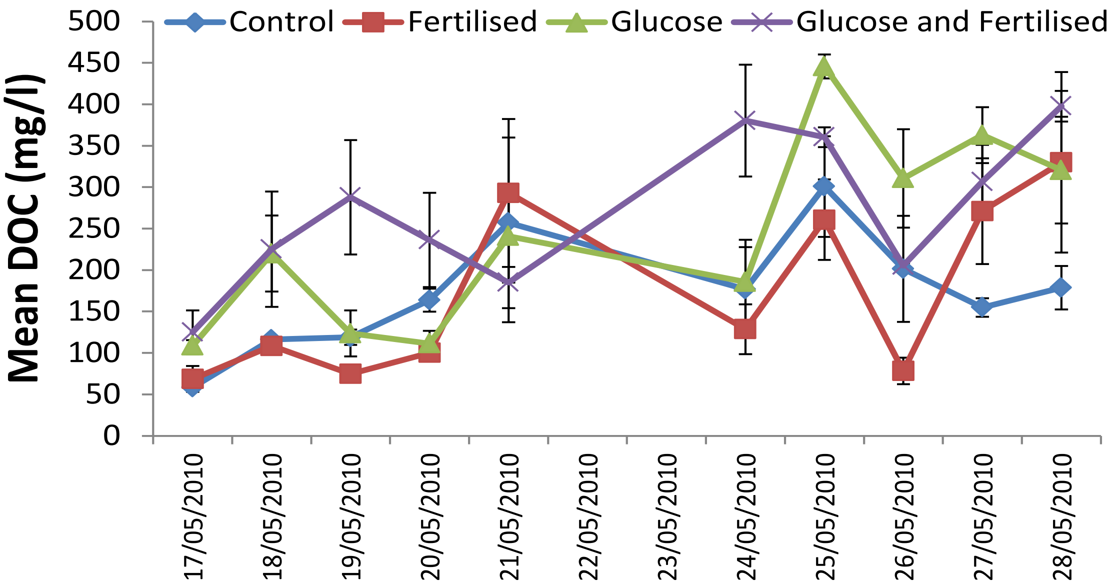


Figure 6.3.1.7 **–** Daily mean soil pore water DOC concentration by treatment for site a1. The error bars denote one standard error.

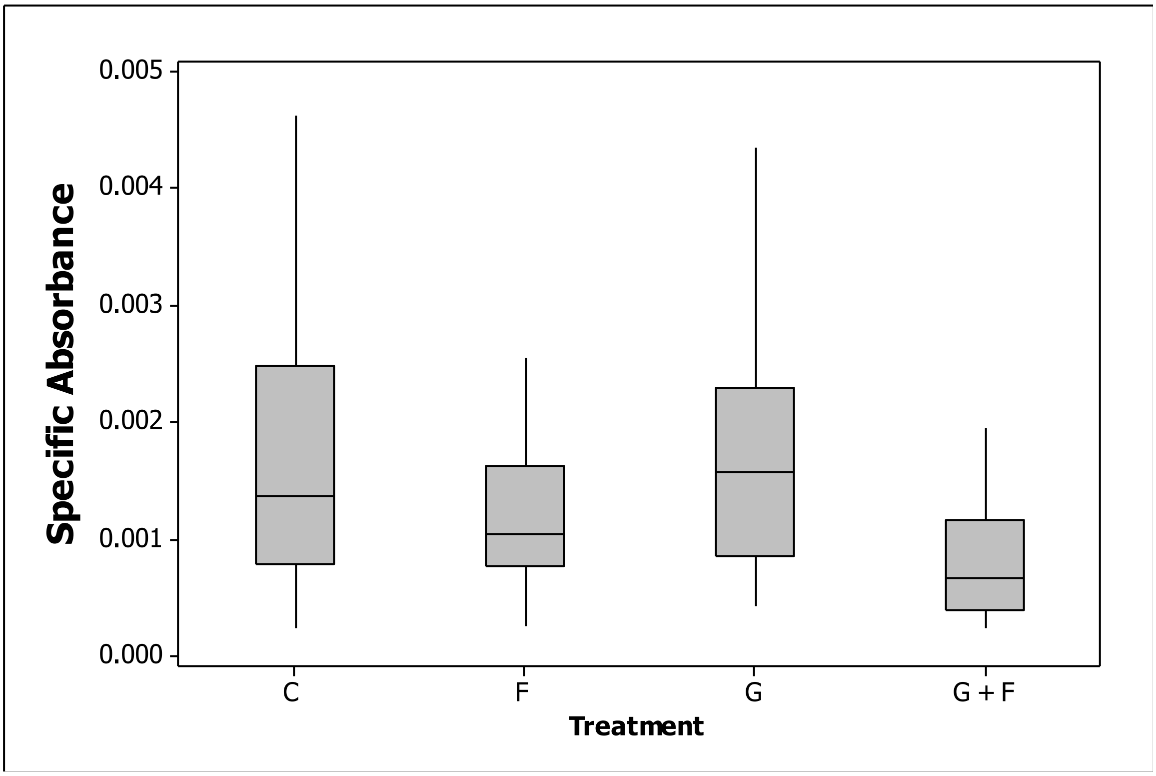


***Figure 6.3.1.8* –** Boxplot showing the distribution of specific absorbance (Abs400/DOC) data by treatment. The box boundaries represent the interquartile range, the line in the middle represents the median and the 'whiskers' denote the 95% confidence limits on the dataset distribution.

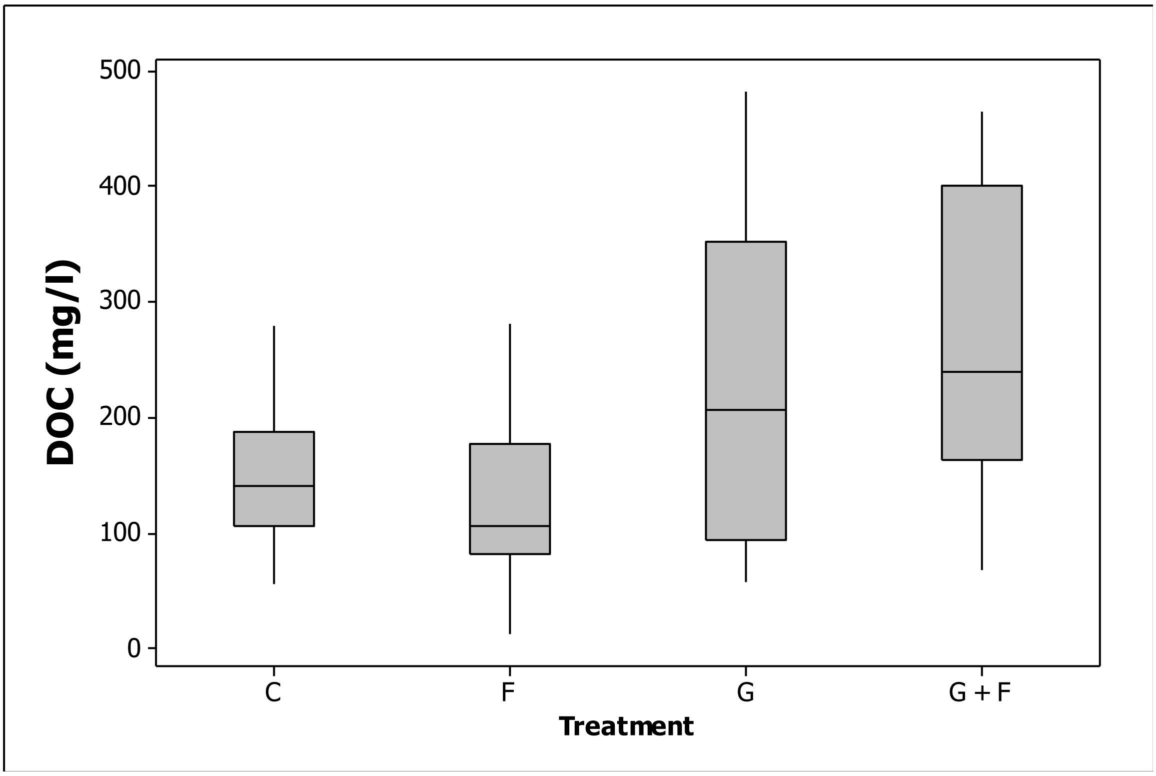


***Figure 6.3.1.9* –** Boxplot showing the distribution of DOC concentration (mg/l) data by treatment. The box boundaries represent the interquartile range, the line in the middle represents the median and the 'whiskers' denote the 95% confidence limits on the dataset distribution.

Table 6.3.1.1 – ANOVA and ANCOVA results for the Acute Trial

All Data

ANOVA

Ln Reco				NEE				DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
FF	Site	< 0.0001	36.08%	FF	Site	< 0.0001	27.93%	FF	Site	< 0.0001	1.68%
FF	Date	< 0.0001	7.61%	FF	Date	< 0.0001	8.74%	FF	Date	< 0.0001	20.85%
FF	Treatment	< 0.0001	7.32%	FF	Treatment	< 0.0001	9.74%	FF	Treatment	0.004	2.77%
R-Sq	52.78%			**R-Sq**	48.32%			**R-Sq**	29.26%		
Tukey: C(a), F(a), G(b) and G+F(b)				**Tukey: C(a), F(a), G(b), G+F(b)**				**Tukey: C(a), F(a), G(ab) and G+F(b)**			

ANCOVA

Ln Reco				NEE				Ln DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
Cov	Ln Conductivity	< 0.0001	22.60%	Cov	Conductivity	0.002	9.42%	Cov	Ln Abs400	< 0.0001	13.94%
Cov	Ln Pg	< 0.0001	28.56%	Cov	Pg	0.021	3.50%				
FF	Site	< 0.0001	11.40%	FF	Site	< 0.0001	5.16%				
FF	Date	< 0.0001	7.67%	FF	Date	< 0.0001	23.04%	FF	Date	< 0.0001	10.94%
FF	Treatment	< 0.0001	9.06%	FF	Treatment	< 0.0001	14.92%	FF	Treatment	< 0.0001	4.10%
R-Sq	80.98%			**R-Sq**	59.55%			**R-Sq**	33.18%		
Tukey: C(a), F(a), G(b) and G+F(b)				**Tukey: C(a), F(a), G(b), G+F (c)**				**Tukey: C(a), F(a), G(ab) and G+F(b)**			

A1

ANOVA

Reco				NEE				Ln DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
FF	Date	< 0.0001	27.60012	FF	Date	< 0.0001	27.54%	FF	Date	0	32.68%
FF	Treatment	< 0.0001	25.4078	FF	Treatment	< 0.0001	24.62%	FF	Treatment	0	11.17%
IF	Date*Treatment	< 0.0001	10.57606	IF	Date*Treatment	0.002	6.32%	IF	Date*Treatment	0.025	5.12%
R-Sq	71.67%			**R-Sq**	67.67%			**R-Sq**	60.65%		
Tukey: C(a), F(a), G(b) and G+F(b)				**Tukey: C(a), F(a), G(b), G+F (c)**				**Tukey: C(ab), F(a), G(bc) and G+F(c)**			

ANCOVA

Reco				NEE				Ln DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
Cov	Air Temp	0.024	16.52%	Cov	Air Temp	0.022	8.98%	n/a			
Cov	Pg	< 0.0001	36.30%	Cov	Pg	< 0.0001	0.16%				
Cov	DOC	0.025	0.62%								
FF	Date	< 0.0001	14.90%	FF	Date	< 0.0001	27.60%				
FF	Treatment	< 0.0001	11.09%	FF	Treatment	< 0.0001	20.30%				
IF	Date*Treatment	< 0.0001	4.15%	IF	Date*Treatment	< 0.0001	7.75%				
R-Sq	88.30%			**R-Sq**	75.83%			**R-Sq**			
Tukey: C(a), F(a), G(b), G+F (c)				**Tukey: C(a), F(a), G(b), G+F (b)**				**Tukey:**			

A2

ANOVA

Reco				NEE				DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
FF	Date	< 0.0001	11.51%	FF	Date	0.003	7.69%	n/a			
FF	Treatment	< 0.0001	8.17%	FF	Treatment	0.013	3.29%				
R-Sq	25.08%			**R-Sq**	16.82%			**R-Sq**			
Tukey: C(a), F(b), G(b), G+F(b)				**Tukey: C(a), F(ab), G(b), G+F(b)**				**Tukey:**			

ANCOVA

Reco				NEE				DOC			
Coding	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**	**Coding**	**Source**	**P**	**w2**
Cov	Pg	< 0.0001	36.86%	Cov	PAR	0.031	6.01%	n/a			
FF	Date	0.015	14.25%	FF	Pg	< 0.0001	13.86%				
FF	Treatment	0.015	4.91%	FF	Date	0.009	9.70%				
R-Sq	56.28%			**R-Sq**	37.70%			**R-Sq**			
Tukey: C(a), F(b), G(b), G+F(b)				**Tukey: n/a**				**Tukey:**			

Coding: Cov = covariate, IF = interaction factor,FF = fixed factor

In order to estimate the total amount of C released through respiration over the initial monitoring period, the best fit ANCOVA model outputs (table 6.3.1.1) for each site were used to predict hourly respiration. These hourly values were then summed in order to give the total amount of C released through respiration. The input meteorological data used during modelling was obtained from the Upper North Grain (UNG) weather station. To estimate P_g the model of Thornley and Johnson, (1990) was used (equation 6.3.1.1); however, this model requires PAR data. These data are not collected by the UNG weather station which means that the PAR data had to be estimated using a linear regression between total solar radiation, collected at the UNG weather station, and PAR data, collected during CO_2 flux measurement (figure 6.1.3.10).

On site A1 DOC was also a significant predictor of R_{eco}. As DOC was only measured on a daily basis the daily value obtained was used for every hour of the day it was measured on. The factor main effects and interactions from the ANCOVA model were incorporated into the model as constants varying between factor levels.

$$P_g = \frac{(PAR \times \alpha \times P_{gmax})}{(PAR \times \alpha + P_{gmax})} \qquad \textit{Equation 6.3.1.1}$$

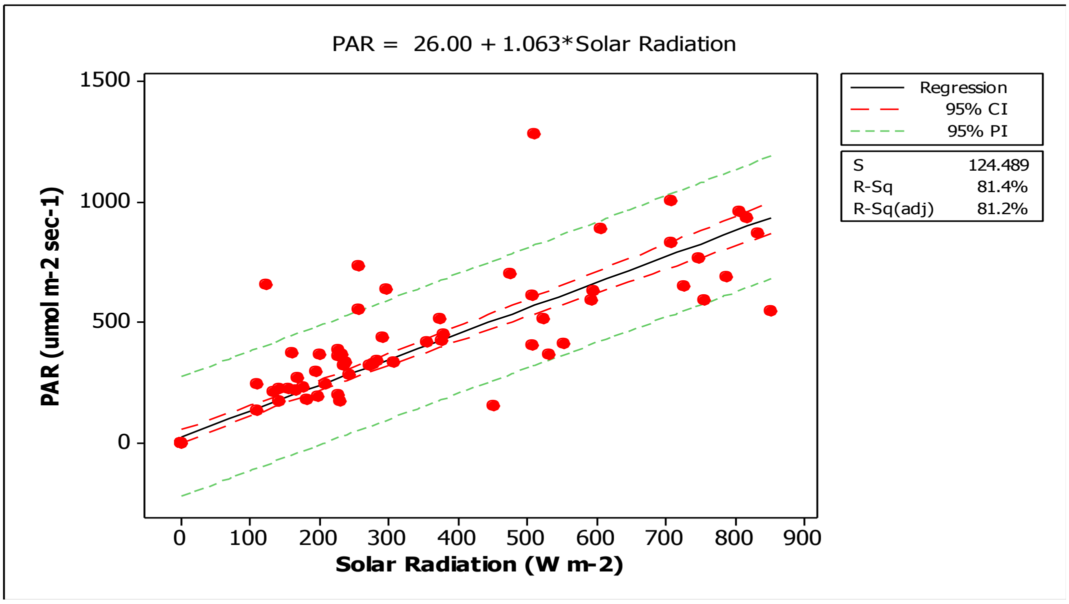


Figure 6.1.3.10 – Plot showing the linear regression between the solar radiation dataset from the Upper North Grain weather station and the PAR dataset recorded in the CPY-2 chamber during the CO_2 flux measurements.

The output of the R_{eco} model for site A1 is given in figure 6.3.1.11. It is apparent that application of glucose, regardless of fertilisation, led to higher rates of respiration than either the fertilised or the control plots. The total amount of CO_2 produced, per quadrat, by each treatment is summarised in table 6.3.1.2. The control plots produced 1.67 g of CO_2-C over the initial 12 days of the experiment. The fertilised plots produced slightly (but not significantly) more at 2.04 g CO_2-C. The glucose and glucose + fertilised treatments produced significantly more than the control at 7.18 and 8.05 g CO_2-C respectively. It can be seen that both the treatments with glucose respired more than the control but less than the total amount of C added from glucose. After 23 days from the start of the experiment it appears that the glucose treatment is no longer different than the control (figure 6.3.1.12); however, for the glucose + fertilised treatment still appears to be higher than the control at 58 days after the start of the experiment.

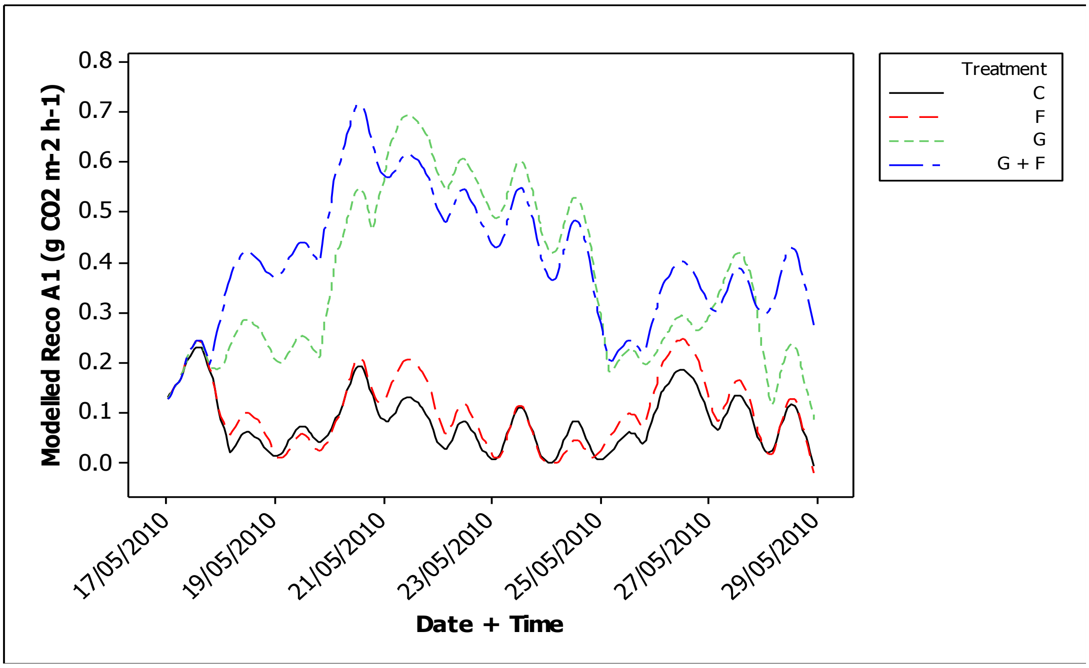


Figure 6.3.1.11 – Plot of the ANCOVA model prediction of the hourly R_{eco} rates from the plots of the four treatment levels on site A1.

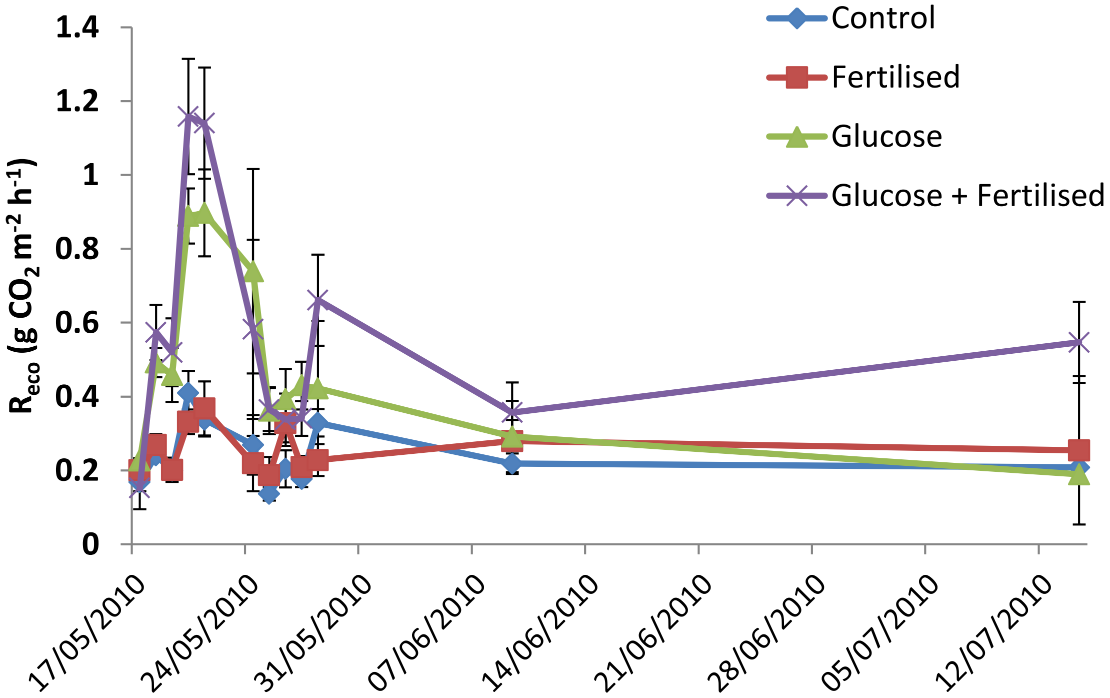


Figure 6.3.1.12 **–** Daily mean values of R_{eco} for each treatment across the whole monitoring period of the experiment for site A1. Error bars are one standard error of the mean.

Table 6.3.1.2 – Predicted amounts of carbon lost through respiration on sites A1 and A2

	A1		
Treatment	**g C added (per quad)**	**g C respired (per quad)**	**Excess Respiration**
C	0.00	1.67	n/a
F	0.00	2.04	0.37
G	28.35	7.18	-22.84
G + F	28.35	8.05	-21.97
	A2		
Treatment	**g C added (per quad)**	**g C respired (per quad)**	**Excess Respiration**
C	0.00	0.87	n/a
F	0.00	1.36	0.49
G	28.35	1.60	-27.62
G + F	28.35	1.61	-27.61

ANCOVA modelling of R_{eco} on site A2 gave a different picture to site A1 (Figure 6.3.1.13). In the same way as A1, respiration was higher from the glucose plots than the control, however, the total magnitude of respiration is much lower from site A1 than A2 with A1 being 1.9, 1.5, 4.5 and 5 times greater than A2 for control, fertilised, glucose and glucose + fertilised respectively. Moreover, there were no interactions between treatment and date on site A2. The total amount of CO_2-C produced from the control was 0.87 g with the fertilised, glucose and glucose + fertilised plots being significantly greater with values of 1.36, 1.60 and 1.61 g CO_2-C respectively. The fertilised plot respired 0.49 g more CO_2 as carbon (CO_2-C) than the control, which was shown by ANCOVA modelling (table 6.3.1.1) to be a significant increase. The effects of the non-control treatments on R_{eco} were still apparent up to 58 days after application (figure 6.3.1.14). This agrees with the model prediction (table 6.3.1.1) which suggests there were no interactions between treatment and date over the 58-day period of the experiment.

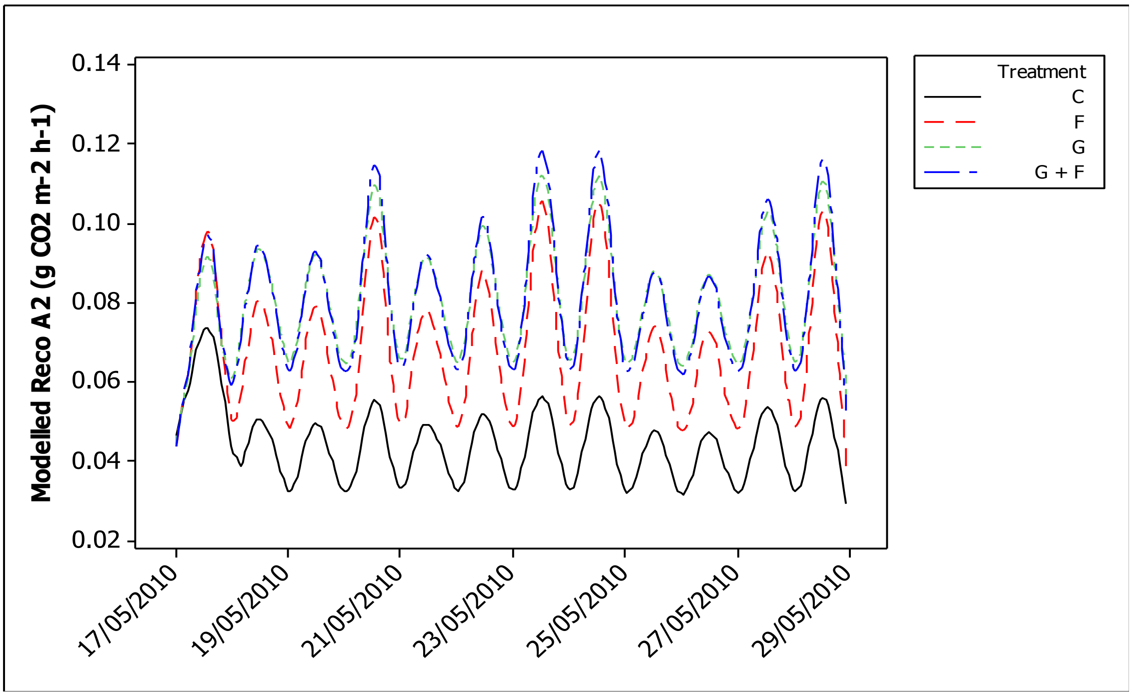


Figure 6.3.1.13 – Plot of the ANCOVA model prediction of the hourly R_{eco} rates from the plots of the four treatment levels on site A2.

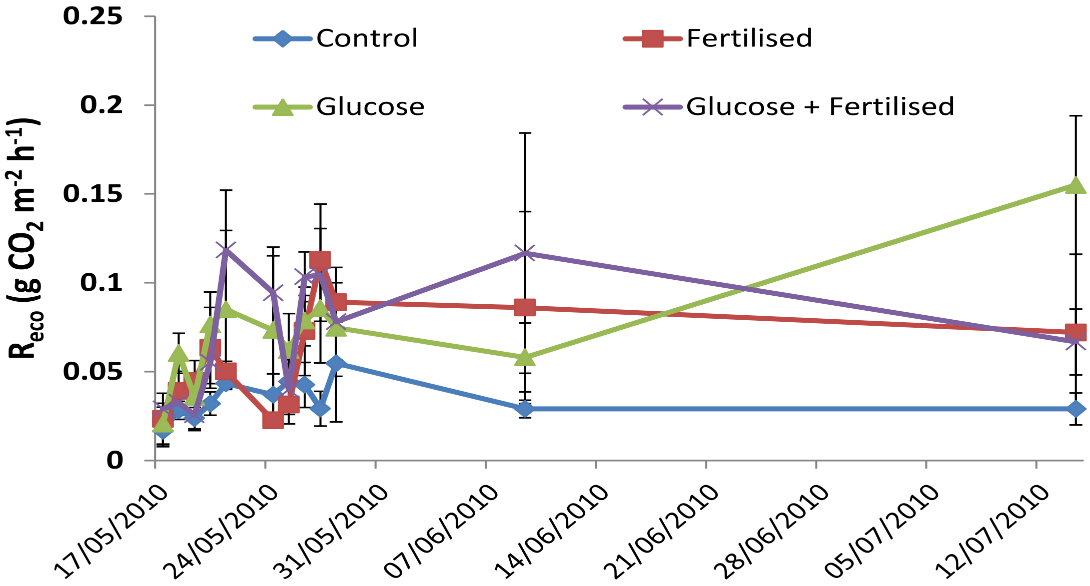


Figure 6.3.1.14 **-** Daily mean R_{eco} values for each treatment across the whole monitoring period of the experiment for site A2. Error bars are one standard error of the mean.

Multiple linear regression analysis of the R_{eco} data by site and treatment showed that the environmental controls on R_{eco} differ between the sites. On site A1, R_{eco} from the control plots were controlled by air temperature, water table depth and gross photosynthesis (table 6.3.1.3). On A2 only water table depth was important. However, the controls also differed between the treatments on each site. On site A1, R_{eco} from the fertilised only plots became insensitive (i.e. no significant correlation found) to air temperature, but plots with glucose added became more sensitive (i.e. increase in the magnitude of the correlation coefficient) to air temperature. However, the importance (as measured by the proportion of the variance explained) of air temperature in the glucose treated plots stayed roughly similar. Plots treated with fertiliser became insensitive to water table depth, regardless of glucose. The glucose only plots became more sensitive to water table depth, and water table depth became more important in these models. All treatment levels were sensitive to gross photosynthesis however the addition of glucose (with or without fertiliser) led to a significantly increased level of sensitivity. Moreover, the importance of gross photosynthesis in the MLR models increased with glucose application also.

Site A2 was only sensitive to water table variations in the control plots (table 6.3.1.3) however the application of any treatment, glucose or fertiliser, made the plots insensitive to water table depth. Instead the treated plots became sensitive to gross photosynthesis, with the fertilised only plots being the most sensitive to gross photosynthesis. Gross photosynthesis explained more dataset variation in R_{eco} with fertiliser alone than the glucose treatments (fertilised or not).

Table 6.3.1.3 – MLR and Partial Regression coefficients for sites A1 and A2. Numbers in brackets represent the standard error of the mean.

	MLR Coefficient					
	A1			**A2**		
	AT	**WTD**	**Pg**	**AT**	**WTD**	**Pg**
C	0.008 (0.002)	0.004 (0.002)	-0.585 (0.138)	-	0.002 (0.0004)	-
F	-	-	-0.553 (0.144)	-	-	-1.271 (0.044)
G	0.015 (0.004)	0.026 (0.005)	-0.917 (0.152)	-	-	-0.604 (0.194)
G+F	0.023 (0.005)	-	-0.852 (0.135)	-	-	-0.5623 (0.238)
	Partial Regression Coefficient					
	A1			**A2**		
	AT	**WTD**	**Pg**	**AT**	**WTD**	**Pg**
C	33.90%	10.20%	28.10%	-	21.10%	-
F	-	-	24.40%	-	-	96.30%
G	25%	44.80%	44.80%	-	-	27.10%
G+F	33.30%	-	51.80%	-	-	19.60%

6.3.2 – Chronic Trial

Bivariate plots of the Reco/NEE versus important predictors are given in figure 6.3.2.1. It can be seen that R_{eco} has apparent significant relationships with air temperature, water table depth and P_g, while NEE has apparent significant relationships with water table depth and PAR. The relationship between NEE and PAR was not present in the equivalent plots for the acute trial, which may imply that such relationships are manifest most strongly on seasonal/annual timescales. These analyses are, however, are unsophisticated as they do not take into account potentially confounding variation related to factors such as site, month, treatment. As such, ANOVA and ANCOVA have been carried out in order to better explore the controls of CO_2 flux and DOC concentration in relation to the effects of the experimental manipulations. The results of these analyses are given below.

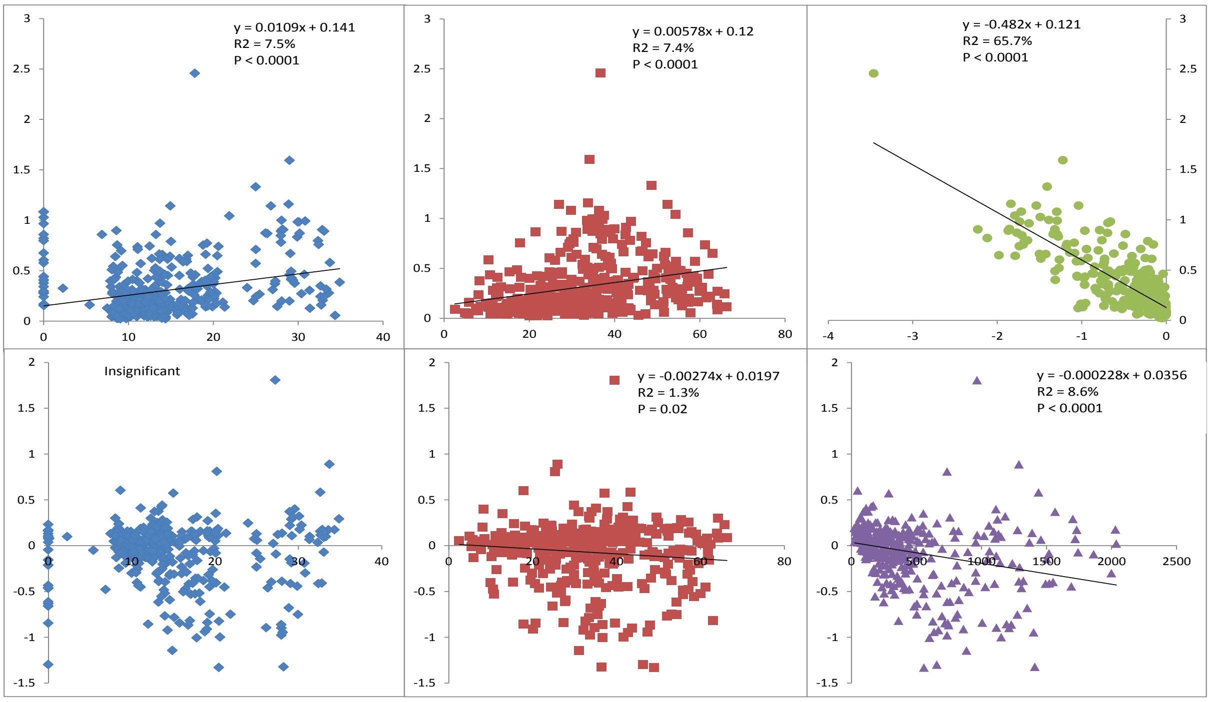


Figure 6.3.2.1 **-** Plots of R_{eco} (top row, g CO_2 m^{-2} h^{-1}) and NEE (bottom row, g CO_2 m^{-2} h^{-1}) (y-axis) versus air temperature (left column, ^{o}C), water table depth (middle column, cm below surface) and P_g (top row, g CO_2 m^{-2} h^{-1}))/PAR (bottom row, µmol s^{-1} m^{-2}) (x-axis) for the acute trial data. Linear regression lines, where significant, are shown.

The ANOVA and ANCOVA results for the chronic trial are summarised in table 6.3.2.1. For R_{eco} the ANOVA and ANCOVA results show that treatment had a significant effect on the datasets of both sites individually and when combined. The specific pattern of results differed slightly between sites (figures 6.3.2.2 and 6.3.2.3). On site C1 R_{eco} on the fertilised only plots (litter removed or not) in the ANOVA models were significantly greater than the litter removed only plots, with the control not being significantly different to any treatment. Changes in the only significant covariate, P_g, in the ANCOVA model of R_{eco} on site C1 appeared to account for about 50% of the observed effect of treatment, with fertiliser apparently increasing the rate of P_g and thus R_{eco}. The remaining effects of treatment seen in the ANCOVA model suggest that even when adjusted for variations in P_g the rate of respiration from the litter removed and fertilised plots was significantly greater than the control and litter removed only plots. On site C2, ANOVA modelling suggested the primary effects of treatment were similar to site C1 with the fertilised plots being significantly greater than the litter removed only plots. However, the effects of treatment had a significant interaction with month. ANCOVA results implied that the only significant covariate, P_g, explained the interaction and further explained about half of the magnitude of the effect of treatment. On site C2 the remaining effects of treatment not accounted for by P_g were that R_{eco} from the fertilised plots was significantly greater than those from the litter removed (fertilised or not) plots.

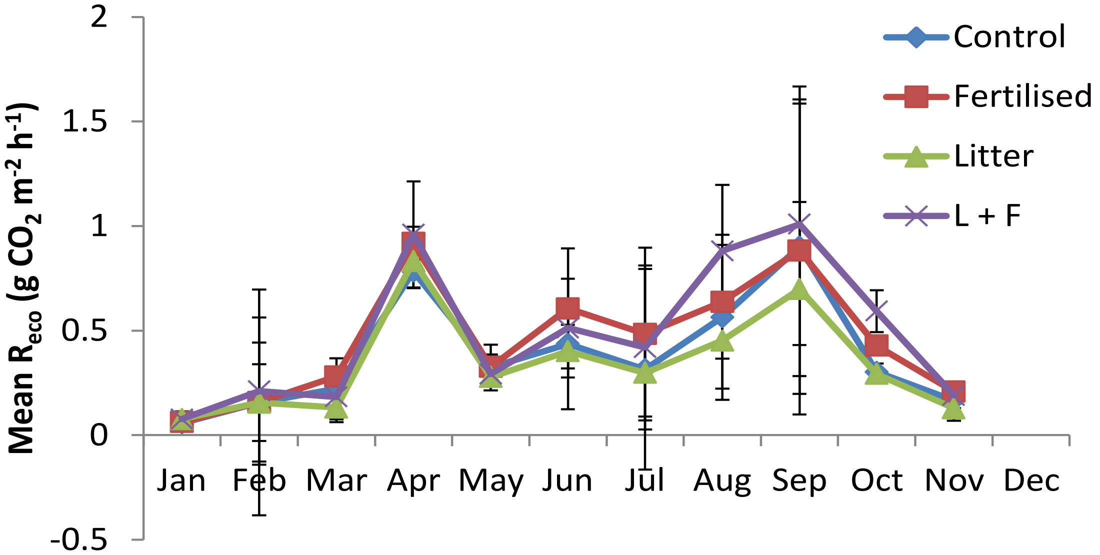


Figure 6.3.2.2 **–** Mean monthly R_{eco} values for each treatment on site C1. The error bars denote one standard error.

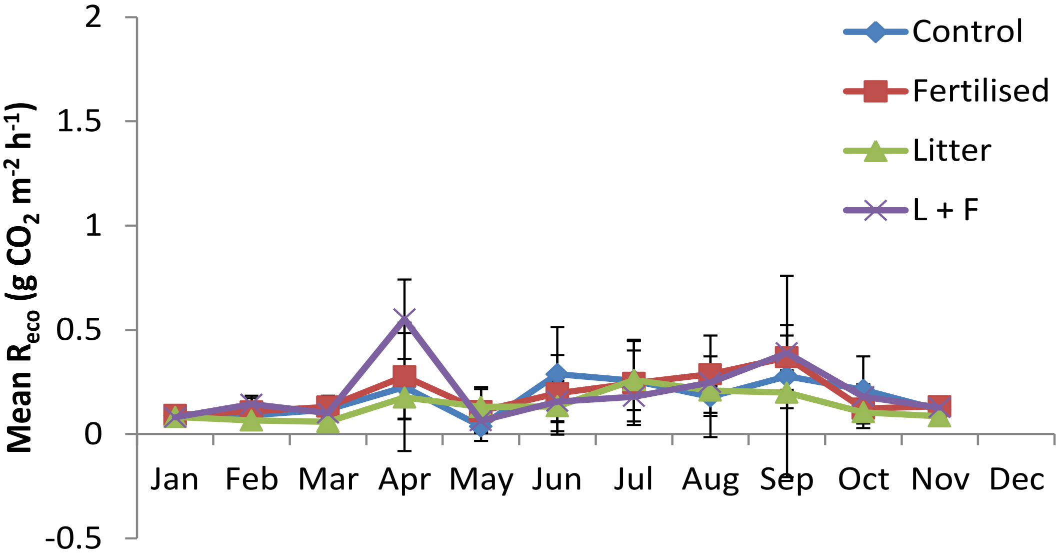


Figure 6.3.2.3 **-** Mean monthly R_{eco} values for each treatment on site C2. The error bars denote one standard error. Axes are identical to figure 6.3.2.1 so as to aid comparison.

The pattern of results for NEE was different to R_{eco} with treatment only having a significant effect on the net exchange of CO_2 from site C2 (i.e. the enhancement in P_g on site C1 counter balanced the increase in R_{eco} with fertilisation). On site C2 ANOVA showed that litter removal (fertilised or unfertilised) led to a positive increase in the value of NEE. Unlike site C1, PAR was not a significant covariate in the NEE ANCOVA model for site C2. Instead P_g alone was significant in the ANCOVA model. Addition of P_g once more accounted for about half of the magnitude of the primary effect of treatment. The residual effect, not accounted for by P_g, indicates that the litter removed plots (fertilised or not) have significantly more positive rates of NEE than the fertilised only plots. Moreover, the litter removed and fertilised treatment has significantly more positive values of NEE than the control.

Table 6.3.2.1 – ANOVA and ANCOVA results for the chronic trial

ANOVA

All Sites

Ln Reco			n	404
Coding	Source	F	P	w2 (%)
FF	**Month**	49.73	0	40.2
FF	**Site**	259.11	0	21.4
FF	**Treatment**	7.08	0	1.5
R-Sq	54.18%			
Tukey	C (a b)	F (a)	L (b)	L + F (a)

NEE			n	409
Coding	Source	F	P	w2 (%)
FF	**Month**	4.7	0	6.0
FF	**Site**	124.96	0	20.3
R-Sq	28.14%			
Tukey	*n/a*			

DOC			n	439
Coding	Source	F	P	w2 (%)
FF	**Month**	18.07	0	26.5
FF	**Site**	16.89	0	2.5
FF	**Pre/Post**	18.8	0	2.8
R-Sq	28.14%			
Tukey	*n/a*			

C1 (Juvenile Calluna)

Ln Reco			n	226
Coding	Source	F	P	w2 (%)
FF	**Month**	62.28	0	71.8
FF	**Treatment**	6.79	0	2.0
R-Sq	75.38%			
Tukey	C (a b)	F (a)	L (b)	L + F (a)

NEE			n	226
Coding	Source	F	P	w2 (%)
FF	**Month**	11.03	0	30.2
FF	**Pre/Post**	5.14	0.024	1.3
R-Sq	34.94%			
Tukey	*n/a*			

DOC			n	245
Coding	Source	F	P	w2 (%)
FF	**Month**	17.23	0	37.4
FF	**Pre/Post**	25.16	0	5.6
R-Sq	45.72%			
Tukey	*n/a*			

C2 (Degenerate Calluna)

Ln Reco			n	178
Coding	Source	F	P	w2 (%)
FF	**Month**	16.35	0	38.9
FF	**Treatment**	3.85	0.011	1.7
IF	**Month*Treatment**	1.73	0.016	5.4
R-Sq	43.86%			
Tukey	C (a b)	F (a)	L (b)	L+F (a b)

NEE			n	183
Coding	Source	F	P	w2 (%)
FF	**Month**	3.71	0	9.7
FF	**Treatment**	7.11	0	6.8
R-Sq	21.42%			
Tukey	C (a)	F (a b)	L (b c)	L + F (c)

DOC			n	194
Coding	Source	F	P	w2 (%)
FF	**Month**	4.33	0	
R-Sq	19.13%			
Tukey	*n/a*			

ANCOVA

All Sites

Ln Reco			n	397
Coding	Source	F	P	w2 (%)
Cov	**Pg**	86.57	0	50.3
FF	**Month**	30.08	0	16.8
FF	**Site**	68.38	0	4.3
FF	**Treatment**	5.6	0.001	1.0
R-Sq	43.86%			
Tukey	C (a b)	F (a)	L (b)	L + F (a)

NEE			n	451
Coding	Source	F	P	w2 (%)
Cov	**Ln PAR**	24.31	0	20.3
Cov	**Pg**	770.96	0	48.6
FF	**Month**	13.98	0	7.6
R-Sq	62.63%			
Tukey	*n/a*			

DOC			n	388
Coding	Source	F	P	w2 (%)
Cov	**400**	19.86	0	11.4
Cov	**Chloride**	8.76	0.003	0.6
Cov	**Sulphate**	8.54	0.004	2.5
Cov	**WTD**	11.49	0.001	9.5
FF	**Month**	8.54	0	12.4
R-Sq	38.70%			
Tukey	*n/a*			

C1 (Juvenile Calluna)

Ln Reco			n	219
Coding	Source	F	P	w2 (%)
Cov	**Pg**	55.62	0	49.1
FF	**Month**	31.29	0	28.7
FF	**Treatment**	4.52	0.004	1.0
R-Sq	80.25%			
Tukey	C (a)	F (a b)	L (a)	L+F (b)

NEE			n	209
Coding	Source	F	P	w2 (%)
Cov	**pH**	5.2	0.024	0.1
Cov	**400**	5.12	0.025	0.6
Cov	**Ln PAR**	31.71	0	34.4
Cov	**Pg**	205.42	0	32.4
FF	**Month**	16.55	0	14.0
R-Sq	82.53%			
Tukey	*n/a*			

DOC			n	180
Coding	Source	F	P	w2 (%)
Cov	**Cond**	7.85	0.006	3.4
Cov	**400**	25.32	0	8.6
Cov	**Sulphate**	7.11	0.008	3.5
Cov	**Air Temp**	4.1	0.044	0.0
FF	**Month**	9.84	0	25.1
FF	**Pre/Post**	8.93	0.003	2.5
R-Sq	48.04%			
Tukey	*n/a*			

C2 (Degenerate Calluna)

Ln Reco			n	178
Coding	Source	F	P	w2 (%)
Cov	**Pg**	55.9	0	24.3
FF	**Month**	15.91	0	32.7
FF	**Treatment**	5.34	0.002	2.9
R-Sq	63.18%			
Tukey	C (a b)	F (a)	L (b)	L+F (b)

NEE			n	179
Coding	Source	F	P	w2 (%)
Cov	**Pg**	92.88	0	27.9
FF	**Month**	9.68	0	21.9
FF	**Treatment**	5.45	0.001	3.5
R-Sq	57.06%			
Tukey	C (a b)	F (a)	L (b c)	L + F (c)

DOC			n	181
Coding	Source	F	P	w2 (%)
Cov	**Cond**	6.26	0.013	4.4
Cov	**400**	26.33	0	7.8
Cov	**Sulphate**	8.52	0.004	2.8
FF	**Month**	10.87	0	27.6
R-Sq	46.41%			
Tukey	*n/a*			

Coding: cov = covariates, IF = interaction factor, FF = fixed facor

Soil pore water DOC concentrations were not significantly affected by any of the treatments. On site C1, in addition to the expected monthly variation, ANOVA showed that there were differences in DOC concentrations between pre- and post-application of the treatments. ANCOVA demonstrated that the differences between pre and post application were partly explained by variations in the significant covariates; Abs_{400}, sulphate, conductivity and air temperature. A similar pattern of results for DOC was apparent for site C2, however pre/post and air temperature were not significant. Apart from that the predictors remain the same between sites C1 and C2, and, on no site were treatments found to have a significant effect.

MLR analysis (table 6.3.2.3) of the R_{eco} dataset by site and treatment revealed that the controls on respiration differed between sites. On site C1 R_{eco} from the control plots was controlled by air temperature and gross photosynthesis. Addition of fertiliser (irrespective of litter removal) caused the plots to be insensitive to air temperature. Litter removal alone did not cause large shifts in sensitivity to the significant predictors. However, litter removal and fertilisation together caused air temperature to cease to be effective and increased the importance of, and sensitivity to, gross photosynthesis in the model. On site C2, R_{eco} on all plots was controlled by gross photosynthesis, however, all treatments were noticeably more sensitive to P_g than their counterparts on site C1. The control plots were only sensitive to P_g. Fertilisation alone caused air temperature and water table depth variations to become significant in the model, whilst increasing the sensitivity and importance of R_{eco} to P_g in the model. Removal of litter led to air temperature becoming significant in the model with the sensitivity to, and importance of P_g, increasing relative to the control. Litter removal and fertilisation caused no apparent changes in sensitivity to P_g relative to the control, however, the importance of P_g in the model increases by a large amount.

Table 6.3.2.3 – MLR results for Chronic Trial R_{eco} data. Numbers in brackets represent the standard error of the mean.

	MLR Coefficient					
	C1			**C2**		
	AT	**WTD**	**Pg**	**AT**	**WTD**	**Pg**
C	0.011	-	-0.357	-	-	-0.682
	(0.004)		(0.045)			(0.308)
F	-	-	-0.39775	0.007	0.004	-0.899
			(0.051)	(0.002)	(0.001)	(0.123)
L	0.007	-	-0.397	0.004	-	-0.874
	(0.003)		(0.064)	(0.001)		(0.141)
L+F	-	-	-0.576	-	-	-0.654
			(0.043)			(0.076)

	Partial Regression Coefficient (%)					
	C1			**C2**		
	AT	**WTD**	**Pg**	**AT**	**WTD**	**Pg**
C	13.30%	-	52.30%	-	-	11.70%
F	-	-	53.20%	25.60%	22.90%	56.40%
L	7.50%	-	43.40%	17.40%	-	46.70%
L+F	-	-	77.00%	**-**	**-**	61.60%

In order to determine more general groupings within the water quality datasets gathered principal component analysis (PCA) was carried out. All the input data were transformed to their z-scores such that variables with differing units could be compared. In order to maximise the dataset size for analysis all data from both sites were amalgamated. Selection of principal components of interest was done by taking the all of the principal components with an eigenvalue greater than one and the first component with a value less than one. In table 6.3.2.3 variables with a large effect on that particular component are highlighted in green. A large effect was defined as a coefficient greater than +/- 0.3. The selection of this level was subjective and does not relate to statistical significance, this is a primary limitation of the PCA approach (e.g. Mazlum et al., 1999). This analysis (table 6.3.2.4) showed that there were five principal components that jointly explain 74.8% of water quality variation.

Table 6.3.2.4 – Loadings of parameters on the first five principal components in the water quality PCA

	PC1	PC2	PC3	PC4	PC5
Z pH	-0.32	0.278	0.112	-0.059	0.609
Z Cond	0.386	0.252	0.28	0.394	-0.015
Z 400	0.478	0.172	0.122	0.117	-0.236
Z E4:E6	0.082	0.134	-0.329	0.628	0.497
Z Nitrate	0.086	0.213	0.707	-0.182	0.155
Z Chloride	0.085	0.621	-0.025	-0.07	-0.067
Z Phosphate	-0.062	-0.428	0.446	0.073	0.308
Z Sulphate	0.265	-0.423	0.136	0.34	-0.024
Z DOC	0.453	-0.116	-0.185	-0.371	0.353
Z Spec Abs	-0.469	0.073	0.185	0.37	-0.278
Eigenvalue	2.4834	1.7757	1.1703	1.1485	0.9008
Proportion	0.248	0.178	0.117	0.115	0.08
Cumulative	0.248	0.426	0.543	0.658	0.748

Table 6.3.2.5 – ω^2 results for Principle Components ANOVA

	Month	**Site**	**Treatment**
PC1	15.39%	5.92%	-
PC2	40.37%	10.00%	-
PC3	14.37%	-	-
PC4	13.76%	1.77%	2.91%
PC5	5.74%	-	-

Component 1 (PC1) accounted for 24.8% of water quality variation. Most important in the component were variables related to DOC (i.e. DOC, Abs$_{400}$, specific absorbance) and soil moisture (i.e. pH and conductivity), ANOVA (table 6.3.2.5) of the component showed that treatment had no significant effect. Month and site accounted for 15.39% and 5.92% of PC1 variation respectively.

Component 2 (PC2) accounted for 17.8% of water quality variation. Most important in the component were variables related to nutrient status (i.e. phosphate and sulphate). ANOVA of the component showed that treatment had no significant effect. Month and site accounted for 40.37% and 10.00% of PC2 variation respectively.

Component 3 (PC3) accounted for 11.7% of water quality variation. Most important in the component were variables related to the nutrients added to the fertilised plots (i.e. nitrate and phosphate) and DOC humification (i.e. E4:E6). However, despite nitrate and phosphate being important in PC3 there were no significant effects of treatment observed in the ANOVA. Month alone accounted for 14.37% of PC3 variation.

Component 4 (PC4) accounted for 11.5% of water quality variation. Most important in the component were variables relating to DOC (i.e. DOC, E4:E6) and ionic/nutrient status (i.e. conductivity, sulphate). This was the only component where ANOVA showed that treatment explained a significant fraction of dataset variation. Month, site and treatment accounted for 13.76%, 1.77% and 2.91% of PC4 variation respectively.

Component 5 (PC5) accounted for 8% of water quality variation. Most important in the component were DOC (i.e. DOC, E4:E6) and nutrient status (i.e. pH, phosphate). Treatment was not significant in ANOVA with month alone accounting for 5.74% of PC5 variation.

Examination of the C:N ratios of the *C. vulgaris* and peat (5 cm depth) samples showed that the data gathered in this chapter are comparable to those in chapter 3. The ANOVA demonstrated that treatment had a significant effect upon the C:N ratios of the *C. vulgaris* samples but not the peat samples. The model (table 6.3.2.6) shows that treatment alone accounts of 10.8% of dataset variation. Additionally, the interaction between material (i.e. peat or *C. vulgaris*) and treatment accounts for a further 9.8% and site had no significant effect. The *post hoc* Tukey comparisons showed that, in general, the fertilised plots were more enriched in N relative to the unfertilised plots (figure 6.3.2.4). Litter removal appeared to make little difference overall.

Table 6.3.2.6 – ANOVA results for the C:N data

C:N ANOVA				
Source	**DF**	**F**	**P**	**w2**
Treatment	3	6.68	<0.0001	10.8%
Material	1	26.23	<0.0001	11.6%
Treatment*Material	3	7.99	<0.0001	9.8%
R-Sq	35.65%			
Tukey: C (ab) F (b) L (a) L+F (b)				

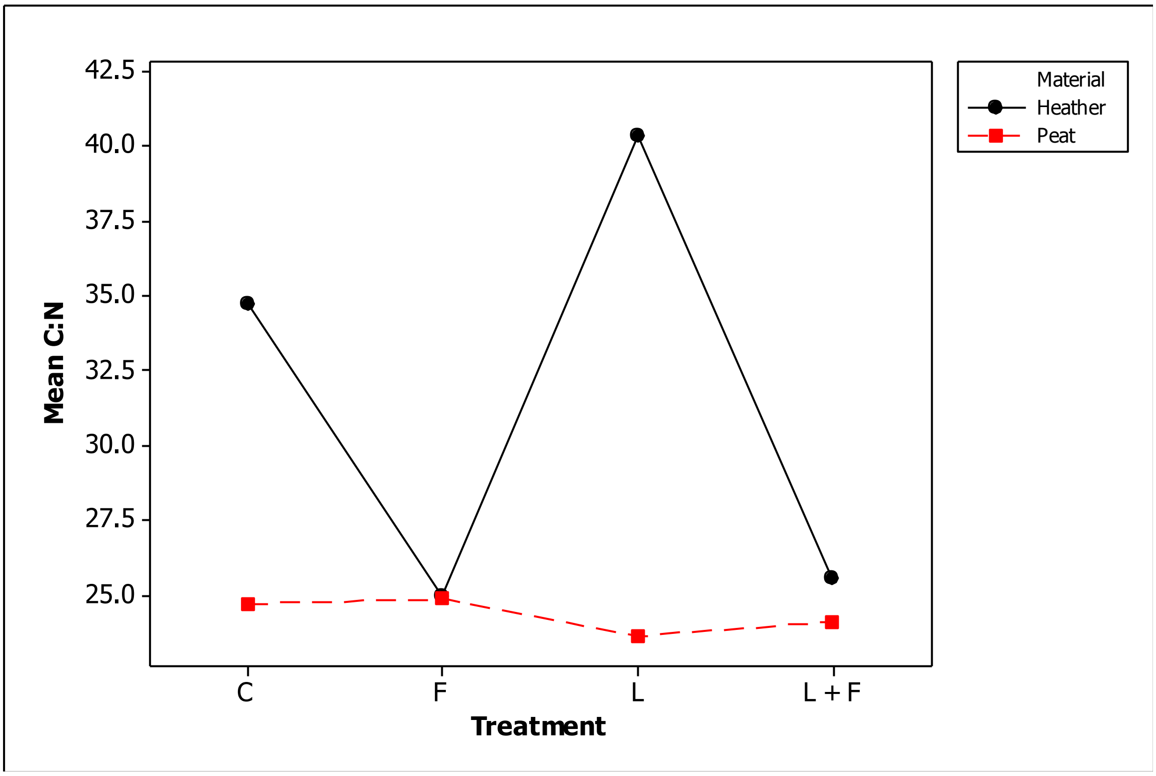


***Figure 6.3.2.4* –** Interactions plot showing the effects of treatment on intra-plot mean C:N by material.

6.4 – Discussion

In respect of the hypothetical predictions made earlier, the observations in the acute trial gave a mixed set of results, with differences between the sites. On site A1 addition of glucose, with or without fertiliser, caused an increase in the magnitude R_{eco}; this conformed to hypothetical predictions and previous research (e.g. Bremer and Kuikman, 1993; Hoyle et al., 2008; Larionova et al., 2007; Sparling et al., 1981). Moreover, addition of glucose to the plots caused an apparent increase in the sensitivity of R_{eco} to air temperature. This was expected and is supported by the findings of other studies (Gershenson et al., 2009; Larionova et al., 2007). The major point of difference between the hypotheses established and the outcomes observed were in respect of the sensitivity of R_{eco} to P_g when glucose has been added. It was expected that the sensitivity of R_{eco} to P_g would reduce; however, the opposite was shown to be true, where the addition of glucose to the soil increased the modelled sensitivity of R_{eco} to P_g. In order to investigate why this result had occurred additional ANOVA and *post hoc* Tukey tests on the P_g dataset were carried out. These tests demonstrated that the rate of photosynthesis had increased significantly on the plots that had glucose added (figure 6.4.2) regardless of fertilisation. This implied that glucose, in the high quantities applied, was acting as a fertiliser.

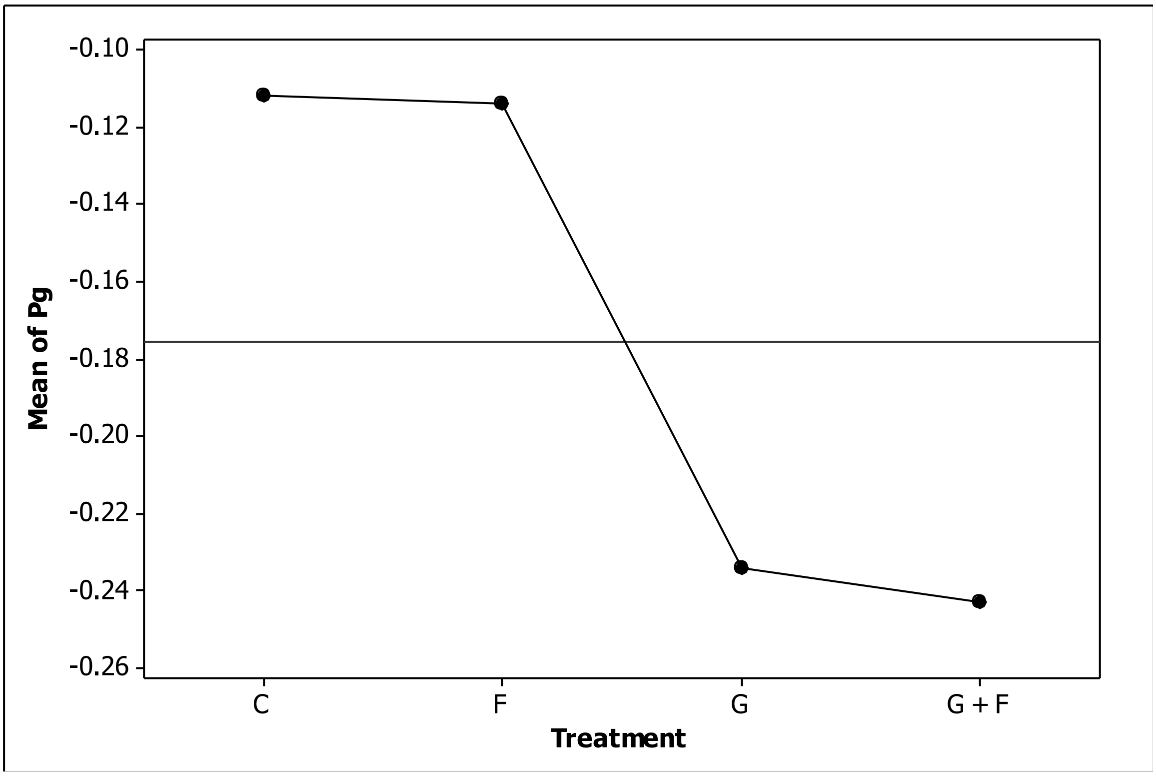


Figure 6.4.2 **–** Main effects plot showing mean P_g by treatment for site A1. The treatments with glucose are significantly different to the treatments without.

As noted above, the increases in photosynthesis were unexpected and imply that glucose acts as a fertiliser in *E. vaginatum* blanket peat environments. This result may be explained by evidence from Keeling et al. (1996) who demonstrated that low concentrations (0.028 M) of glucose added to *Lolium perenne* (perennial ryegrass) significantly increased dry matter yields (i.e. biomass production). The explanation given for their result was that a permanent source of labile C in the soil allowed asymbiotic N_2-fixation to occur thereby increasing available N for the plant. Their proposed mechanism, however, was entirely hypothetical. While this chapter has found a similar result to the Keeling et al. (1996) study, there are two important differences: firstly the effect found in Keeling et al. (1996) was over an annual timescale with only small differences in the first few weeks; and secondly, only the lower of two doses of glucose (which were both lower than this study) was effective at increasing plant productivity. As such, it seems unlikely that the mechanism invoked to explain the Keeling et al. (1996) result can be invoked in the case of this study.

Given this, it is necessary to find an alternate explanation; however, as glucose is a by-product of photosynthesis, it is hard to imagine why glucose in the soil zone would increase photosynthesis. The work of Kuzyakov and Jones (2006) demonstrated that maize roots are able to directly remove glucose from soil water. They noted that there would be intense competition for low molecular weight compounds (i.e. glucose) from soil micro-organisms which would reduce the efficiency of this process but that despite this up to 8% of added C was taken in by the plant roots. However, as the experiment performed in this chapter added a very large amount of glucose to the soil, in a single pulse, it could be argued that this limitation may no longer apply. Thus, the plant roots may be taking up a proportion of the glucose added. However, this potential uptake of glucose by plant roots does not explain why plant productivity increases or why R_{eco} would become more sensitive to photosynthesis. Work by Takahashi et al. (2003), however, suggested that glucose (and other low molecular weight sugars) induce adventitious root (i.e. out of sequence with the primary root path) growth in hydroponically grown *Arabidopsis* spp. It is possible to speculate that a similar process of plant growth induction could have taken place in this study explaining the need for additional atmospheric carbon fixation to provide the raw material to support this growth. However, this hypothesis is untestable with the current dataset and as such remains, at best, speculative.

Analysis of the DOC dataset for site A1 revealed that only the combination of glucose and fertiliser caused a significant difference relative to the control. Box plots of DOC by treatment (figure 6.3.1.8) suggests that both the glucose and glucose + fertiliser treatments increase the total concentration of DOC in the soil pore water, which is to be expected as glucose is highly soluble in water. These results confirm that some of the glucose did make it to the soil pore water rather than being left on the surface. There was not enough soil pore water data from site A2 to make an analysis of the DOC concentrations possible.

On site A2 the application of glucose and/or fertiliser caused increases in the magnitude of R_{eco} relative to the control, in line with the working hypotheses. In addition, these treatments also increased the sensitivity of R_{eco} to P_g. Respiration from the control plots was insensitive to P_g so, in the case of site A2, finding a significant relationship between R_{eco} and P_g was enough to confirm an increase in sensitivity. This finding is again in line with the predictions made earlier in this chapter. Fertilisation was found to have the largest effect on R_{eco} sensitivity to P_g, increasing the coefficient to a value greater than one. This implies that more than 100% of the total amount of photosynthesis is being given out again as respiration. An interpretation for this effect is that fertilisation increases microbial biomass which will also increase the utilisation of the peat itself as a substrate. Hardie et al., (2009) demonstrated that respiration of 'old' carbon (i.e. carbon derived from the peat soil itself) was a significant fraction of the overall R_{eco} flux from a similar upland UK environment, accounting for about 10-23% of the total R_{eco} flux. This finding supports the interpretation given above. However, this is not to say that the fertilisation has caused respiration of peat substrates to begin, as respiration is greater than zero on the control plots, merely, that fertilisation has caused an increase in a process already ongoing within the soil. In addition, the application of glucose (with or without fertiliser) increased R_{eco} sensitivity to P_g, but not by as much as fertiliser alone. This could imply that the soil micro-organisms respired the glucose preferentially, thus making ecosystem respiration less sensitive to the supply of photosynthate than treatments without fertiliser, a finding in agreement with earlier predictions.

As the only organisms actively photosynthesising on the plots of site A2 were surficial algae (see also chapter 4), it is likely that the transfer of recent photosynthate to the soil zone through exudation is negligible. Therefore, another explanation is needed to explain the magnitude of the enhancement of R_{eco} sensitivity to P_g on the fertilised only plots. A plausible explanation is that while, in this case, P_g does not directly drive R_{eco}, the rate of P_g covaries with drivers (e.g. soil temperature, soil moisture) that also pose a control on R_{eco} and that R_{eco} in the presence of fertiliser has become more sensitive to these drivers, rather than P_g itself. Thus, P_g and R_{eco} correlate while still being mechanistically (in a biochemical sense) independent. Another explanation could be that R_{eco} and P_g are only correlated due to 'self-correlation' (see chapter 2) and thus the model coefficients have no meaning. However, as the existence of the P_g-R_{eco} relationship is widely accepted (e.g. Raich and Tufekcioglu, 2000), has been reported elsewhere (e.g. Hogberg et al., 2001; Tang et al., 2005) and has been used to improve models of R_{eco} (e.g. Larsen et al., 2007) this seems unlikely. Moreover, the measurement protocols used in this thesis (chapter 2) were established on the basis of literature recommendations that were designed to minimise the issue of 'self-correlation'. Indeed, all CO_2 fluxes, be they R_{eco} or NEE, were measured using standard protocols and subject to subsequent data quality control procedures (i.e. removal of outliers and logically inconsistent values). Furthermore, where fertiliser has been employed with glucose, the sensitivity of R_{eco} to P_g is within errors of plots where glucose alone had been applied. This effect was consistent between sites and thus it would be highly coincidental for it to be due to the issue of self-correlation. Hence, this would imply that, at the dosage rates employed, the supply of labile substrates was more important than fertilisation on the time scale of the acute trial because the effect of fertiliser appears to have been overprinted by the effect of glucose.

Enhancement of autotrophic respiration by the treatments on site A2 is thought to be minimal as the site was bare and any ongoing photosynthesis on this site has been attributed (in chapter 4) to the presence of surficial algae. Thus, on site A2 at least, it can be said that application of glucose has increased heterotrophic respiration. On site A1, however, the MLR results suggested an increase in autotrophic respiration (i.e. that closely coupled to photosynthesis). As such, it appears that the manipulations enhanced both respiratory pathways, but on vegetated sites autotrophic respiration may be more important than heterotrophic respiration. This interpretation is in line with a literature review by Ryan and Law (2005) where it was shown that autotrophic respiration is generally the more important pathway of soil respiration (when compared to heterotrophic respiration).

Modelling of R_{eco} on both sites using the ANCOVA models provided a method to estimate how much CO_2 was respired from the system over the initial monitoring period of the experiment. For site A1, there were interactions between treatment and date in the ANCOVA model. These interactions reflected the fact that the effects of the treatments were largest in the first three days post application, with a decreasing trend in the subsequent days (figure 6.3.1.10). There is a slight increase in the final three days of the primary monitoring period, which likely reflects the rainfall on these days dissolving and transporting precipitated residues of the treatments from the ground surface to the soil water.

Overall, the control plots gave out a total of 1.67 g C quadrat^{-1}, the glucose and glucose + fertilised plots (i.e. the plots that were significantly different to the control) gave out 7.18 and 8.05 g C quadrat^{-1} respectively. Taking into account the baseline rate of respiration (i.e. the control plots) and the amount of C added from glucose (i.e. 23.32 g C) the glucose and glucose + fertilised plots gave out 17.81 and 16.84 g C less than they received from glucose respectively. As the glucose added was not labelled it is impossible to determine; how much of the glucose was used directly for respiration, how much was lost from the system in soil water and how much was left in the soil.

Figure 6.3.1.10 shows that the glucose + fertilised plots appeared to have greater rates of R_{eco} than the control on the final monitoring campaign (i.e. 58 days after the initial application). Given that the glucose only treatment seemed to have returned to control plot levels by 23 days after application, it seems unlikely that respiration of added glucose was responsible for this effect. As such, it is reasonable to speculate that the addition of labile substrates (i.e. glucose) in combination with fertiliser increased the soil microbial biomass which thus caused the soil microbial community to mineralise the peat substrates at a faster rate (Sparling et al., 1981). However, without directly measuring the soil microbial biomass it is impossible to prove this conjecture.

Site A2 lacked the interaction between date and treatment, suggesting that the system was more nutrient and substrate limited than A1, hence the longer duration of treatment effects relative to the vegetated site A1. This makes sense as A2 is completely bare and a legacy of surface erosion has exposed relatively recalcitrant, former catotelm peat, reducing overall respiratory activity, when compared with vegetated sites (chapter 4). The total amount of C respired from the control plots on site A2 was 0.87 g C quadrat^{-1}. The fertilised, glucose and glucose + fertilised plots respired 1.36, 1.60, 1.61 g C quadrat^{-1} respectively. Taking into account baseline respiration (i.e. respiration levels from the control plots) and the amount of carbon added, the fertilised plots respired 0.49 g C quadrat^{-1} more than the control (table 6.3.1.2) whereas the glucose and glucose + fertilised plots respired 22.59 and 22.58 g C quadrat^{-1} less than the amount of C added. Supporting the suggestion that the impacts of the treatments were longer lived on site A2 than site A1 is figure 6.3.1.12 which shows that all non-control treatments appear to be greater than the control up to and most likely after the last monitoring campaign. A potential explanation for the lack of a significant effect of fertilisation on site A1 is that *Eriophorum* spp. is known to be a relatively good sink of nutrients through its nutrient-rich litter (Silvan et al., 2004) and as such the fertiliser added may have been relatively superfluous.

The chronic trial manipulations produced results which indicated the null hypothesis was most appropriate. The null hypothesis was accepted on all occasions apart from site C1, where the working hypothesis was accepted for the R_{eco}-P_g sensitivity test on the litter removed and fertilised plots. These results imply that research hypotheses posed should be rejected however this may represent a type II error if the experimental manipulations were not of sufficient magnitude to produce the shifts expected. Careful examination of the results suggests that this explanation may be correct. The reason for this is that, while the treatments were (mostly) not significantly different to the control, there were significant differences between the treatments themselves, which were in line with expectations. For example on site C1 the litter removed plots had significantly lower R_{eco} than the fertilised plots. This is to be expected as removing litter removes a source of nutrients and labile carbon and as such suppression of R_{eco} is expected. This should be especially evident when compared to plots that have been fertilised as the metabolic rate of the plants and soil micro-organisms should be enhanced. Another reason to believe that the modelling interpretations are valid is that when comparing treatments between site C1 and site C2 it can be seen that R_{eco} on site C2 is more sensitive to P_g than on site C1. This makes sense as the total amount of biomass on site C2 was much greater than on C1, given the differing stand ages of *C. vulgaris* present. Increasing amounts of biomass on the plots would be expected to increase both the amount of autotrophic and heterotrophic respiration due to photosynthesis, thus making the system more sensitive to the R_{eco}-P_g relationship. In addition to the effects on R_{eco}, the treatments were found to have significantly affected the nitrogen contents of the *C. vulgaris*, with the fertilised plots having significantly lower C:N ratios than the unfertilised plots (figure 6.3.2.3 and table 6.3.2.6). This implies that the litter produced by the *C. vulgaris* exposed to the fertiliser will be more decomposable than that produced by the unfertilised plants (e.g. Aerts et al., 1995).

The overall pattern of results from the PCA and subsequent ANOVA implied that water quality variation is mainly driven by monthly (i.e. seasonally) varying processes. DOC concentration and composition dominates two of three most important components and as such could be argued to be the most important aspect of annual water quality variation. Nutrient levels were also found to be important, but perhaps not to the same extent as DOC. The most important finding from this analysis is that treatment was only found to be very weakly effective on the fourth principal component, leading to the conclusion that water quality and gas fluxes are somewhat decoupled as there has been a lot more evidence found for treatment effects on CO_2 fluxes. Indeed, DOC was not found in any of the ANOVAs to be significantly different with respect to treatment.

6.5 – Conclusions

This chapter has produced some intriguing findings. Working hypotheses set up to test whether the manipulations undertaken would be recognised in changes in magnitude and modelled sensitivity of R_{eco} to P_g were fulfilled on almost all occasions in the acute trial. Unexpected effects of glucose addition on plant photosynthetic activity were found, however; these effects did not suggest a problem with the modelling technique rather they demonstrated that the system was more complex than initially conceived. In fact, it was the unexpected increase in the sensitivity coefficient between R_{eco} and P_g that gave the first evidence that photosynthesis had been enhanced by glucose. This interpretation was subsequently confirmed by ANOVA. The implications of this finding may be important from the perspective of upland blanket peat restoration and further work to determine whether this glucose fertilisation is repeatable in laboratory conditions is recommended.

The chronic trial was not successful in producing the expected pattern of result with respect to the control plots with the null hypothesis being accepted on all but one occasion. However, detailed examination of the ANOVA/ANCOVA results suggested that, while the treatments themselves were not of sufficient magnitude to shift the system significantly with respect to the control they were of sufficient magnitude to shift the treatments in the expected directions with respect to each other.

Improvements to this experiment, implied by the results, are that the dosage rate of fertiliser should be increased (in both trials) as there was little evidence for a fertilisation effect. Moreover, the dose of glucose may have been larger than necessary in the acute trial; thus, a repeat experiment would reduce this dosage or apply the glucose in varying dosages in order to examine the effects of labile substrate additions in more detail. However, despite the limitations of this experiment, the results implied that the MLR approach to investigating is robust and is reflective of ongoing processes within the system.

7 – Conclusions

7.1 – Overview of Thesis

The central goal of this research has been to investigate and refine the understanding of carbon cycling processes, particularly as they relate to CO_2 flux, from upland blanket peat in the Peak District/South Pennine areas of England. The motivation for such research has been, in part, to provide real world data to inform decisions regarding what factors should be introduced into the Durham Carbon Model (DCM) and more broadly to provide insights into management and conservation issues in this region.

Of course, there are many processes and factors that affect carbon cycling on peatlands, and this thesis was never intended to provide a comprehensive account of them all. Instead, it has identified and studied a number of important areas not currently considered in the DCM. In addition to this, novel, in-field experiments were set up to manipulate the peatland carbon cycle and investigate the physical interpretability of the MLR modelling framework, which is frequently used in the sub-model terms within the Durham Carbon Model.

The remainder of this chapter will give an account of the key objectives, implications and conclusions of this thesis alongside a discussion of the principal limitations and areas for further work.

7.2 – Key Objectives

- Chapter 3 – The Role of Altitude. An assessment was made, employing two different experimental set ups, to determine whether a relationship between altitude and CO_2 flux was present, which was not explained by variations in the other predictive variables measured, i.e. an intrinsic effect of altitude.

- Chapter 4 – The Role of Vegetation. This chapter used a dataset of CO_2 flux, with DOC concentration and (limited) CH_4 data to study the comparative effects of vegetation type on carbon sources and fluxes. The second objective was to discern whether the canopy height of *C. vulgaris* had a significant effect on CO_2 flux or DOC concentration. The third objective was to compare the fits of literature models and empirically derived models of R_{eco} between vegetation types and models.
- Chapter 5 – The Role of Diurnal Processes. The primary goal of this chapter was to characterise what processes control CO_2 flux on a diurnal time scale, as all previous research in this thesis had been at a monthly time-scale. As a part of this analysis, the temporal dynamics of the relationship between R_{eco} and P_g were investigated.
- Chapter 6 – Manipulation Trials. Operating on differing time scales and using differing methods, the objective of these trials was to investigate the robustness of the assumption that empirically derived models of R_{eco} can be physically interpretable.

7.3 – Key Findings

7.3.1 – The Role of Altitude

This chapter presented results from the first study to investigate the role of altitude in UK blanket peat carbon cycling. The aim was to identify whether a statistically significant altitudinal trend was apparent in CO_2 flux datasets, when the effects of other environmental variables and factors were taken into account. The experiment consisted of two parts: part one used existing monitoring sites, covering a range of vegetation types, altitudes and localities, to investigate the effects of altitude (in aggregate and by vegetation type); part two used a transect of sites installed down the flank of the Goyt Valley in degenerate *C. vulgaris* specifically for the experiment.

Given the limitations imposed by the design of experiment I and the use of P_g as a predictor in experiments I and II, four distinct statistical techniques were employed to investigate the effects of altitude. In experiment I, altitude was found to have a general effect on R_{eco} within the whole dataset of about 4-9% of dataset variation. When the dataset was broken into subsets by vegetation type, it was apparent that rooting *Calluna vulgaris* (in experiments I and II) was insensitive to variations in altitude (in both experiments) while non-rooting bryophytes were the most sensitive to altitude. The importance of the effect found varied between vegetation types from no effect for *C. vulgaris* to 10-13% of variance explained for *Sphagnum* spp, the average effect being 4-9% of dataset variation. Despite the use of different statistical methods to investigate the effect of altitude, it was apparent that all estimates of a R_{eco} dataset's sensitivity to altitude were similar regardless of design, implying that the estimates were not biased by experimental limitations. Altitude was generally less important in NEE than R_{eco} and the results partly suggested that it was in fact the R_{eco} component of NEE responding to altitude.

Overall, the results suggested that altitude does indeed exert some control on CO_2 flux from blanket peat. The effect of this control is to reduce CO_2 losses as altitude increases (i.e. R_{eco} and NEE become more negative). The effect observed, however, differs between vegetation types and these differences may, in part, be attributable to rooting depth. Moreover, the effect observed was much larger than the effect expected if it were due solely to a lapse rate in air temperature.

7.3.2 – The Role of Vegetation

This chapter presented the results from the largest, in situ, comparative study of the role of vegetation in carbon cycling on Peak District/South Pennines region (and perhaps on UK as a whole) upland blanket peat. The chapter was split into three general sections: firstly, it investigated CO_2, CH_4 and DOC datasets to determine whether there were differences between common upland vegetation types in terms of carbon cycling. Secondly, the role of *C. vulgaris* canopy height was investigated with respect to CO_2 flux and DOC concentration. Finally, a comparison between the MLR modelling technique utilised in this thesis and more generally in the sub-models of the DCM and literature derived, theoretical (process-based) models of R_{eco} flux was presented.

Fluxes of CO_2 and soil pore water DOC concentrations were shown to significantly differ between vegetation types. The data for CH_4 were of very low temporal resolution but a qualitative assessment suggested that differences may also exist between some vegetation types with respect to this carbon flux pathway. *Molinia caerulea* was shown to be the least preferable species from a CO_2 flux perspective, having uniformly greater fluxes of CO_2 to the atmosphere (in both a net and gross sense) than all other vegetation types studied. Bare peat was shown to have the lowest R_{eco} fluxes, close to zero NEE and relatively low concentrations of soil pore water when compared to the other groups. Encouragingly (from a peatland restoration perspective), areas of bare peat sown with lawn grass seed were found to have the largest net daylight hours sink of CO_2 while also having low soil pore water concentrations of DOC. This result is encouraging from a carbon perspective, however, it should be borne in mind that this is a transient vegetation state. Nonetheless sowing lawn grass and thus allowing re-vegetation on bare peat surfaces may, in time, allow for the establishment of upland species and thus be of benefit from a biodiversity perspective. When looking at the vegetation types most typical of upland conditions (i.e. ignoring bare peat and re-vegetated areas), it was apparent that *Sphagnum* spp. represented the only daylight hours sink of CO_2, *Eriophorum* spp. had a rate of NEE of close to zero, with the remaining vegetation types all being net daylight hours sources of CO_2.

The results of the *C. vulgaris* canopy height section of this chapter showed that canopy height can be used as a predictor of a peatland's carbon cycling status (with respect to CO_2 flux and DOC concentration). The key finding of this investigation was that canopy heights in excess of 30 cm are indicative of relatively high rates of net CO_2 emission to the atmosphere and high soil-pore water concentrations of DOC. From a CO_2 perspective it was apparent that as the canopy height increased the ratio of P_g/R_{eco} decreases progressively from values greater than 1 (i.e. more P_g than R_{eco} between 0-20 cm to values less than 1 (i.e. more R_{eco} than P_g) between 20-40 cm.

The modelling section of this chapter demonstrated that MLR models of CO_2 flux, derived from two thirds of the observed data and validated against the remaining third of the data, fit the data better than equivalent theoretical models of R_{eco}/NEE. Using the MLR modelling framework also provided more insights into differing environmental controls on CO_2 flux than using theoretical models whose predictive variables are rigidly defined. Models of R_{eco} using P_g as a predictor, MLR or theoretical, were uniformly found to predict R_{eco} better than those without. If, bearing in mind the potential for self-correlation, this result represents a real dependency of R_{eco} on P_g then this implies that there is a component of the relationship between R_{eco} and P_g that varies on a seasonal timescale, rather than it simply being a diurnal relationship.

7.3.3 – The Role of Diurnal Processes

The motivation for this chapter was two-fold. Firstly, when considering carbon balance the DCM has thus far been calibrated to monthly data only and as such it was felt that it was important to investigate the dynamics of CO_2 flux on a diurnal time-scale in the South Pennies/Peak District region order to make recommendations for modifying the DCM to deal with diurnal time-scale variation. Secondly, within the confines of the discussion related to self-correlation, the relationship between P_g and R_{eco} has so far only been demonstrated on a monthly/seasonal time-scale in this thesis. A mechanism invoked to explain diurnal scale relationships between P_g and R_{eco} in other temperate ecosystems relates to below-ground transfers of recently assimilated photosynthates. If a relationship between P_g and R_{eco} was apparent on a diurnal time scale on blanket peatlands, and such a mechanism was wholly or partly responsible for it, then there may be a lag time between P_g and R_{eco}. As such, the second aim of this chapter was to establish whether such a lag exists.

Comparing the means of R_{eco} from the all day time and all night time data demonstrated that, for the cycles where enough data were obtained, there was no significant difference in flux magnitude between night and day. However, this masks to some extent individual hours, usually 12:00-13:00, during the day time when R_{eco} was significantly greater than the rest. As such, this implied that in order to use daytime fluxes to approximate night time fluxes, data would have to be collected in the mid-morning or late-afternoon in order to minimise biases.

It was found that daytime and night-time rates of R_{eco} were controlled by different processes. Mirroring the findings of other chapters in this thesis, P_g was found to be the most important predictor of R_{eco} during daytime hours. The other predictors of daytime R_{eco} varied between cycles, but were generally related to the meteorological conditions during the sampling hours. In contrast to the daytime models, the night-time models of R_{eco} had fewer significant predictors with water table depth (July and August), and to a much smaller extent air temperature (June) being the only significant night time covariates.

The incorporation of a lagged P_g term into full cycle (i.e. night and day) MLR models improved overall model fits, and in the June sampling run, when it did not rain during the sampling period, including a lag effect noticeably reduced the magnitude of model underestimation during the hours of darkness. Cross-correlation analysis of P_g-R_{eco} demonstrated that a significant lag effect was apparent with a magnitude of ~3 hours in both raw and residual analyses in June. This effect was not repeated in the two subsequent months, which may be related to rainfall and consequent sub-optimal conditions for the production of photosynthates in those months.

7.3.4 – Manipulation Trials

This chapter presents the results of novel, in-situ experimental manipulations of the blanket peat ecosystem, which to the author’s knowledge have not been carried out elsewhere. Following on from the idea examined in chapter 5, this chapter aimed to investigate the link between P_g and R_{eco}

in terms of below-ground carbon cycling. Additions/subtractions of labile substrate (with and without fertiliser) were made to investigate whether R_{eco} becomes less/more sensitive to P_g as a result. MLR analyses (alongside ANCOVA) were used to investigate the effects of the manipulations and as such the results of this chapter also presented a chance to investigate whether the MLR approach can be said to be physically interpretable

The principal conclusion of this chapter is that structural, empirical MLR modelling of R_{eco} does appear to be physically interpretable in that changes in the coefficients in the model appear to reflect actual changes in the ecosystem. Indeed, hypothetical predictions about the ecosystem were largely accepted in the acute trial. However, the experimental hypotheses in the chronic trial were generally rejected with respect to the control. Nonetheless, there were significant differences between the treatment levels themselves in the chronic trial. Thus, the fact few differences were found between treatments and the control was attributed to limitations within the experimental treatments applied, rather than a failure of the model itself. In this acute trial the additions of glucose to the ecosystem, regardless of fertiliser, led to an apparent fertilisation effect leading R_{eco} to have an enhanced sensitivity to P_g.

7.4 – Principal Limitations

Every experimental study can be improved with a greater number of replicate readings or longer time series etc. This section aims to cover limitations of the datasets used in this thesis that should be borne in mind when considering the conclusions being drawn from these results.

- ***Self-Correlation*** – this issue has been discussed throughout the thesis. The assumption has been made that the issue of self-correlation is minimised by the experimental method and data quality controls; however, there are no data provided in this thesis to unequivocally confirm this assumption. Thus, it is important to bear in mind that all results and subsequent interpretations pertaining to regressions between R_{eco}/NEE and P_g are subject to the caveat that self-correlation has been minimised and thus its magnitude is small relative to the magnitude of the real relationship.

- ***Site Disturbance*** – the installation of dip-wells and gas collars into the peat inevitably disturbs the carbon cycle of the peat profile in the vicinity of these pieces of equipment. The principal issues relate to damage done to root systems and subsequent modifications to the growth of the vegetation in the area. The effects of this disturbance are dealt with, partly, by leaving the site to settle for at least one month after initial installation. Aside from disturbance related to equipment installation, frequent visits to and flux sampling on the sites will have inevitably disturbed the vegetation. All that could be done to minimise these effects was to take care when moving around the site and setting up flux monitoring equipment.
- ***Site Setup*** – the datasets employed for the altitude (chapter 3) and vegetation (chapter 4) studies were amalgams of data taken from sites that were not necessarily designed with the objective of investigating vegetation or altitude. As such, the setup of ANOVA and ANCOVA models had to be carefully designed in order to avoid including factors that are not cross-classified.
- ***Temporal Overlap*** – following on from the previous point, the amalgamated datasets suffer from a lack of temporal overlap between some sites. This has meant that 'year' could not be considered as a fixed factor in ANOVA/ANCOVA models. While it has been considered as a random factor, this method of analysis has less power than a full factorial design with year as a fixed factor.
- ***Confounded Factors*** – for a fully factorial ANOVA/ANCOVA to be valid all factors must be cross-classified, that is, all levels of each factor must be present in the levels of every other factor. In many cases, when looking at vegetation types, sites would only contain one vegetation type. Occasionally, more than one vegetation type would be sampled on a site;

however, there was never a site that sampled all vegetation types considered in this thesis. This limitation is impossible to get around when the distribution of vegetation in the uplands is considered as it is highly unlikely that so many, functionally different vegetation types will be present on a small enough area of land to fit into a single site. Thus, ‘site’ was never considered as a discrete factor in ANOVA/ANCOVA models. This means the effects of being on different sites will not have been removed from the ‘vegetation’ factors and as such it can be said that these factors are confounded.

- ***Uncontrolled Variables*** – the manipulation (chapter 6) study deals with in situ experimental manipulations of the carbon cycle. While the novel part of these experiments was that they were conducted in situ, this experimental setup is limited by the issue of uncontrolled variables. The benefit of working in a laboratory is that many variables, i.e. water table, sunlight, temperature, wind speed etc. could be directly controlled and manipulated. In situ experiments cannot control for these variables. However, the experimental design employed replicated treatments that were compared to a control such that the prevailing environmental conditions on each plot were roughly similar.
- ***Homogeneity and Distribution of Replicates*** – when establishing replicate plots on sites the issue of replicate homogeneity has had to be considered. In studies where sampling a particular vegetation/ground cover type was important, plots were installed in areas where the pre-existing vegetative cover and density (as judged by eye) was similar. After installing plots into areas with similar amounts of *Eriophorum* spp., the distribution of the experimental plots in the manipulation trials (chapter 6) was determined by the following rule: that no plot could be installed in the same column or row as a plot of the same treatment (in a this would satisfy a Latin-Square design if enough there were the same number of rows as columns). In this way biases due to poor homogeneity and uneven distributions of replicates were minimised.

7.5 – Implications

7.5.1 – Management and Conservation

Peatlands are complex and dynamic ecosystems; aside from their aesthetic, economic and cultural value they provide important ecological functions as a habitat for diverse and in many cases rare wildlife, a storage component within the hydrological cycle and as an important capacitor within the terrestrial carbon cycle. It is this latter role that the research in this thesis has paid most attention to. However, the findings of this research fit into the wider narrative of peatland conversation.

Charman (2002) defined the three most important conservation values of peatlands as rarity, naturalness and fragility. The findings in this thesis underline the concept of peatland fragility from a carbon cycling perspective in that it was seldom found, in any chapter, on any time-scale, that a site was a net daylight hours sink of CO_2. Moreover, the results presented in the diurnal chapter (chapter 5) showed that even in the height of the growing season, on the least disturbed of the sites investigated, there were no plots that were net daily sinks of CO_2. This finding may well reflect the climatically marginal location of the Peak District/South Pennies region with respect to the zone of environmental conditions conducive to active blanket bog formation (i.e. Lindsay et al., 1988). Indeed, Clark et al. (2010) showed that most bio-climatic envelope models of environmental conditions conducive to peat formation indicate that UK peatlands will be negatively affected by climatic change over the coming century. Indeed Clark (2011) suggested that the Peak District was the third most vulnerable area of blanket peat in the UK to climate change. The findings of the altitude chapter demonstrate that conditions more conducive to carbon storage increase with increasing altitude. Projected changes in climate and environment over the coming century may increase the altitude at which net carbon sinks become favourable resulting in degradation of peatlands at lower altitude faster than those at higher elevations.

In order to mitigate against such change in climate and environment, it is important that peatland ecosystems are carefully managed to ensure a biotic and hydrological regime suitable for carbon storage. Results from chapter 4 (on the role of vegetation) suggest strongly that promotion of *Sphagnum* mosses at the expense of *M. caerulea* and *C. vulgaris* is important to produce net sinks of CO_2. Moreover, there was evidence to suggest that the depth to the water table, a specific controlling factor on *Sphagnum* occurrence, was also a more general factor in controlling net CO_2 fluxes and soil pore water DOC concentrations. Thus, this thesis endorses the ongoing programme of gully and drain blocking in some areas of the Peak District with the objective of raising water tables to shallower levels. Furthermore, the results of this thesis also endorse the use of re-vegetation as a method of reducing carbon losses from peatland ecosystems.

During the Annual General Meeting of the British Ecological Society, Clark (2011) suggested that the decreasing amount of UK land surface area predicted to be favourable to blanket peat formation with climate change posed land managers and policy makers with an important question: where should radical interventions be carried out to help conserve these peatlands? Clark (2011) argued that the “common sense” approach to target those areas most vulnerable to climate change could be unfeasible from a resource standpoint as the bioclimatic envelope for blanket peat formation retreats northward and upward over time. Instead, Clark (2011) noted that it could be argued that peatlands that are likely to remain within the bioclimatic envelope but which are degraded due to other factors (e.g. mismanagement) should be targeted and may produce the best results with the limited resources available to tackle the problem. The results from this thesis demonstrate that, if the latter strategy is taken and thus the blanket peatlands of the Peak District/South Pennines are not conserved by radical changes in current land use (e.g.. replacement of heathland with *Sphagnum* dominated communities) due to their climatic marginality, then there are still strategies to current management practices that can be of benefit to the carbon cycle. A specific recommendation in relation to this point and resulting from the research presented in this thesis is that heathland burning/cutting can be targeted to canopy height (rather than being rotational on a temporal scale) in order to minimise the carbon loss via R_{eco} and DOC release. In agreement with other studies from differing perspectives (e.g. Burch 2008), the results of the canopy height study would support a target burn/cut height of 20-30 cm. Furthermore, using techniques like cutting, which lead to less vigorous re-growth of *C. vulgaris* than burning, may allow for a floristic composition less dominated by *C. vulgaris*. If the flora replacing the *C. vulgaris* is graminiod (e.g. *Eriophorum* spp.) or bryophyte (e.g. *Sphagnum*) then the results of chapter 4 suggest that carbon losses from the current heathlands on blanket peat could be reduced.

7.5.3 – The Durham Carbon Model

One of the primary motivations of this thesis was to investigate areas not currently considered within the Durham Carbon Model. The three areas investigated with this objective in mind were altitude, diurnal-scale fluxes and vegetation type. The broad questions being asked with respect to the DCM were:

- Do altitude and vegetation type have an identifiable effect on blanket peat CO_2 flux?
- Does *C. vulgaris* canopy height (an easily mapped parameter representing land management) affect CO_2 flux and DOC concentrations?
- Is the MLR technique robust in terms of physical interpretability and in relation to other modelling techniques?

For altitude, the pattern of results implied that the effect differed between different vegetation types, with *C. vulgaris* showing no apparent effect and bryophytes being the most sensitive to altitude. As such, any attempt to incorporate altitude into the DCM should take these vegetation specific differences into account, perhaps by introducing the altitudinal effect into vegetation specific sub-models. Indeed, this procedure would accord with the findings of chapter 4, which demonstrated that there are significant differences, some very large, between vegetation types. As such, vegetation specific sub-models calibrated to the vegetation type present would seem to be appropriate on this basis. This view is in agreement with Couwenberg et al. (2011) who recommended the use of vegetation type as a proxy for carbon flux from restored Belarusian peatlands.

The results of the canopy height section of the vegetation chapter demonstrated that canopy height is effective on CO_2 fluxes and DOC concentrations. As such, sub-model structures related to *C. vulgaris* canopy height could be used to take into account (some of) the effects of land management in the uplands. The primary benefit of canopy height is that it is now becoming possible to estimate vegetation canopy height from remote sensing data (e.g. Buchanan et al., 2005; Chapman et al., 2010) and thus apply this sub model to large areas of the UK uplands without the necessity of additional fieldwork.

Results from many sections of this thesis implied that MLR models of R_{eco} and NEE were better fitting than widely used theoretical alternatives (e.g. Lloyd and Taylor, 1994). As such, this thesis would endorse the continued use of the MLR framework within the DCM structure as it has been shown (even on validation data) to explain more dataset variation than the theoretical alternatives tested. Moreover, the manipulation chapter demonstrated that the MLR model framework could be used to characterise differences in CO_2 flux dynamics due to experimental manipulation.

7.6 – Further Work

The results of this thesis, and the limitations of the methods employed, raise additional research questions that could be dealt with in future experiments. Most frequently, ambiguity has been introduced into the results of this thesis due to its in situ nature, or experimental deficiencies. An important focus of many of the chapters of this thesis has been on the relationship between P_g and R_{eco}. The potential for self-correlation was an important limiting factor in the results presented in this thesis. The assumption that the ‘real’ magnitude of the correlation between P_g and R_{eco} is much larger than the error-induced self-correlation has not been tested formally in this thesis. This is due to the lack of independent measures of P_g and R_{eco}. Therefore, an experiment employing independent measurements to estimate P_g and R_{eco} should be employed in order to determine whether this assumption is more than theoretically justifiable.

An important area of research emerged from the acute experiment of the manipulation trials (chapter 6). There was an apparent 'fertilisation' effect from the addition of glucose to the soil that led to an increase in R_{eco} sensitivity to P_g, the opposite of what the hypotheses had predicted. A satisfactory explanation for this effect was not forthcoming and thus a controlled laboratory experiment to determine if this result is reproducible and if so what mechanism controls it is recommended.

More generally, the research in this thesis has been entirely in situ in nature using relatively low resolution (spatially and temporally) techniques to investigate the carbon cycle on upland blanket peatlands. These methods have been sufficient to demonstrate important controls on carbon cycling but are not sufficient to accurately trace the carbon cycle at the molecular/biochemical level.

Relationships between R_{eco} and P_g demonstrate the importance of the above-below ground linkages in the peatland ecosystem from a carbon cycling perspective. However, as mentioned above the methodologies available to this thesis were not sufficient to study these linkages in detail. As such, an important area of future research would be to explore the linkages in the soil-litter-vegetation system on a blanket peatland using isotopic tracer studies. Such research will help to examine how photosynthates are allocated above and below ground and on what time scale these processes occur. Laboratory tracer experiments with controlled environmental conditions could add further insight into the dynamics of this system by examining the system under varying environmental conditions and over differing temporal scales.

The vegetation chapter explored the issue of bare peat re-vegetation with lawn grass seeding. The results obtained indicated that this method of peatland restoration has had a beneficial impact from a carbon cycling perspective. However, this thesis would advocate continued monitoring of these areas in order to characterise the long-term impact of re-vegetation on blanket peat carbon cycling. Specifically, more ‘natural’ vegetation types expected in the upland areas have yet to establish themselves on these sites. As such, it is important to work out on what time scale this process would occur and, moreover, it is important to see whether the current relatively large net sink of CO_2 reported on the site continues or whether this sink (with increasing replacement of sown vegetation by ‘natural’ upland species) causes the sites to become net sources of CO_2 in accordance with the general pattern observed at the other less disturbed sites monitored in this thesis.

References

- Adkinson A.C., Syed K.H. and Flanagan L.B., 2011, “Contrasting responses of growing season ecosystem CO2 exchange to variation in temperature and water table depth in two peatlands in northern Alberta, Canada”, Journal of Geophysical Research, 116: G01004
- Aerts R., Bakker C. and de Caluwe H., 1992, “Root turnover as determinant of the cycling of C, N and P in a dry heathland ecosystem”, Biogeochemistry, 15: 175-190
- Aerts R. and de Caluwe H., 1999, “Nitrogen Deposition effects on Carbon Dioxide and Methane Emissions from Temperate Peatland Soils”, Oikos, 84: 44-54
- Aerts R., van Logtestijn, van Staalduinen M. and Toet S., 1995, “Nitrogen supply effects on productivity and potential leaf litter decay of *Carex* species from peatlands differing in nutrient limitation”, Oecologia, 104: 447-453
- Allott T.E.H., Evans M.G., Lindsay J.B., Agnew C.T., Freer J.E., Jones A. and Parnell M., 2009, “Water tables in Peak District blanket peatlands – Report 17”, Moors for the Future, Edale
- Anderson D.E., 2002, “Carbon accumulation and C/N ratios of peat bogs in North-west Scotland” Scottish Geographical Journal, 118: 323-341
- Anderson, P. and Yalden, D.W., 1981, “Increased sheep number and the loss of heather moorland in the Peak District, England”, Biological Conservation, 20: 195-213
- Armentano T.V. and Menges E.S., 1986, “Patterns of change in the carbon balance of organic soil-wetlands of the temperate zone”, Journal of Ecology, 74: 755-774
- Arrhenius S., 1889, “Uber die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren”, Zeitschrift fur Physik Chemique, 4: 226-248
- Avery B.W., 1980, “Soil classification for England and Wales; Higher categories (Techincal Monograph 14”, Soil Survey, Harpenden

- Bahn M., Schmitt M., Siegwolf R., Richter A. and Bruggemann N., 2009, “Does photosynthesis affect grassland soil-respired CO_2 and its carbon istope composition on a diurnal timescale?” New Phytologist, 182: 451-460
- Bardgett, R.D. and Marsden, J.H., 1995, “The extent and condition of heather on moorland in the uplands of England and Wales”, Biological Conservation, 71: 155-161
- Bartlett R.J. and Ross D.S., 1988, “Colorimetric Determination of Oxidizable Carbon in Acid Soil Solutions”, Soil Science Society of America Journal, 52: 1191-1192
- Bekku Y., Koizumi H., Nakadai T. Iwaki H., 1995, “Measurement of soil respiration using closed chamber method: and IRGA technique”, Ecological Research, 10: 369-373
- Bell M.J. and Worrall F., 2009, “Estimating a region’s organic carbon baseline: The undervalued role of land-management”, Geoderma, 152: 74-84
- Bellamy P.H., Loveland P.J., Bradley R.I., Lark R.M. and Kirk G.J.D., 2005, “Carbon losses from all soils across England and Wales 1978-2003”, Nature, 437: 245-248
- Berendse F., 1998, “Effects of Dominant Plant Species on Soils during Succession in Nutrient-poor Ecosystems”, Biogeochemistry, 43: 73-88
- Bhupinderpal-Singh A., Nordgren A., Ottosson-Lofvenius M., Hogberg M.N., Mellander P.-E. and Hogberg P., 2003, “Tree root and soil heterotrophic respiration as revealed by girdling of boreal Scots pine forest: extending observations beyond the first year”, Plant, Cell and Environment, 26: 1287-1296
- Billett M.F., Palmer S.M., Hope D., Deacon C., Storeton-West R., Hargreaves K.J., Flechard C. and Fowler D., 2004, “Linking land-atmosphere-stream carbon fluxes in a lowland peatland system”, Global Biogeochemical Cycles, 18: Article Number GB1024
- Blunier T., Chappellaz J., Schwander J., Stauffer B. and Raynaud D., 1995, “Variations in atmospheric methane concentration during the Holocene epoch”, Nature, 374: 46-49

- Bond-Lamberty B., Wang C. and Gower S., 2004, "A global relationship between the heterotrophic and autotrophic components of soil respiration?", Global Change Biology, 10: 1756-1766
- Bonn A., Allott T., Hubacek K. and Stewart J., 2008, "Drivers of environmental change in uplands", Routledge, Abingdon
- Boone R.D., Nadelhoffer K.J., Canary J.D. and Kaye, J.P., 1998, "Roots exert a strong influence on the temperature sensitivity of soil respiration", Nature, 396: 570-572
- Bower M.M., 1961, "Distribution of Erosion in Blanket Peat Bogs in the Pennines", Transactions of the Institute of British Geographers, 29:17-30
- Bragazza L. and Gerdol R., 1996, "Response surfaces of plant species along water-table and pH gradients in a poor mire on the southers Alps (Italy)", Annals Botanici Fenici, 33:11-20
- Bradley R.I., Milne R., Bell J., Lilly A., Jordan C. and Higgins A., 2005, "A soil carbon and land use database for the United Kingdom", Soil Use and Management, 21: 363-369
- Breeuwer, A., Heijmans M., Robroek B.J.M, Limpens, J. and Berendse F., 2008, "The effect of increased temperature and nitrogen deposition on decomposition in bogs." Oikos, 117: 1258-1268
- Breeuwer A., Robroek B.J.M., Limpens J., Heijmans M.M.P.D., Schouten M.G.C. and Berendse F., 2009, "Decreased summer water table depth affects peatland vegetation", Basic and Applied Ecology, 10: 330-330
- Bremer E. and Kuikman P., 1994, "Microbial utilisation of 14C[U]glucose in soil is affected by the amount of timing if glucose additions", Soil Biology and Biochemistry, 26: 511-517
- Brook G.A., Folkoff M.E. and Box E.O., 1983, "A world model of soil carbon dioxide", Earth Surface Processes and Landforms, 8: 79-88

- Bubier J.L., Crill P.M., Moore T.R., Savage K. and Varner R.K., 1998, “Seasonal patterns and controls on net ecosystem CO_2 exchange in a boreal peatland complex”, Global Biogeochemical Cycles, 12:703-714
- Buffam I., Carpenter S.R., Yeck W., Hanson P.C. and Turner M.G., 2010, “Filling holes in regional carbon budgets: Predicting peat depth in a north temperate lake district”, Journal of Geophysical Research, 115: G01005
- Burch J., 2008, “The relationship of bryophyte regeneration to heather canopy height following moorland burning on the North York Moors”, Journal of Bryology, 30: 208-216
- Burt T.P. and Ferranti E.J.S., 2012, “Changing patterns of heavy rainfall in upland areas: a case study from northern England”, International Journal of Climatology, 32: 518-532
- Burt T.P. and Holden J., 2010, “Changing temperature and rainfall gradients in the British Uplands”, Climate Research, 45; 57-70
- Cannell M.G.R. and Milne R., 1995, “Carbon pools and sequestration in forest ecosystems in Britain”, International Journal of Forest Research, 68: 361-378
- Carroll, J., Anderson, P., Caporn, S., Eades, P., O’Reilly, C. and Bonn, A., 2009, “Sphagnum in the Peak District current status and potential for restoration - Moors for the Future Report No 16”, Moors for the Future Partnership, Edale
- Chapman S.B., Hibble J. and Rafarel C.R., “Litter accumulation under Calluna vulgaris on a lowland heath in Britain”, Journal of Ecology, 63: 259-271
- Chapman S.J. and Thurlow M., 1996, “The influence of climate on CO_2 and CH_4 emissions from organic soils”, Agricultural and Forest Meteorology, 79: 205-217
- Charman D.J., 2002, “Peatlands and Environmental Change”, Wiley, Chichester
- Chen Y. and Murrell C., 2010, “Geomicrobiology: Methanotrophs in moss”, Nature Geoscience, 3: 595-596

- Chen Y., McNamara N., Dumont M.G., Bodrossy L., Stralis-Pavese N. and Murrell J.C., 2008*,* *"*The impact of burning and *Calluna* removal on below-ground methanotroph diversity and activity in a peatland soil", Applied Soil Ecology, 40: 291-298
- Clark J.M., Ashley D., Wagner M., Chapamn P.J., Lane S.N., Evans C.D. and Heathwaite A.L., 2009, Increased temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down", Global Change Biology, 15: 794-807
- Clark J.M., Billett M.F., Coyle M., Croft S., Daniels S., Evans C.D., Evans M., Freeman C., Gallego-Sala A.V., Heinemeyer A., House J.I., Monteith D.T., Nayak D., Orr H.G., Prentice I.C., Rose R., Rowson J., Smith J.U., Smith P., Tun Y.M., Vanguelova E., Wetterhall F. and Worrall F., 2010, "Model inter-comparison between statistical and dynamic model assessments of the long-term stability of blanket peat in Great Britain (1940-2099)", Climate Research, 45: 227-248
- Clay G.D., Dixon S., Evans M.G., Rowson J.G. and Worrall F., 2012, "Carbon dioxide fluxes and DOC concentrations of eroding blanket peat gullies", Earth Surface Processes and Landforms, Article In Press, DOI: 10.1002/esp.3193

- Clymo R.S. and Hayward P.M, 1982, "The ecology of Sphagnum". In *Bryophyte Ecology*, by A.J.E Smith, Chapman and Hall, New York

- Clymo R.S., 1984, "The limits to peat bog growth", Philosophical Transactions of the Royal Society of London, 303: 605-654
- Cope F.W., 1998, "Geology explained in the Peak District – 2nd Revised Edition", Scarthin Books, Cromford
- Couwenberg J., Thiele A., Tanneberger F., Augustin J., Barisch S., Dubovik D., Liashchynskaya N, Michaelis D., Minke M, Skuratovich A. and Joosten H.., 2011, "Assessing greenhouse gas emissions from peatlands using vegetation as a proxy"., Hydrobiologia, 674: 67-89

- Davidson E.A., Richardson A.D., Savage K.E. and Hollinger D.Y., 2005, “A distinct pattern of the ratio of soil respiration to total ecosystem respiration in a spruce-dominated forest”, Global Change Biology, 12: 230-239
- Davis R.C., 1983, “Prediction of Net Primary Production in two Antarctic Mosses by two Models of Net CO_2 Fixation”, British Antarctic Survey Bulletin, 59:47-51
- Dawson J.J.C., Tetzlaff D., Speed M., Hrachowitz M. and Soulsby C., 2010, “Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland”, Hydrological Processes, 25: 1647-1658
- DEFRA, 2007, “The heather and grass burning code: 2007 version”, DEFRA, London
- Dilkes N.B., Jones D.L. and Farrar J., 2004, “Temporal dynamics of carbon partitioning and rhizodeposition in wheat”, Plant Physiology, 134: 706-715
- Dixon R.K., Brown S., Houghton R.A., Solomon A.M., Trexler M.C. and Wisniewski J., 1994, “Carbon pools and flux of global forest ecosystems”, Science, 263: 185-190
- Dorrepaal E., Corneilssen J.H.C., Aerts R., Wallén B. and van Logestijn R.S.P.,2005, “Are growth forms consistent predictors of leaf litter quality and decomposability across peatlands along a latitudinal gradient?”, Journal of Ecology, 93: 817-828
- Dorrepaal E., Cornelissen J.H.C. and Aerts R., 2007, “Changing leaf litter feedbacks on plant production across contrasting sub-arctic peatland species and growth forms”, Oecologica, 151: 251-261
- Doyle G., “Blanket bogs: An interpretation based on Irish blanket bogs”, in “Conserving peatlands”, eds. Parkyn L., Stoneman R.E. and Ingram H.A.P., 1997, CAB International, Wallingford
- Epron D., Le Dantec V., Dufrene E. and Granier A., 2001, “Seasonal dynamics of soil carbon efflux and simulated rhizosphere respiration in a beech forest”, Tree Physiology, 21: 145-152
- Eswaran H., Van Den Berg E. and Reich P., 1993, “Organic carbon in soils of the world” Journal of the Soil Science Society of America, 57: 192-194

- Evans J.R. and von Caemmerer S, 1996, “Carbon dioxide diffusion inside leaves”, Plant Physiology, 100: 339-346
- Evans M. and Warburton J., 2005, “Sediment budget for an eroding peat-moorland catchment in northern England”, Earth Surface Processes and Landforms, 30: 557-577
- Evans M. and Warburton J., 2007, “Geomorphology of upland peat: erosion, form and landscape change”, Blackwell Publishing, Oxford
- Evans M. and Lindsay J., 2010a, “High resolution quantification of gully erosion in upland peatlands at the landscape scale”, Earth Surface Processes and Landforms, 35: 376-386
- Evans M. and Lindsay J., 2010b, “The impact of gully erosion on carbon sequestration in blanket peatlands”, Climate Research, 24: 31-41
- Evans M., Allott T., Holden J., Flitcroft C. and Bonn A., 2005, “Understanding gully blocking in deep peat: Moors for the future report No 4”, Moors for the Future, Castleton
- Evans M., Warburton J. and Yang J., 2006, “Eroding Blanket Peat Catchments: Global and Local Implications of Upland Organic Sediment Budgets”, Paper presented at the Conference on Sediment and Geochemical Budget in Geomorphology, University of British Columbia, 27-30 June 2004
- Fang C. and Moncrieff J.B., 1999, “A model for soil CO_2 production and transport 1: model development” Agricultural and Forest Meteorology, 95: 225-236
- Farrick K.K. and Price J.S., 2009, Ericaceous shrubs on abandoned block-cut peatlands: implications for soil water availability and Sphagnum restoration”, Ecohydrology, 2: 530-540
- Faure H., Adams J.M. and Debenay J.P., 1996. “Carbon Storage and Continental Land Surface Change since the last Glacial Maximum”, Quarternary Science Reviews, 15: 843-849
- Fenner N., Ostle N., Freeman C., Sleep D. and Reynold B., 2004, “Peatland carbon efflux partitioning reveals that *Sphagnum* photosynthate contributes to the DOC pool”, Plant and Soil, 259: 345-354

- Fenner, N., Ostle N.J., McNamara N., Sparks T., Harmens H., Reynolds B. and Freeman C., 2007, “Elevate CO_2 effects on peatland plant community carbon dynamics and DOC production”, Ecosystems, 10: 635-647
- Field C.B., Behrenfeld M.J., Randerson, J.T. and Falkowski P., 1998,” Primary Production of the Biosphere: Integrating Terrestrial and Oceanic Components”, Science, 281: 237-240
- Forrest G.I. and Smith R.A.H., 1975, “The productivity of a range of blanket bog vegetation types in the northern Pennines”, Journal of Ecology, 63: 173-202
- Frolking S., Roulet N.T., Moore T.R., Richard P.J.H., Lavoie M. and Muller S.D., 2001, “Modeling northern peatland decomposition and peat accumulation”, Ecosystems, 4: 479-498
- Gamnitzer U., Schaufele R. and Schnyder H., 2009, “Observing ^{13}C labelling kinetics in CO_2 respired by a temperate grassland ecosystem”, New Phytologist, 184: 376-386
- Garnet K.N., Megonigal J.P., Litchfield C. and Taylor Jr. G.E., 2005, “Physiological control of leaf methane emission from wetland plants”, Aquatic Botany, 81: 141-155
- Gerdol R., Bragazza L. and Brancaleoni L., 2008, “Heatwave 2003: highsummer temperature, rather than experimental fertilization affects vegetation and carbon dioxide exchange in an alpine Bog”, New Phytologist, 179: 142–154
- Gershenson A., Bader N.E. and Cheng W., 2009, “Effects of substrate availability on the temperature sensitivity of soil organic matter decomposition”, Global Change Biology, 15: 176-183
- Gimingham, C.H., 1972, “Ecology of Heathlands”, Chapman and Hall, London
- Gorham E., 1991, “Northern peatlands: Role in the carbon cycle and probable responses to climatic warming”, Ecological Applications, 1: 182-195
- Gorham E., Lehman C., Dyke A., Janssens J. and Dyke A., 2007, “Temporal and spatial aspects of peatland initiation following deglaciation in North America”, Quaternary Science Review, 26: 300-311

- Grace J., 2004, “Understanding and managing the global carbon cycle”, Journal of Ecology, 92: 189-202
- Hamer U. and Marschner B, 2002, “Priming effects of sugars, amino acids and catechol on the mineralization of lignin and peat”, Journal of Plant Nutrition and Soil Science, 165: 261-268
- Hansen G.K., 1977, “Adaptation to photosynthesis and diurnal oscillation of root respiration rates for *Lolium multiflorum*”, Physiologia Plantarum, 39: 275-279
- Harris A. and Bryant R.G., 2009, “A multi-scale remote sensing approach for monitoring northern peatland hydrology: Present possibilities and future challenges”, Journal of Environmental Management, 90: 2178-2188
- Heinemeyer A., Croft S., Garnett M.H., Gloor E., Holden J., Lomas M.R. and Ineson P., 2010, “The MILLENNIA peat cohort model: predicting past, present and future soil carbon budgets and fluxes under changing climates in peatlands”, Climate Research, 4: 207-226
- Hinde S., Rosenburgh A., Wright N., Buckler M. and Caporn S., 2010, “*Sphagnum* re-introduction project: A report on research into the re-introduction of *Sphagnum* mosses to degraded moorland: Moor for the future research report 18”, Moors for the Future, Edale
- Hogberg P., Nordgren A., Buchmann N., Taylor A.F.S, Ekblad A., Hogberg M.N., Nyberg G., Ottosson-Lofvenius M. and Read D.J., 2001, “Large-scale forest girdling shows that current photosynthesis drives soil respiration” Nature, 411: 789-792
- Holden J., 2005a, “Controls on Soil Pipe Frequency in Upland Blanket Peat”, Journal of Geophysical Research, 110: F01002
- Holden J., 2005b, “Peatland hydrology and carbon release: why small-scale process matters” Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 363: 2891-2913
- Holden J. and Rose R., 2001, “Temperature and surface lapse rate change: a study of the UK’s longest upland instrumental record”, International Journal of Climatology, 31: 907-919

- Holden J., Shotbolt, L., Bonn, A., Burt, T.P., Chapman, P.J., Dougill, A.J., Fraser, E.D.G., Hubacek, K., Irvine, B., Kirkby, M.J., Reed, M.S., Prell, C., Stagl, S., Stringer, L.C., Turner, A. and Worrall., F, 2007, “Environmental change in moorland landscapes”, Earth-Science Reviews, 82: 75-100
- Howell D.C., 1992, “Statistical methods for psychology – third edition”, PWS-Kent Publishing, Boston
- Hoyle F.C., Murphy D.V. and Brookes P.C., 2008, “Microbial response to the addition of glucose in low-fertility soils”, Biology and Fertility of Soils, 44: 571-579
- Hulme P.D., 1986, “The origin and development of wet hollows and pools on Craigeazle mire, south west Scotland”, International Peat Journal, 1: 15-28
- Immirzi C.P., Maltby E. and Clymo R.S., 1992, “The global status of peatlands and their role in carbon cycling”, Friends of the Earth, London
- IPCC, 2007, “Climate Change 2007 – The Physical Science Basis”. Cambridge University Press, Cambridge
- Janssens I.A., Freibauer A., Schlamadinger B., Ceulemans R., Ciais P., Dolman A.J., Heimann M., Nabuurs G.-J., Smith P, Valentini R. and Schulze E.-D., 2005, “The carbon budget of terrestrial ecosystems at country-scale – a European case study”, Biogeosciences, 2: 15-26
- Jensen L.S., Mueller T., Tate K.R., Ross D.J., Magid J. and Nielsen N.E., 1996, “Soil surface CO_2 flux as an index of soil respiration in situ: a comparison of two chamber methods”, Soil Biology and Biochemistry, 28: 1297-1306
- Joosten H., 2009, “The global peatland CO2 picture: Peatland status and drainage related emissions in all countries of the world”, Wetlands International, Ede
- Kaplan J.O, Krumhardt K.M, Ellis E.C, Ruddiman W.F., Lemmen C. and Goldewijk K.K., 2011, “Holocene carbon emissions as a result of anthropogenic land cover change”, The Holocene, 21: 775-791

- Kenney B.C., 1982, “Beware of spurious correlations!”, Water Resources Research, 18: 1041-1048
- Kenney B.C., 1991, “Comments on ‘Some misconceptions about the spurious correlation problem in the ecological literature’ by Y.T. Prairie and D.F. Brid”, Ocecologia, 86: 152
- Keselman H.J. and Rogan J.C., 1978, “A comparison of the modified Tukey and Scheffé methods for multiple comparisons of pairwise contrasts”, Journal of the American Statistical Association, 73: 47-52
- Kivimaki S.K., Yli-Petays M., and Tuittila E.S., 2008, “Carbon sink function of sedge and Sphagnum patches in a restored cut-away peatland: increased functional diversity leads to higher production.” Journal of Applied Ecology, 45: 921-929
- Koehler A-K, Murphy K., Kiely G. and Sottocornola M., 2009, “Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland”, Biogeochemistry, 95: 231-242
- Koerselman W. and Meuleman A.F.M., 1996, “The vegetation N:P ratio: a new tool to detect the nature of nutrient limitation”, Journal of Applied Ecology, 33: 1441-1450
- Kuzyakov Y., 2002, “Separating microbial respiration of exudates from root respiration in non-sterile soils: a comparison of four methods”, Soil Biology & Biochemistry, 34: 1621-1631
- Kuzyakov Y. and Cheng W., 2001, “Photosynthesis controls of rhizosphere respiration and organic matter decomposition”, Soil Biology & Biochemistry, 33: 1915-1925
- Kuzyakov Y. and Jones D.L., 2006, “Glucose uptake by maize roots and its transformation in the rhizosphere”, Soil Biology and Biochemistry, 38: 851-860
- Kuzyakov Y., Raskatov A. and Kaupenjohann M., 2003, “Turnover and distribution of root exudates of *Zea mays*” Plant and Soil, 254: 317-327
- Lambers H., Chapin F.S. III, Pons T.L., 2006, ”Plant physiological ecology”, Springer, New York

- Larionova A.A., Yevdokimov I.V. and Bykhovets S.S., 2007, "Temperature response of soil respiration is dependent on concentration of readily available decomposable C", Biogeosciences, 4: 1073-1081
- Larsen K.S., Ibrom A., Beier C., Jonasson S. and Michelsen A., 2007, "Ecosystem respiration depends strongly on photosynthesis in a temperate heath", Biogeochemistry, 85: 201-213
- Lasslop G., Reichstein M., Detto M., Richardson A.D. and Baldocchi D.D., 2010, "Comment on Vickers et al.,: Self-correlation between assimilation and respiration resulting from flux partitioning of eddy-covariance CO_2 fluxes", Agricultural and Forest Meteorology, 150: 312-314
- Lavoie C., Marcoux K., Saint-Louis A. and Price J.S., 2005, "The dynamics of a cotton-grass (*Eriophorum vaginatum* L.) cover expansion in a vacuum-mined peatland, southern Quebec, Canada", Wetlands, 25: 64-75
- Le Dantec V., Epron D. and Dufrêne E., 1999, "Soil CO_2 efflux in a beech forest: comparison of two closed dynamic systems", Plant and Soil, 214: 125-132
- Lee N-J, 2010, "An evaluation of empirical regression models for predicting temporal variations in soil respiration in a cool-temperate deciduous broad-leaved forest", Journal of Ecology and Field Biology, 33: 165-173
- Leigh H., 1975, "Modeling the primary production of the world", in "Primary production of the biosphere", eds. Leigh H. and Whittaker R.H., Springer-Verlag, New York
- Leppälä M., Kukko-Oja K., Laine J. and Tuittila E.-S., 2008, "Seasonal dynamics of CO_2 exchange during primary succession of boreal mires as controlled by phenology of plants", Ecoscience, 15: 460-471
- Limbach W.E., Oechel W.C and Lowell W., 1982, "Photosynthetic and respiratory responses to temperature and light of three Alaskan Tundra growth forms", Holarctic Ecology, 5: 150-157

- Lindsay R.A., 1995, “Bogs: the Ecology, Classification and Conservation of Ombrotrophic Mires”, Scottish Natural Heritage, Perth
- Lindsay R.A., 2010, “Peatbogs and Carbon: a critical synthesis to inform policy development in oceanic peat bog conservation and restoration in the context of climate change”, RSPB Scotland, Edinburgh
- Lloyd J. and Taylor J.A., 1994, “On the Temperature Dependence of Soil Respiration”, Functional Ecology, 8: 315-323
- Lundegaardh H., 1927, “Carbon dioxide evolution of soil and crop growth”, Soil Science, 23: 415-453
- MacDonald G.M., Beilamn D.W., Kremenetski K.V., Sheng Y., Smith L.C. and Velichko A.A., 2006, “Rapid early development of circumarctic peatlands and atmospheric CH_4 and CO_2 variations”, Science, 314: 285-288
- Marinier M., Glatzel S. and Moore T.R., 2004, “The role of cotton-grass (*Eriophorum vaginatum*) in the exchange of CO_2 and CH_4 at two restored peatlands, eastern Canada”, Ecoscience, 11: 141-149
- Martini I.P. and Glooshenko W.A., 1985, “Cold climate peat formation in Canada, and its relevance to Lower Permian coal measures in Australia”, Earth-Science Reviews, 22: 107-140
- Mazlum N., Özer A. and Mazlum S., 1999, “Interpretation of water quality data by Principle Components Analysis”, Turkish Journal of Engineering and Environmental Science, 23: 19-26
- McMorrow J, Aylen J., Albertson K., Cavan G., Lindley S., Handley J. and Karooni R., 2006, “Climate change and the visitor economy: Technical report 3: Moorland wild fires in the Peak District National Park”, Centre for Urban and Regional Ecology, Manchester
- McNamara N.P., Plant T., Oakley S., Ward S., Wood C. and Ostle N., 2008, “Gully hotspot contribution to landscape methane (CH_4) and carbon dioxide (CO_2) fluxes in a northern peatland”, Science of the Total Environment, 404: 354-360

- McNeil P. and Waddington J.M., 2003, "Moisture Controls on *Sphagnum* Growth and CO_2 Exchange on a Cutover Bog", Journal of Applied Ecology, 40: 354-367
- Metcalfe D.B., Fisher R.A. and Wardle D.A., 2011, "Plant communities as drivers of soil respiration: pathways, mechanisms, and significance for global change", Biogeosciences, 8: 2047-2061
- Migliavacca M., Reichstein M., Richardson A.D., Colombo R., Sutton M.A., Lasslop G., Tomelleri E., Wohlfahrt G., Carvalhais N., Cescatti A., Mahecha M.D., Montagnani L., Papale D., Zaehle S., Arain A., Arneth A., Black T.A., Carrara A., Dore S., Gianelle D., Helfters C., Hollinger D., Kutsch W.L., Lafluer P.M., Nouvellon Y., Rebmann C., da Rocha H.R., Seufert G., Soussana J-F. and van der Molen M.K., 2011, "Semiempirical modelling of abiotic and biotic factors controlling ecosystem respiration across eddy covariance sites", Global Change Biology, 17: 390-409
- Mohamed, A., Hardtle W., Jirjahn B., Niemeyer T. and von Oheimb G., 2007, "Effects of prescribed burning on plant available nutrients in dry heathland ecosystems" Plant Ecology, 189: 279–289
- Montanarella L., Jones R.J.A. and Hiederer R., 2006, "The distribution of peatland in Europe", Mires and Peat, article number 1
- Moore P.D. and Bellamy D.J., 1974, "Peatlands", Elek Science, London
- Moore T.R., 1986, "Carbon dioxide evolution from subarctic peatlands in eastern Canada", Journal of Arctic and Alpine Research, 18: 189-193
- Moss, C. E., 1913, "The vegetation of the Peak District", Cambridge University Press, Cambridge
- Mowforth M. and Sydes C., 1989, "Moorland management: a literature review", Nature Conservation, Report No. 25, HMSO, London

- Moyano F.E., Kutsch W.L. and Schulze E-D., 2007, “Response of mychorrhizal, rhizosphere and soil basal respiration to temperature and photosynthesis in a barely field”, Soil Biology and Biochemistry, 39: 843-853
- Moyano F.E., Kutsch W.L. and Rebamann C., 2008, “Soil respiration fluxes in relation to photosynthetic activity in broad-leaf and needle-leaf forest stands”, Agricultural and forest meteorology, 148(1): 135-143
- Nieveen J.P., Jacobs C.M.J. and Jacobs A.F.G., 1998, “Diurnal and seasonal variation of carbon dioxide from a former true raised bog”, Global Change Biology, 4: 823-833
- Nykänen H., Heikkinen P., Pirinen L., Tiilikainen K., Martikainen P.J., 2003, “Annual CO_2 exchanges and CH_4 fluxes on a subarctic palsa mire during climatically different years”, Global Biogeochemical Cycles, 17: article n^o 1018
- O’Connell M., 1990, “Origins of Irish lowland blanket bog”, in “Ecology and conservation of Irish peatlands” ed. Doyle G., Royal Irish Academy, Dublin
- Oberbauer S.F., Gillespie C.T., Cheng W., Sala A., Gebauer R. and Tenhunen J.D., 1996, “Diurnal and seasonal patterns of ecosystem CO_2 efflux from upland tundra in the foothills of the Brooks Range, Alaska, U.S.A.” Arctic and Alpine Research, 28: 328-338
- Olejnik S. and Algina J., 2003, “Generalised Eta and Omega squared statistics: measures of effect size for some common research problems”, Psychological Methods, 8: 434-447
- Otieno D.O., Wartinger M., Nishiwaki A., Hussain M.Z., Muhr J., Borken W. and Lischeid G., 2009, “Responses of CO_2 exchange and primary production of the ecosystem components to environmental changes in a mountain peatland”, Ecosystems, 12: 590-603
- Panikov N.S., Mastepanov M.A., and Christensen T.R., 2007, “Membrane probe array: Technique development and observation of CO_2 and CH_4 diurnal oscillations in peat profile”, Soil Biology & Biochemistry, 39: 1712-1723

- Parkin T.B. and Kaspar T.C., 2003, “Temperature controls on diurnal carbon dioxide flux: implications of estimating soil carbon loss”, Journal of the Soil Science Society of America, 67:1763–1772
- Pellerin S., Lagneau L.A., Lavoie M. and Larocque M., 2009, “Environmental Factors Explaining the Vegetation Patterns in a Temperate Peatland”, Competes Rendus Biologies, 332: 720-731
- Pilkington M.G., Caporn S.J.M., Carroll J.A., Cresswell N., Lee J.A., Ashenden T.W., Brittain S.A., Reynolds B. and Emmett B.A., 2005, “Effects of increased deposition of atmospheric nitrogen on an upland moor: leaching of N species and soil solution chemistry”, Environmental Pollution, 135: 29-40
- Prairie Y.T. and Bird D.F., 1989, “Some misconceptions about the spurious correlation problem in the ecological literature”, Oecologia, 81: 285-288
- Prentice I.C., Farquhar G.D., Fasham M.J.R, Goulden M.L., Heimann M., Jaramillo V.J., Kheshgi H.S, Le Quéré C., Scholes R.J. and Wallace D.W.R., 2001, “The Carbon Cycle and Atmospheric Carbon Dioxide”, IPCC Third Assessment Report: Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge
- Price J.S. and Whitehead G.S., 2001, “Developing Hydrologic Thresholds for *Sphagnum* Recolonization on an Abandoned Cutover Bog”, 21: 32-40
- Pumpanen J., Ilvesniemi H. and Hari P., 2003, “A process-based model for predicting soil carbon dioxide efflux and concentration”, Journal of the Soil Science Society of America, 67: 402-413
- Raich J.W. and Schlesinger, 1992, “The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate”, Tellus, 44: 88-99
- Raich J.W. and Potter C.S., 1995, “Global patterns of carbon dioxide emissions from soils”, Global Biogeochemical Cycles, 9: 23-36

- Raich J.W. and Tufekcioglu A., 2000, “Vegetation and soil respiration: correlations and controls”, Biogeochemistry, 48: 71-90
- Rawes M., 1983, “Changes in two high altitude blanket bogs after the cessation of sheep grazing”, Journal of Ecology, 71: 219-235
- Reichstein M., Falge E., Baldocch D.S., Papale D., Aubinet M., Berbigier P., Bernhofer C., Buchmann N., Gilmanov T., Granier A, Grunwald T., Havrankova K., Ilvesniem H., Janous D., Knohl A., Laurila T., Lohila A., Loustau D., Matteuci G., Meyers T., Miglietta F, Ourcival J.M, Pumpanen J., Rambal S., Rotenburg E., Sanz M., Tenhunen J., Seufert G., Vaccar F., Vesala T., Yakir D. and Valentini R., 2005, “On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm”, Global Change Biology, 11: 1424-1439
- Reyes A.V. and Cooke C.A., 2011, “Northern peatland initiation lagged abrupt increase in deglacial atmospheric CH_4”, Proceedings of the National Academy of Science, 4748-4753
- Richardson D.H.S., 1981, “The biology of mosses”, Blackwell, Oxford
- Risch A.C. and Frank D.A., 2010, “Diurnal and seasonal patterns in ecosystem fluxes and their controls in a temperate grassland”, Rangeland Ecological Management, 63: 62-71
- Riveros-Iregui D.A., Emanuel R.E., Muth D.J., McGlynn B.L., Epstein H.E., Welsch D.L., Pacific V.J. and Wraith J.M., 2007, “Diurnal hysteresis between soil CO_2 and soil temperature is controlled by soil water content”, Geophysical Research Letters, 34: L17404
- Robertson K.P. and Woolhouse H.W., 1984, “Studies of the seasonal course of carbon uptake of *Eriophorum vaginatum* in a moorland habitat: I. Leaf production and senescence”, Journal of Ecology, 5: 423-435
- Rochefort L., 2000, “New Frontiers in Bryology and Lichenology – *Sphagnum* – A Keystone Genus in Habitat Restoration”, Bryologist, 103:503-508

- Rothwell J.J., Evans M.G., Liddaman L.C. and Allott T.E.H., 2007, "The role of wildfire and gully erosion in particulate Pb export from contaminated peatland catchments in the southern Pennines, U.K.", Geomorphology, 88: 276-284
- Rovira A.D., "Plant root exudates", The Botanical Review, 35: 35-53
- Rowson J.G., 2007, "Carbon emissions from managed upland peat", Ph.D Thesis, Durham University Library
- Rutherford A., 2001, "Introducting ANOVA and ANCOVA a GLM Approach", Sage, London
- Ryan M.G., L:avigne M.B. and Gower S.T., 1997, "Annual carbon cost of autotrophic respiration in forest ecosystems in relation to species and climate", Journal of Geophysical Research, 102: 871-883
- Ryan M.G. and Law B.E., 2005, "Interpreting, measuring and modeling soil respiration", Biogeochemistry, 73: 3-27
- Ryan M.G., Binkley D., Fowns J.H., Giardina C.P. and Senock R.S., 2004, "An experimental test of the causes of forest growth decline with stand age", Ecological Monographs, 74: 393-414
- Rydin H., Gunnarsson U. and Shunberg S., 2006, "The role of Sphagnum in peatland development and persistence", Boreal Peatland Ecosystems, 188: 47-65
- Schlesinger W.H., 1997, "Biogeochemistry: An analysis of global change, Second Edition" Academic Press, London
- Silvan N., Tuittila E.S., Vasander H. and Laine J., 2004, "Eriophorum vaginatum plays a major role in nutrient immobilisation in boreal peatlands." Annales Botanici Fennici, 41: 189-199
- Simmons, I.G., 2003, "The Moorlands of England and Wales", Edinburgh University Press, Edinburgh
- Singh, J.S. and Gupta, S.R., 1977, "Plant decomposition and soil respiration in terrestrial ecosystems", The Botanical Review, 43: 449-428
- Skeffington, R., Wilson, E., Maltby, E., Immirzi, P. and Putwain, P., 1997, "Acid deposition and blanket mire degradation and restoration", In: "Blanket mire degradation: causes,

consequences and challenges", eds Tallis, J.H., Meade, R. and Hulme, P.D., British Ecological Society - Mires Research Group

- Smith P., Smith J., Flynn H., Killham K., Rangel-Castra I., Foereid B., Aitkenhead M., Chapman S., Towers W., Bell J., Lumsdon D., Milne R., Thomson A., Simmons I., Skiba U., Reynolds B., Evans C., Frogbrook Z., Bradley I., Whitmore A. and Falloon P., 2007, "ECOSSE – Estimating carbon in organic soils – Sequestration and emission", Environmental and Rural Affairs Department, Scottish Executive, Edinburgh
- Sottocornola M. and Kiely G., 2010, "Hydro-meteorological controls on the CO2 exchange variation in an Irish blanket bog", Agricultural and Forest Meteorology, 150: 287-29
- Sparling G.P., Ord B.G. and Vaughan D., 1981, "Microbial biomass and activity within soils amended with glucose", Soil Biology and Biochemistry, 13: 99-104
- Strand L.T., Abrahamsen G. and Stuanes A.O., 2002, "Leaching from Organic Matter–Rich Soils by Rain of Different Qualities.", Journal of Environmental Quality, 31: 547-556
- Taiz L. and Zeiger E., 2002, "Photosynthesis: Physiological and Ecological Considerations", In: Taiz L. and Zeiger E., "Plant Physiology, 3rd edition", Sinauer Associates, Sunderland
- Tallis, J.H, 1964, "Studies on southern Pennine peats. III. The behaviour of sphagnum", Journal of Ecology, 52: 345-353
- Tallis J.H., 1965, "Studies on Southern Pennine Peats: IV Evidence of Recent Erosion", Journal of Ecology, 53: 509-520
- Tallis J.H., 1985, "Mass movement and erosion of a southern Pennine blanket peat" Journal of Ecology, 73: 283-315
- Tallis J.H., 1991, "Forest and moorland in the South Pennine uplands in the Mid-Flandrian period. III. The spread of moorland – local, regional and national", Journal of Ecology, 79: 401-415

- Tallis J.H., 1997. "The Southern Pennine Experience: An overview of blanket mire degradation. In: Blanket mire degradation: causes, consequences and challenges", eds Tallis, J.H., Meade R.and Hulme, P.D., British Ecological Society - Mires Research Group
- Tallis J.H., 1998a, "Growth and degradation of British and Irish blanket mires", Environmental Reviews, 6: 81–122
- Tallis J.H., 1998b, "The uplands: human influences on the plant cover", in "Ecology and Landscape Development: History of the Mersey Basin", ed. Greenwood E.F., Liverpool University Press, Liverpool
- Tallis J.H. and Switsur V.R., 1983, "Forest and moorland in the South Pennine Uplands in the Mid-Flandrian period: I. Macrofossil evidence of the former forest cover" Journal of Ecology, 71: 585-600
- Tang J., Baldocchi D.D. and Xu L., 2005, "Tree photosynthesis modulates soil respiration on a diurnal time scale", Global Change Biology, 11: 1298-1304
- Taylor J.A. and Tucker R.B., 1968, "The Peat Deposits of Wales: an inventory and interpretation", Proceedings of the 3rd International Peat Congress, International Peat Society, Duluth
- Thornley J.H.M. and Johnson I.R., 1990, "Plant and crop modelling: a mathematical approach to plant and crop physiology", Clarendon, Oxford
- Thomas K.L., Benstead J., Davies K.L. and Lloyd D., "Role of wetland plants in the diurnal control of CH_4 and CO_2 fluxes in peat", Soil Biology and Biochemistry, 28: 17-23
- Thurman E.M., 1985, "Organic geochemistry of natural waters", Kluwer, Lancaster
- Trinder C.J., Artz, R.R. and Johnson, D., 2008, "Contribution of plant photosynthate to soil respiration and dissolved organic carbon in a naturally recolonising cutover peatland", Soil Biology and Biochemistry, 40: 1622-1628
- Trumbore S., 2006, "Carbon respired by terrestrial ecosystems – recent progress and challenges", Global Change Biology, 12: 141-153

- Verburg P.S.J., Gorissen A. and Arp W.J., 1998, "Carbon allocation and decomposition of root-derived organic matter in a plant-soil system of Calluna vulgaris as affected by elevated CO_2", Soil Biology and Biochemistry, 30: 1251-1258
- Verhoeven J.T.A. and Liefveld W.M., 1997. "The ecological significance of organochemical compounds in Sphagnum", Acta Botanica Neerlandica, 46: 117-130
- Vickers D., Thomas C.K., Martin J.G.and Law B., 2009, "Self-correlation between assimilation and respiration resulting from flux partitioning of eddy covariance CO_2 fluxes", Agricultural and Forest Meteorology, 149: 1552-1555
- Wallèn B., 1987, "Growth pattern and distribution of biomass of *Calluna vulgaris* on an ombrotrophic peat bog", Holarctic Ecology, 10: 73-79
- Wang W.J., Zu Y.G., Wang H.M., Hirano T., Takagi K., Sasa K. and Koike T., 2005, "Effect of collar insertion on soil respiration in a larch forest measured with a LI-6400 soil CO_2 flux system", Journal for Research of the Japanese Forest Society, 10: 57-60
- Warburton J., 2003, "Wind-splash erosion of bare peat on UK uplands moorlands", Catena, 52: 191-207
- Ward S.E., Bardgett R.D, McNamara N.P. and Ostle N.J., 2009, "Plant functional group identity influences short-term ecosystem carbon flux: evidence from a plant removal experiment", Functional Ecology, 23: 454-462
- Ward S.E., Ostle N.J., McNamara N.P. and Bardgett R.D., 2010, "Litter evenness influences short-term peatland decomposition processes" Oecologia, 164: 511-520
- Williams B.L. and Sikcock D.J., 2000, "Impact of NH_4NO_3 on microbial biomass C and N and extractable DOM in raised bog peat beneath *Sphagnum capillifolium* and *S. recurvum*", Biogeochemistry, 49: 259-276
- Wilson D., Alm J., Laine J., Byrne K.A., Farrell E.P. and Tuittila E-S., 2009, "Rewetting of cutaway peatlands: are we re-creating hot spots of methane emissions?" Restoration Ecology, 17: 796-806

- Wilson L., Wilson J., Holden J., Johnstone I., Armstrong A. and Morris M., 2011, "Ditch blocking, water chemistry and organic carbon flux: evidence that blanket bog restoration reduces erosion and fluvial carbon loss", Science of the Total Environment, 409:2010-2018
- Wood-Gee V., 1996, "Taking the heat out of burning", Farming and Conservation, January: 24-26
- Worrall F. and Burt T., 1998, "Decomposition of river water nitrate time series – comparing the agricultural and urban signals", Science of the Total Environment, 201: 153-162
- Worrall F. and Burt T., 2005, "Predicting the future DOC flux from an upland peat catchments", Journal of Hydrology, 300: 126-139
- Worrall F., Burt T., Adamson J., Reed M., Warburton J., Armstrong A. and Evans M., 2007, "Predicting the future carbon budget of an upland peat catchment", Climatic Change, 85: 139-158
- Worrall F., Burt T.P., Jaeban R.Y., Warburton J. and Shedden R.,2002, "Release of dissolved organic carbon from upland peat." Hydrological Processes, 16: 3487-3504
- Worrall F., Reed M., Warburton J. and Burt T., 2003, "Carbon budget for a British upland peat catchment", Science of the Total Environment, 312: 133-146
- Worrall F., Burt T.P., Rowson J.G., Warburton J. and Adamson J.K., 2009a, "The multi-annual carbon budget of a peat covered catchment", Science of the Total Environment, 407: 4084-4094
- Worrall F., Evans M.G., Bonn A., Reed M.S., Chapman D. and Holden J., 2009b, "Can carbon offsetting pay for ecological restoration?", Science of the Total Environment, 408: 26-36
- Worrall F., Rowson J.G., Evans M.G., Pawson R., Daniels S. and Bonn A., 2011, "Carbon fluxes from eroding peatlands – the carbon benefit of revegetation following wildfire", Earth Surface Processes and Landforms, 36: 1487-1498

- Wu Hu Q., Wu Q., Cao G.-M., Li D., Long R.-J. and Wang Y.-S., 2008, “Growing season ecosystem respirations and associated component fluxes in two alpine meadows on the Tibetan plateau”, Journal of Integrative Plant Biology, 50: 271-279
- Yan W., Artz R.R.E. and Johnson S., 2008, “Species-specific effects of plants colonising cutover peatlands on patterns of carbon source utilisation by soil microorganisms”, Soil Biology and Biochemistry, 40: 544-549
- Yuan W., Luo Y., Li X., Liu S., Yu G., Zhou T., Bahn M., Black A., Desai A.R., Cescatti A., Marcolla B., Jacobs C., Chen J., Aurela M., Bernhofer C., Gielen B., Bohrer G., Cook D.R., Dragoni D., Dunn A.L., Gianelle D., Grunwald T., Ibrom A., Leclerc M.Y., Lindroth A., Liu H., Marchesini L.B., Montagnani L., Pita G., Rodeghiero M., Rodrigues A., Starr G. and Stoy P.C., 2011, “Redefinition and global estimation of basal ecosystem respiration rate”, Global Biogeochemical Cycles, 25: GB4002
- Yu Z., 2011, “Holocene carbon flux histories of the world’s peatlands: Global carbon-cycle implications”, The Holocene, 21: 761-774
- Zhao L., Li Y., Xu S., Zhou H., Gu S., Yu G. and Zhao X., 2006, “Diurnal seasonal and annual variation in net ecosystem CO_2 exchange of an alpine shrubland on Qinghai-Tibetan plateau”, Global Change Biology, 12: 1940-1953

Appendices

Appendix 1 (electronic)

Chapter 3 – Altitude Raw Data

This file contains the collation (i.e. CO_2, DOC etc.) sheets for experiments I and II as well as the C/N data for experiment II.

Chapter 4 – Vegetation Raw Data

This file contains the collation (i.e. CO_2, DOC etc.) sheet for all the vegetation types and a methane data collation sheet.

Chapter 5 – Diurnal Raw Data

This file contains the collation (i.e. CO_2, DOC etc.) sheet for each cycle sampled and the UNG weather station data corresponding to the sampling periods.

Chapter 6 – Acute Trial Raw Data

This file contains the CO_2, DOC concentration, water quality and data collation sheets for all plots in the acute trial.

Chapter 6 – Chronic CN Raw Data

The file contains the raw CN data for the chronic trial.

Chapter 6 – Chronic Trial Raw Data

This file contains the CO_2, DOC concentration, water quality, PCA and data collation sheets for all plots in the chronic trial.

UNG Weather Data 2006-2010

This file contains the meteorological data from the Upper North Grain (UNG) weather station.