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The drivers of soil organic matter turnover across spatial scales and the effect of climate change on gaseous losses of C and N from heathland systems

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The drivers of soil organic matter turnover across spatial scales, and the effect of climate change on gaseous losses of C and N from heathland systems.

A thesis submitted to Bangor University by Robert Thomas Edmund Mills in candidature for the degree of Philosophiae Doctor at the School of the Environment, Natural Resources and Geography, Bangor, Gwynedd LL57 2DG

May, 2011.

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Abstract

Understanding the turnover and storage of C and N in soils is central to the wider study of biogeochemical cycles. The loss of C and N to the atmosphere can be monitored using simple analytical techniques both in the field and under laboratory conditions, with the loss of C (soil respiration) being one of the most studied components of terrestrial biogeochemistry. The sensitivity of these processes to climate change, and the general driving by edaphic, vegetation and climatic conditions are variable and still poorly understood. This thesis considers three issues in contemporary biogeochemistry; 1. How do warming and throughfall reduction (i.e. climate change) alter soil respiration in an upland heathland. 2. What are the drivers of gaseous losses of C (and N) over spatial scales. 3. What controls the turnover of long residence-time soil C on a national scale.

Reduction in summer throughfall had a significant effect on soil respiration when monitored over a three year period. Passive night time warming also had a significant effect on soil respiration, and both treatments increased the temperature sensitivity of soil respiration. There was a strong seasonal element though which suggests a greater temporal resolution is needed to further understand the nature of these fluxes. Assessment of C fluxes on across a national scale suggested that the quantity (and possible quality) of Soil Organic Matter (SOM) was a major factor alongside vegetation type when explaining large-scale soil respiration rates under controlled conditions. Using radiocarbon to model the turnover of SOM on a national scale suggested a fundamental difference between vegetation types with regard to the storage of SOM on decadal or millennial timescales.

These results reinforce the sensitivity of shorter-term processes, such as soil respiration, to fluctuations in prevailing climatic conditions, but suggest that vegetation type (and therefore litter input quantity and quality) may be more important when considering the longer-residence time SOM stored in GB soils. Linking concepts across scales is therefore deemed the way forward

in an attempt to integrate model predictions of the resilience of different pools of SOM to perturbations such as climate and land-use change.

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It has been a long road. Eventful and varied, but always providing new routes to explore and new questions to get stuck in to. I have met so many great people during the course of the PhD, and some friendships have been formed which I know will last. I would first like to thank Bridget Emmett and Davey Jones for their supervision of the project. For their enthusiasm, friendship, support and creative discussion I am indebted. Ed Tipping is also thanked for inspiration and the positive and productive support during the radiocarbon chapter. Working alongside Alwyn Sowerby, Chris Hinton and Dave Williams on the roof projects was always good fun and Alwyn is thanked especially for the long chats and support on life the universe and everything! To all my peers and friends made whilst at CEH: Mark, Hilary, Helen, Kirsten, Imogen, Simon, Miles, Ed, Katie, Steph, Susie, Jackie Cooper, Jackie Chaplow, Laurence, Jenny, Steve, Gareth, Aarron, Tom, Bev, David and the rest of CEH staff I thank you for happy times, support and creating such a great place to work. Also, thanks are extended to NERC for generous funding of this project.

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Chapter 1. Introduction

1.1 Carbon in soil: introduction

Carbon within soils represents the largest terrestrial C store, and is estimated somewhere in the order of 2500 Pg C (Lal, 2004). This value is approximately three times that which is found within the atmospheric pool, and consequently represents a highly valuable resource. Roughly 1550 Pg of the total soil-C is organic (SOC) (Lal, 2004, Schlesinger & Andrews, 2000), with Soil Inorganic Carbon (SIC) accounting for the remaining 950 Pg C (Lal, 2004). The use of the word 'store' implies this C is stable and will remain within the soil, especially for SOC this is not the case, and all SOC exists at a point along a decomposition continuum. This ultimately leads to C being lost from soil as a gas (principally CO_2), as Dissolved Organic Carbon (DOC), or as Particulate Organic Material (POM) through erosion or leaching processes. The input and eventual loss of C can be measured as the flux. The flux of carbon in terrestrial systems can be simplified into two main processes:

1. The removal of C from the atmosphere by autotrophic fixation (photosynthesis).
2. The loss of C through mineralization by autotrophs and heterotrophs (respiration) and loss as dissolved organic carbon in soil water.

The incorporation of CO_2 into sugars via photosynthesis is the primary route by which carbon enters terrestrial systems. After autotrophic respiration of fixed C, C contained within plant biomass will invariably enter the soil as plant litter at some stage in the plants life cycle. The construction of various materials, such as cellulose, starch, lipids, proteins and lignin within a plant cause the derived litter to be complex, and have a range of decomposition pathways within the soil. Plant derived carbon will enter the soil in three main pathways: directly as dead litter, as partially decomposed material from animal excrement, or as an exudate from the plant root system either directly (Kuzyakov, 2006) or via a mycorrhizal association (Johnson *et al.*, 2002).

The state and complexity of the three different input pathways suggest a hugely variable quality of carbon input to the soil, and subsequently a diverse flora and fauna thrive on decomposing the residue of plant material (Bardgett, 2005).

1.2 Decomposition and Soil respiration

All organic carbon input to soil enters a continuum of decomposition which can be summarised by three main processes:

- mineralisation, whereby SOC is metabolised by the biomass and lost as gaseous carbon
- assimilation, whereby organic material is incorporated into the biomass of soil flora/fauna
- Alteration, whereby the original substrate is transformed into a material with a different chemical structure, often following some form of chemical action (often a form of metabolism).

Conceptual views of the decomposition and soil respiration of SOC appear in many reviews within the literature and range in complexity from simple overview approaches such as that by Trumbore (2009) (Figure 1.1), through a construction where SOC pool have distinct turnover times (Figure 1.2), to more complex approaches where turnover is expressed as complicated by substrate sources and mode of turnover such as that proposed by Kuzyakov & Gavrichkova (2010) (Figure 1.3). These examples are few among many, and serve to demonstrate the complexity of studying and conceptualising the decomposition of SOC.

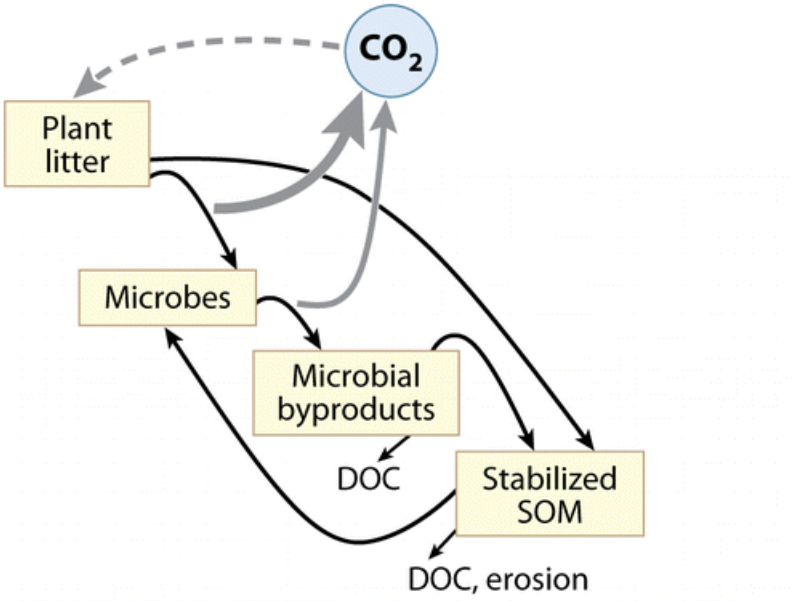


Figure 1.1 Conceptual View of C cycling within surface soils. From Trumbore (2009)

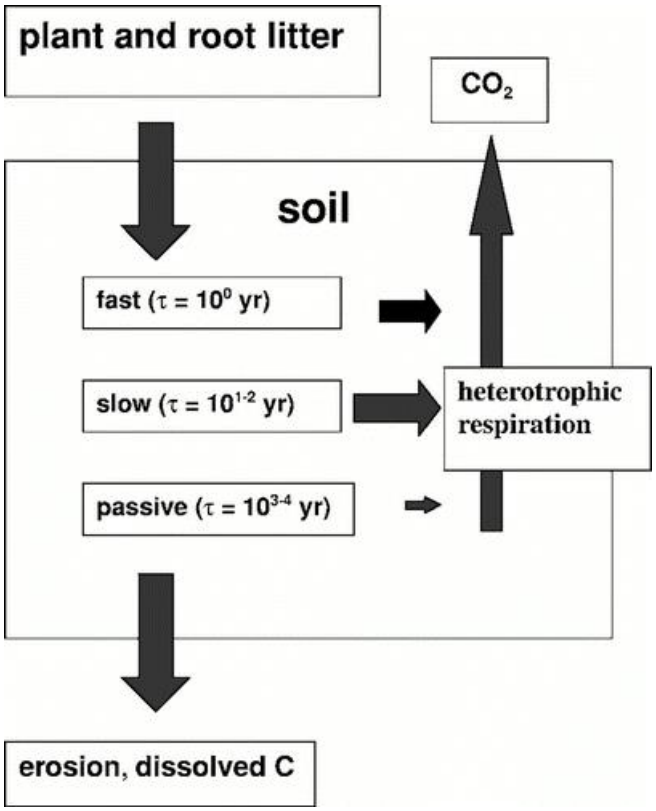


Figure 1.2 Conceptual view of SOC contained within pools of distinct turnover times. From Amundson (2001)

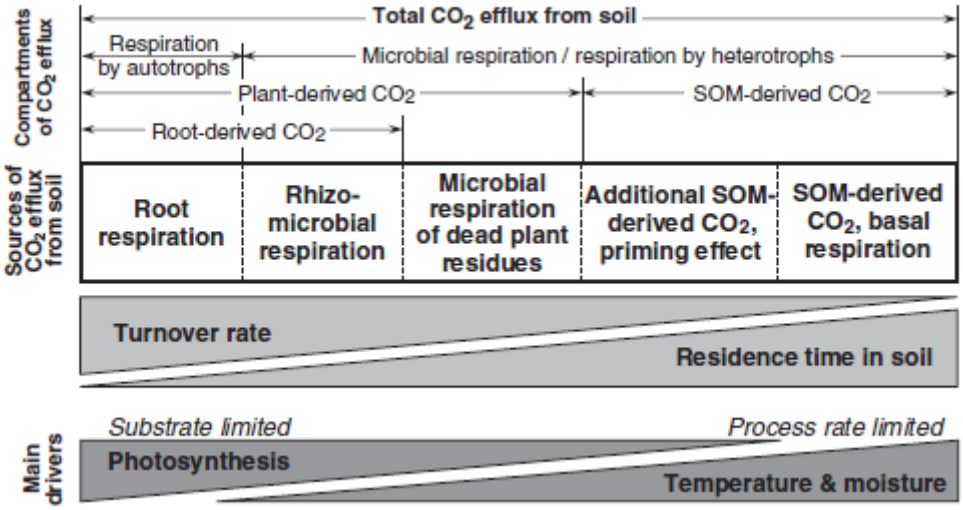


Figure 1.3 Conceptual view linking the source, mode and turnover time of components of SOC. From Kuzyakov & Gavrichkova (2010).

Soil respiration combines the measurement of CO_2 efflux from a number of components which can be broadly split into autotrophic and heterotrophic sources (Bond-Lamberty *et al*, 2004). This approach relies on the assumption that the total heterotrophic component is physically separate from, and therefore not reliant upon, the autotrophic component. Of course, this is not the complete picture, and although there will inevitably be a portion of the heterotrophic component which relies on bulk SOC for substrate, the contribution of rhizosphere microbes to total respired-C is great. As rhizosphere respiration can be considered the combination of microbial and root respiration, splitting further into source components at the rhizosphere level is difficult. The components of soil respiration can therefore be summarised in a simple relationship:

Eqn. 1. *Soil Respiration (SR) = autotrophic respiration + rhizosphere respiration + SOM respiration*

Given the understanding that rhizosphere respiration is complex, and the source components are potentially inseparable (i.e. rhizosphere microbes, by

definition, cannot function adequately in the absence of the root), a broad picture of dependence can be formed, such that total soil respiration will be root dependent, or root independent. This allows a simplification of equation 1 to:

Eqn. 2. *SR = Root dependent respiration (R_{rd}) + Root independent respiration (R_{ri})*

This approach avoids having to make a differentiation between autotrophic and heterotrophic contribution, more it recognises the role of roots in both directly contributing to respiration, but also stimulating a portion of heterotrophic respiration. To argue that the R_{ri} fraction is completely root independent would be flawed, as ultimately all soil biology is interdependent in some extraneous form or another. However, in reasonably short timescales R_{ri} can probably be seen as independent.

1.3 Controls on Soil respiration

Soil respiration is the benchmark measure of carbon turnover in soil, and as such, has been employed in the field and in laboratory settings to assess the impact of soil conditions on microbial and plant root activity. Using this technique, many authors (Beier *et al.*, 2004, Chapman, 1998, Davidson *et al.*, 1998a, Kuzyakov, 2002b, Kuzyakov & Cheng, 2001b, Lloyd & Taylor, 1994, Saleska *et al.*, 1999, Schlesinger, 1977, Trumbore, 1993) have reported sensitivity of soil respiration to changes in temperature and soil moisture, this being the fundamental principal underpinning concern for upland soils.

1.3.1 Temperature

The temperature sensitivity of organic matter decomposition is the key factor determining the response of the terrestrial carbon balance to climate change (Reichstein *et al.*, 2005a). Despite the common acceptance that soil carbon efflux is highly sensitive to temperature (Davidson *et al.*, 2000, Fang, 2001, Kirschbaum, 2006, Trumbore, 1993, Trumbore *et al.*, 1996) there is still an amount of uncertainty, and there certainly can't currently be a 'one size fits all' attitude to temperature sensitivity across world soils. Because of this uncertainty, the issue has received a considerable about of interest (Davidson *et al.*, 1998a, Lloyd & Taylor, 1994, Sanderman *et al.*, 2003).

In principle, the rate of all chemical reactions and enzymatic processes are linked to temperature, this making them ultimately variable with temperature. Temperature response of soil respiration is most commonly expressed as Q_{10}. This value signifies the change in rate of the reaction (in this case CO_2 production) with an increase in temperature of 10°C. This figure is especially useful when used to assess how the rate of respiration may change over different temperature ranges. This may allow better understanding of the sensitivity of a system to fluctuations in temperature within certain parameters. Broad Q_{10} values for whole system response are not sensitive to the varying contributors to bulk soil respiration. Although metabolic theory suggests that the rate of a reaction should relate to temperature such that a Q_{10} of around two should be found (assumes no other limiting factors), the varying sensitivities of the components of soil respiration allow for variation about this value (Davidson, 2006, Flanagan & Johnson, 2005, Janssens & Pilegaard, 2003, Panagiotis Dalias, 2001, Vanhala *et al.*, 2008, Yuste *et al.*, 2004)

The link between temperature and cycling of organic material in soils has been subject to some considerable debate within the literature (Davidson *et al.*, 2000, Giardina & Ryan, 2000, Knorr *et al.*, 2005). Although the relationship is based on the enhanced activity of decomposition processes at elevated temperatures, the application of this is difficult in a system which is

both highly heterogeneous and subject to temporal and spatial variation in other factors which affect decomposition and soil respiration. In order to quantify the sensitivity of soil to temperature change, the different pools of carbon within soils, both the labile and the stable pools, must be assessed for their sensitivity (Trumbore *et al.*, 1996). This assessment remains the major stumbling block in understanding organic matter decomposition, and remains the key topic of debate within the literature. Some authors suggest that the more recalcitrant pool of organic matter is much more sensitive to temperature than more labile fractions (Vanhala *et al.*, 2007, Xu *et al.*, 2010), whereas it has also been argued that temperature sensitivity is not dependent upon stability or recalcitrance indices (Fang *et al.*, 2005, Plante *et al.*, 2009).

Giardina and Ryan (2000) suggest that organic matter decomposition in some soils are not controlled primarily by temperature. The same authors also imply that our limited understanding of biophysical factors and inappropriate application of laboratory and field tests has led to a false emphasis on temperature sensitivity. This conclusion was drawn from a study of forest soils which, according to Davidson *et al* (2000) contained crucial flaws in application of methods and use of inappropriate field sites which had undergone significant disturbance. Davidson *et al* (Davidson *et al.*, 2000) continue to add that Giardina and Ryan (2000) assume homogeneity in soil carbon pool response to temperature, instead of recognising the different pools of labile and stable carbon. Giardina and Ryan (2000) insist that their methods were robust enough to assume homogeneity in soils, and that disturbance was relative between soils.

Assumption of homogeneity has been addressed by Trumbore (1993) when using a compartment model to assess turnover times in soils. Using radiocarbon methods, Trumbore (1993) was able to differentiate between compartments which had a range of turnover times between 10-10000 years within this study, the surface labile pools were shown to respond more rapidly to changing temperature. The response time of the labile pool would initially indicate that labile pools are more sensitive to changing temperature,

but Knorr *et al* (2005) conclude that the more stable pools of carbon are in fact more sensitive to long term temperature variation and could exert a stronger positive feedback to global warming that currently assumed. This raises the issue of what unlocks the more stable pools? Although Trumbore (1993) shows that rapid turnover compartments are more sensitive to short term changes in temperature, these soils are more easily cycled due to the relatively few chemical and physical constraints operating in the surface and litter layers. The modified, often deeper stable pools are likely to be constrained by chemical and physical factors, such as anoxia, extremes of pH and accumulation of recalcitrant matter as well as consistently low temperatures. Removal or amelioration of these factors could allow for more substantial decomposition of 'stable' pools.

Reichstein (2005a) argues that the higher sensitivity or stable pools is in fact false, and that Knorr *et al* (2005) used an inappropriate data from Katterer *et al* (1998) and that short term incubations (as used by Knorr et al (2005)) are less reliable when turnover is inherently slow. Reichstein (2005a) extends this point, stating that by allowing for comparison with a two compartment model, whereby the decomposition rates of the labile and the stable pools can vary independently, shows that there is a reverse relationship from the original findings of Knorr *et al* (2005).

The response of microbial communities to elevated temperature over long periods of time has been seen to decline in many experimental studies (Bradford *et al.*, 2008, Hartley *et al.*, 2008, Luo *et al.*, 2001). Two opposing theories have been suggested for this phenomena, that microbial communities acclimate to the elevated temperature, or that substrate depletion occurs, both causing a reduced temperature response. Root respiration is a major contributor to total soil respiration, acclimation to elevated soil temperatures for root production needs to considered alongside that of the microbial community. Burton and Pregitzer (2003) found no acclimation to temperature when studying the seasonal fluctuations of fine root respiration in sugar maple (Acer saccharum Marsh.) and red pine (*Pinus resinosa* Ait.) forests. Thermal acclimation to experimentally raised

temperature was found in some *Rannunculus* species (Cooper, 2003), in some ectomycorrhizal fungi (Malcolm *et al.*, 2008) and in the roots of citrus trees (Bryla *et al.*, 1997), however many studies observe acclimation over short periods of time, which may not be true of systems under extended periods of elevated temperature.

1.3.2 Soil moisture

The presence of water within soil is essential for biological activity, both in terms of the fundamental role water plays in metabolism, and by providing a solution within the soil facilitating movement of soil organisms and the diffusion and availability of nutrients (Killham, 1994). Excessive amounts of soil moisture, whereby the diffusion of oxygen throughout the soil is inhibited, can lead to a reduction in metabolic activity, especially the oxidative processes associated with organic matter decomposition (Orchard and Cook, 1983, Davidson *et al* 2000). An excess of water can become the dominant factor controlling biogeochemical cycles, and in many upland systems, it is the consistent excess of soil moisture which retards decomposition, and leads to the accumulation of organic material within soil. This excess can be driven by precipitation, or water table movements. Water limited soils will also exhibit low metabolic activity, but rather than the biogeochemical cycles shift from aerobic to anaerobic, oxidative processes will remain dominant, but at much lower rate, often responding in flushes of activity to precipitation events. It is therefore important to consider the initial climatic conditions of a system before attempting to estimate response to climatic change (Falloon *et al*, 2001), as sensitivity to fluctuations in moisture will much depend upon the preceding soil moisture regime.

The idea that systems limited by either the excess of moisture, or the lack of it will respond to events of precipitation (or the lack of for moist soils) is one of the key issues when considering the controlling effect soil moisture regimes have on carbon cycling. In the case of carbon rich soils, the omnipresence of water may be periodically interrupted by episodic drought,

thus creating conditions more favourable for aerobic decomposition pathways. The incidence of summer drought punctuated by more extreme storm events (IPCC, 2007) may become more prevalent for some northern latitude systems. These more volatile climatic conditions could have profound effects on the cycling of carbon within highly organic soils, previously constrained by a year round excess of soil moisture.

The anoxic conditions within peaty soils caused by excess moisture have been seen to be lifted by experimentally induced droughts, and the subsequent onset of oxidative processes noted (Emmett *et al.*, 2004, Haesebroeck *et al.*, 1997, Hogg *et al.*, 1992, Knorr *et al.*, 2008, Petrone *et al.*, 2005, Sowerby *et al.*, 2008). In an excessively wet heathland, reducing the summer rainfall input caused a 22% increase in the production of bulk CO_2 from soil, (Jensen *et al.*, 2003). Bulk soil respiration does not indicate the relative contributions from soil microbes and from root respiration, but it is highly likely that under reduction of excessive moisture conditions, previously stable organic matter within soil is more easily mineralized, and thus will contribute a large amount to bulk soil respiration. In an attempt to partition respiration from a peatland system, Crow and Wieder (2005) found that vascular plants generally accounted for anything between 35-57% of total respiration, the majority of this being derived from root respiration and the microbial turnover of rhizosphere root products. Similar figures were found by Knorr et al (2008) where 55-65% of total respiration was autotrophic derived. It would seem reasonable then to assume that a significant portion of the increased C mineralization observed in Jensen et al (2003) was from microbial sources. Knorr et al (2008) found that autotrophic respiration to be less sensitive to drought during a lowering of water table in a temperate fen, but soil respiration rates near the surface of the droughted soil to increase notably.

A shift in substrate utilization would suggest a shift in microbial population structure (diversity, mass), Jensen et al (2003) found a shift to a more fungal-dominated microbial population structure, but no significant change in total biomass. Jensen at el (2003) suggest that this shift in population structure is

a result of greater tolerance of drought stress than bacterium, and also the more efficient use of poor substrate by fungi. Jaatinen et al (2007) found nutrient status to be a significant factor in controlling the nature of microbial diversity change under droughting of peatlands, with a more dominant fungal population found during drying of a mesotrophic fen and fungal populations suffering during the drying of an ombrotrophic bog. These data suggest that the type of peatland/highly organic soil interacts with the hydrology to potentially favour different microbial groups during drought.

Groundwater level appears to be one of the major controlling factors in reducing the check placed on C mineralization (Jungkunst *et al.*, 2008). Natural droughting of a boreal bog system in Finland during the summer of 1994 was reported by Alm et al (1999) as having a significant effect of carbon efflux. Using static chamber measurements, Alm et al (1999) reported a shift from net carbon uptake to net carbon efflux via CO_2 production during drought induced water table draw down. This loss of carbon was deemed a product of both enhanced soil organic matter decomposition, and reduced photosynthetic capacity due to desiccation of Sphagnum species. Water table draw down manipulations to intact bog monoliths were reported by Updergraff et al (2001) to have no effect upon CO_2 emissions, even though the continuation of water table draw down was for a much greater period of time than that noted by Alm et al (1999). Glatzel et al (2006) also noted a significant increase (approx. 33%) in CO_2 production at a restored bog in north west Germany following a drop in the water table (42cm) caused by a 59% reduction in summer rainfall.

Soil fauna population dynamics have also been shown to be influenced by drought (Lindberg *et al.*, 2002) both directly and indirectly. Direct response includes the reduced motility of some soil animals under drought, and indirect effects include the population response to changes is prey item distribution. Lindberg *et al* (2002) showed mycophagous soil animals to have highly variable response to drought, this perhaps being due to the relative abundance of drought tolerant fungi as seen in Jensen *et al* (2003). Differential response to drought across microbial populations and soil

macrofauna indicate that a more variable hydrological regime could cause a significant shift in soil ecology towards favouring more tolerant species, species capable of multiple substrate utilization, and species capable of making rapid population recoveries in response to substrate starvation.

Drought induced changes in the water holding and repellence characteristics of soil has been well documented in the literature (Dekker, 2000, Doerr *et al.*, 2000, Doerr & Thomas, 2000, Jaramillio, 2000, McHale, 2005). The occurrence of water repellence in soils can be due to the presence of hydrophobic substances within the soil matrix, as well as physical modification of soil components. Even without these additions and changes, a soil will have an inherent degree of hydrophobicity due to the physical structure of soil particles and pore spaces (Doerr *et al.*, 2000). The simple attractive forces which exist between water and solid surfaces cannot be broadly applied to soils in scales greater than the grain size, due to the highly heterogeneous nature of soils and the variable content of hydrophilic and hydrophobic substances and surfaces. The lack of uniformity in repellency characteristics is pointed out by Ma'shum *et al* (1988) when stating that many layers of a hydrophobic substance are required to render a mineral grain completely hydrophobic. So even with the presence of a hydrophobic material, grains will not be entirely covered, and indeed, scaling this idea up to the catena level is highly complex.

The presence of hydrophobic material in organic matter is stated as being the main driver behind water repellency in natural soils (Doerr *et al.*, 2000) and it is the variety of naturally occurring waxes, aliphatic and amphiphillic compounds within organic matter which hive hydrophobic properties. The amount of these materials within any given soils is dependent upon the vegetation type and cover, and the microbial communities within a soil. The presence of resin-rich plants, such as pines and eucalyptus (Ferreira, 2000) would increase the hydrophobic quality of litter layer soil, and this will also be true of stable organic matter in deeper soils originating from resin-rich litter. Water repellency has also been noted in heathland ecosystems under

Calluna (Mallik & Rahman, 1985) and *Vaccinium* (Richardson & Hole, 1978) species as well as Mediterranean shrubland (Giovannini *et al.*, 1987).

Soil micro organisms have also been noted as significant contributors to soil hydrophobicity (Doerr *et al.*, 2000). Hallett and Young (1999) describe how the production of water repellent microbial biomass and exudates which alter the hydraulic properties of soil are the main factors which determine microbial input to hydrophobicity. Hallett and Young (1999) go on to state that this is most sever when soil is under drought, as the exudates become highly hydrophobic when dry. Feeney ((2004), in Feeney (2006)) showed a strong relationship between fungal mass and water repellency, and this correlates with the well-known presence of highly hydrophobic fungi within soils (Unestam, 1995). Not all fungi are hydrophobic; indeed, many fungi have highly hydrophilic hyphae and can be found alongside hydrophobic fungi within soils (Unestam, 1995). Attempting to determine the contribution of fungi to water repellency, Feeney *et al*(2006) used biocides to remove bacterium from the soil, but failed to link individual fungal species biomass with water repellency. This a likely result of the inability to distinguish between fungal species, and consequently their hydrophobic nature.

As with data from Jensen at el (2003), fungi were seen to be more dominant under drier soil conditions. This study also was unable to determine the actual fungal species present, and perhaps represents a situation whereby hydrophobic fungi become more successful due to their ability to thrive under dry conditions. *Aspergillus niger* was shown to induce water repellency by Bornemisza (1964) but not by Savage *et al*, (1972) concluding that even when the fungi can be isolated and identified, it does not always exhibit the same repellency characteristics.

1.3.3 Perturbations – freeze-thaw and dry-rewet

Within the controlling factors of temperature and soils moisture, it is the cyclical nature of seasonal alterations to prevailing conditions and the onset

of perturbations (freezing events, extreme droughts, storms etc.) which can cause shifts in the nature of carbon cycling in organic soils.

Carbon cycling and general metabolic activity within frozen soil is reasonably poorly studied (Schimel, 2005) and requires significant amounts of study to fully quantify the role many frozen arctic and northern latitude soils play in global carbon fluxes (Robinson, 2002). The sensitivity of soil respiration in organic soils under cold conditions is very high, with Q_{10} values between 60 and 200 (Mikan *et al.*, 2002) reported for conditions below 0°C. This temperature sensitivity is key to understanding the way in which soil respiration and substrate use may change in a thawing soil. Upon thawing, a flush of respiration has been noted, (Schimel & Clein, 1996) this perhaps being rapid turnover of microbial biomass-derived low molecular weight carbon after cell lysis (Feng *et al.*, 2007). Studies have suggested that low molecular weight organic material, such a root exudates and that sourced from the microbial biomass may be key to maintaining carbon turnover in arctic systems (Boddy *et al.*, 2008) and indeed regulate microbial activity through tight substrate supply constraints. The rapid turnover of low molecular weight material) in some agricultural soils has been shown to be almost instantaneous after input (Jones & Murphy, 2007), indicating the substrate induced respiration cause by rhizosphere products. The turnover of more complex material was shown by Boddy et al (2008) to be much slower than that of substrates such as glucose and amino acids at low temperatures, suggesting temperature sensitivity of decomposition for material more complex than simple sugars and amino acids. The tight relationship between root- derived-substrate supply and microbial respiration could suggest that under warmer conditions a substrate-source change might occur to a more complex material, this was shown by Schimel and Mikan (2005) when microbial communities switched from within pool cycling of microbial biomass at .5°C to more plant detritus dominated pool at 2°C. This is a significant change over such a small temperature range, and at higher temperatures, greater rates of substrate induced respiration may occur.

Reduced snow cover to upland areas of the UK could sensibly be accompanied by the occurrence of more soil freezing events, as the insulating properties of snow are lost. This could lead to more substrate-induced respiration during winter months, as soil respiration is primed by the lysed products of freeze-thaw events. It is important then to consider that the turnover of high quality plant detritus during winter months could be increased under a changing climate, not only by increased temperature, but potentially by the occurrence of freeze-thaw events priming decomposition.

The nature of precipitation patterns coupled with soil hydrological conditions mean that soils can be subjected to drying and rewetting cycles on a range of severities and temporal scales. Similarly to the incidences of prolonged drought events, the impact of dry-rewet events on soil microbial communities and carbon turnover are much dependent upon the normal soil conditions. Fierer et al (2003b) found a grassland soil microbial community to be relatively unaffected by dry-rewet cycles when compared to an oak soil, where community composition changed significantly. This is explained by the inherently different microbial communities seen under the contrasting vegetation types, and the soil moisture stresses normally placed on the two communities. Altering the microbial community structure could potentially affect soil processes (Fierer *et al.*, 2003b) such as carbon turnover, or leached nutrients (Gordon *et al.*, 2008) and partly explain any change in soil respiration seen during dry-rewet events.

Gordon et al (2008) found a significant shift in microbial community composition of two grasslands under dry-rewet treatments, with a shift to a more bacteria dominated system and the loss of many fungi (as inferred from PLFA). This suggests that bacteria might be more resistant to dry-rewet episodes due to the physical stress of desiccation being less marked in the smaller pore spaces colonised by bacteria, rather than the larger pores where fungal communities tend to dominate (Gordon *et al.*, 2008). Soils which are generally subject to a drier climate are less affected by dry-rewet episodes than soils which are generally moist (Zornoza *et al.*, 2007) and modifications to microbial biomass carbon and substrate induced respiration

are most pronounced in soils which are dried down from a typically moist field state.

The flush effect of rewetting a soil is similar to that of freeze-thaw, in that a significant proportion of the respired C is derived from turnover of the microbial biomass (Utomo & Dexter, 1982, Wu & Brookes, 2005) as well as the enhanced availability and physical release of non-biomass soil organic matter (Halverson *et al.*, 2000, Wu & Brookes, 2005). The flush of mineralization after a rewetting event has been noted to be greater than pre cycle rates (Wu & Brookes, 2005) and it is possible that these events could make up a substantial part of a systems C flux. Episodic rewetting enhanced CO_2 release in soils studied by Miller et al (2005) in the order of 2.2-3.7 times greater than those incubated at equivalent mean soil moisture, and this was reported to be equivalent to 12-18% of the total soil C pool. This study suggests the potential for significant loss of soil C through a series of dry-rewet events, especially if they occurred in a system limited by water stress. Reasonably dry forest soils in many temperate and boreal systems accumulate organic material as a function of litter quality, soil temperature, soil moisture, soil fertility and soil mineralogy (Borken *et al.*, 2003). Soil carbon tends to be at or near steady state (Borken *et al.*, 2003) in many northern latitude forest systems, regulated by the aforementioned factors, so extreme precipitation events in these systems could induce enhanced respiration. This is noted by Borken et al (2003) in a study on forest O horizon response to dry-rewet cycles, and when considered in the light of potential temperature change, enhanced losses of carbon from boreal systems could represent a significant efflux of carbon form northern latitude systems. Soil respiration response to wetting events appears to be as responsive on larger scales (whole system response to precipitation events) as to small-scale dry-rewet events (Lee *et al.*, 2004). Indeed, the timing and quantity of rainfall events appears to have a marked effect on whole system response (Chou *et al.*, 2008) and should be considered in potential ecosystem response to a changing climate.

1.3.4 SOM quality and availability

Storage of carbon within SOM occurs on a variety of timescales, from minutes, to thousands of years (Sollins *et al.*, 2007, Trumbore, 2000, van Hees, 2005). The residence time of SOM can be influenced by a range of intrinsic chemical and physical, properties of the SOM (Marschner *et al.*, 2008), climate (Cou *et al.*, 1995), but also by the range of stabilisation mechanisms which operate within soil (Sollins *et al.*, 2007). Generally, the intrinsic chemical and physical properties of a substrate are highly relevant for initial litter decomposition (Cou *et al.*, 1995, Hattenschwiler & Jorgensen, 2010). However, the usefulness of these indices seems to decrease over the duration of decomposition (Cortez *et al.*, 2007). The quality of substrate input has been shown to stimulate certain components of the decomposer community (Chigineva *et al.*, 2009, Paterson *et al.*, 2008), and certain litters are often decomposed more rapidly when familiar to the decomposer biomass (Ayres *et al.*, 2009).

Light fractions of soil organic matter, such as dissolved organic carbon, represent a major energy source for soil microbes (Haynes, 2000) and the rapid response of soil respiration to input of high quality material reflects this (Jones & Murphy, 2007, Paterson *et al.*, 2008, Roberts *et al.*, 2007, Yuste *et al.*, 2007). Low molecular weight simple substrate materials such as glucose are mostly sourced from root exudates and turnover of microbial biomass (Kuzyakov & Cheng, 2001a). Because of the source of these simple materials and the rapid rate of their mineralization, low molecular weight material tends not to accumulate in soil. More complex, less favourable material will accumulate in soils, and it is the modification and availability of this material that will influence the rate of mineralization when soil conditions (moisture, temperature, nutrient supply etc.) change. These factors interact with each other to create a continuum of partially decomposed material within a given soil, and the challenge is to find appropriate methods which can separate SOM into externally distinct fractions with a known chemistry.

Baring in mind the complex range of substrates within soil, soil organic matter can be broadly grouped into reasonably distinct fractions (Crow & Wieder, 2005). The use of these fractions as substrates for carbon mineralization depends much upon the microbial community and its requirements to access a given fraction. Paterson et al (2008) used a variety of ^{13}C labelled plant material added to soil cores and found greater recovery of labile (lighter fraction/soluble) organic matter in bacteria and more recalcitrant (less soluble fraction) in fungal biomass. This pattern was not complicated by the presence or absence of roots and mycorrhizal fungi, suggesting that root exudates are not necessary to prime respiration when litter derived substrate is in abundance, and also that different fractions of soil organic matter are utilised by distinct microbial communities.

The application of fresh litter itself is seen as a primer for respiration (Paterson *et al.*, 2008). In work carried out by De Nobili et al (2001) trace concentrations ($\mu g\ g^{-1}$ quantities) of 'trigger solutions' of glucose, amino acids and root exudates caused the evolution of about 2 to 5 times more C as CO_2 than was contained in the original 'trigger solution'. This priming effect is likely to have caused the onset of further substrate utilisation from other soil fractions, as metabolic activity is elevated (Kuzyakov, 2002a) Priming is not universally observed though, and in some studies, the increase in respiration was confined to the turnover of N-rich material and the absence of priming turnover of more recalcitrant SOC (Weintraub *et al.*, 2007).

1.4 Soils and trace gas flux

Due to a range of biogeochemical cycles within soils, trace gas production (CH_4 and N_2O) is a notable facet of gaseous carbon and nitrogen loss from soils. The controls on the production of trace gases are lengthy and complex, but as both gases are sourced mainly from anaerobic processes in soils, it is clear that moisture will play a key role in regulating trace gas

production. A changing climate may alter these processes and lead to large scale changes in trace gas production.

1.4.1 Soil flux of methane

Methane (CH_4) is produced under anaerobic conditions within soils, and as such, soils which are generally high in organic material and subject to excessive moisture will be important sources of CH_4 (Flessa *et al.*, 1998, Maltby & Immirzi, 1993). CH_4 is a significant greenhouse gas, having 23 times the warming potential than CO_2 over a 100 year period (Smith *et al.*, 2003).

Highly organic soils have been seen in a number of studies to be sources of CH_4 (Greenup *et al.*, 2000, Hutchin *et al.*, 1996, Maltby & Immirzi, 1993, van Huissteden, 2004) due to the anaerobic decomposition of organic matter, leading to CH_4 as a terminal electron acceptor (Killham, 1994). The role of water table depth has been shown to have a major role in the production of CH_4 in organic soils (Jungkunst *et al.*, 2008), with continuous inundation (highest water table) favouring CH_4 production (Altor & Mitsch, 2008), but a more variable water table favouring CO_2 production (Aerts & Ludwig, 1997). Aerts and Ludwig, (1997) found CH_4 emission of intact peat monoliths to be about one order of magnitude lower at a low static water table compared with static high water-table, the difference in water table heights being only 10 cm. This suggests that methanogenic metabolism is highly water table sensitive. Coupled with the evidence that CO_2 production increases 15.3 times with the same lowering, carbon turnover overall is water table sensitive. The relationship between water table and gas production is not clear cut, indeed Blodau and Moore (2003) found that although water table draw down resulted in a net reduction in CH_4 production and increase in CO_2 production, the change was complex and by no means linear. The varying equilibration times of gas production to moisture regimes (varying from days to months) would help explain why in-situ measurements of gas fluxes are not always correlated well to environmental variables (Blodau *et al.*, 2004). Hughes et al (1999) noticed a downward translocation of methanogenic

activity during droughting of a peatland soil, coupled with cyclical trends (seasonal) of CH_4 production throughout the year. Low recovery of emissions of CH_4 following such droughts were suggested by Dowrick et al (2006) to be heavily influenced by the increase in sulphate concentration within soil. This appears to be the case in-situ, and the same authors suggest that a possible interaction with low productivity following drought may act to further control methanogenic activity. The link between productivity and CH_4 production in bog systems remains uncertain, with some authors finding no significant correlations (Updegraff *et al.*, 2001)

Climate change has been associated with increases in wetland derived CH_4 during Interstadials during the last glaciation, owing mainly to the likely effect of stimulated CH_4 production in wetlands due to increased temperature rather than converse arguments of wetland expansion (van Huissteden, 2004). This is large scale CH_4 production from temperature induced rises in metabolic activity. Temperature sensitivity of CH_4 production under anaerobic conditions is well documented in the literature (Hargreaves and Fowler, 1998), but with variable values, between 1.3 and 28 (van Hulzen *et al.*, 1999). A significant factor in this variation may be due to the competitive success of methanogens at varying temperatures. Van Bodegom and Stams (1999) found that over certain temperature ranges, the Q_{10} of CH_4 production increased greater than any other reduction process, and this was due to increased success at competing for acetate as a substrate. Van Hulzen et al (1999) used a modelling approach to study the dynamic interactions of the temperature dependent sub-processes and simulated CH_4 production at different temperatures, finding that at low temperatures, electron acceptors and methanogenic biomass limit CH_4 production for a longer time leading to low CH_4 production. Thaw of soil has been seen to be a process linked with enhanced mineralization of carbon to CO_2, but the release of CH_4 as trapped bubbles (Tokida *et al.*, 2007) and as a consequence of thawing permafrost (Turetsky *et al.*, 2002) indicates that episodic release of CH_4 associated with temperature fluctuations and freeze-thaw events may make up significant parts of carbon budgets for cold environments.

1.4.2 Soil flux of nitrous oxide

Nitrous oxide (N_2O) is one of the dominant gaseous forms of nitrogen lost from soil due to denitrification, the other gas being molecular nitrogen (N_2). Denitrification occurs when oxygen diffusion rates in soil are too low to satisfy the needs of respiration (Killham, 1994), conditions usually characterised by excessive moisture or water logging. Of the two gases, N_2O is of major concern due to its role as a greenhouse gas and a potential ozone depleting gas. Nitrification-mediated release of N_2O is found in soils where the diffusion of oxygen and substrate not inhibited by excess soils moisture (Bollmann & Conrad, 1998) and below threshold values (~60% WFPS) N_2O loss through nitrification is inhibited. At greater WFPS (~>90%) denitrification is the major pathway through which N_2O is lost from soil (Bollmann & Conrad, 1998). Davidson (1992) also noted that denitrification became the dominant process at higher moisture contents, finding that an initial flush of N_2O and NO after re-wetting a dried soil was followed by N_2O far exceeding NO production at field capacity.

Emission from soil has achieved attention mainly in agricultural settings (Freney, 1995) where efflux as a consequence of mineral N fertiliser application and certain agricultural practices has been noted (Dick *et al.*, 2008). In semi natural systems such as organic rich soils, N_2O production should be relatively small due to the generally acid conditions that prevail, as denitrification optima lies towards neutral pH (Killham, 1994). It would appear from the literature that availability of substrate via nitrification is one of the key factors in controlling denitrification rates (Wray & Bayley, 2007) and that potential denitrification often exceeds actual denitrification, even with a surplus of carbon substrate (van Beek *et al.*, 2004). Koops et al (1996) after finding significantly higher contribution of surface peat layers to N_2O production than sub surface soils, concluded that easily attainable carbon substrate was a limiting factor. It is feasible that these two factors interact, and it is the availability of quality carbon substrate and the availability of denitrification substrates (nitrates) (Aerts & Ludwig, 1997) that ultimately limit denitrification in anaerobic systems.

Weier et al (1993) studied the availability of simple carbon (glucose) and nitrate substrate addition and its effect on denitrification, looking at re-packed cores of four different soils. It appeared in the study by Weier et al (1993) that the availability of carbon substrate increased denitrification rates, even when soils were at relatively low moisture contents (70% WFPS), and excessive nitrate addition reduced the conversion of N_2O to nitrogen, suggesting that systems with large amounts of available nitrate coupled with high quality carbon substrate might emit denitrification products with a high N_2O:N_2 ratio.

Temperature effect on N_2O production has been noted (Godde & Conrad, 1999), however, the regulatory role of temperature on N_2O production appears to much less significant than the factors relating to substrate availability. Indeed, temperature sensitivity was seen by Rosenkranz et al (2006) to only be correlated with N_2O production in a forest soil when high quality litter was available in soil. Soil moisture and soil nutrient interaction with temperature were also seen by McHale et al (1998), again suggesting that temperature only influences N_2O production when substrate availability is high, and soil conditions favour a strong denitrification pathway. This suggests that there may be a substrate threshold within soils which, when reached, temperature response begins to influence N_2O flux.

1.5 Climate system and global change

Predicting the nature of our future climate is significant issue, and one which is of exceptional political, social and environmental importance. As well as using historical records and sophisticated climate models to predict change, understanding the implications of change and the potential feedbacks that may arise further complicate the issue. However, significant gains have been made in recent years to address these issues, as our climate models become more reliable and the depth of work on ecosystem response grows.

1.5.1 Recent change

On a global scale, greenhouse gas forcing of climate change has been seen to increase global mean air temperatures in recent years. Indeed, the most recent IPCC report (IPCC, 2007) ranks eleven recent years (1995-2006) among the 12 warmest on instrumental record, with global average temperature rising by approximately 0.76°C (1850-1899 to 2001-2005). Parker et al (1994) noted that the most recent warmth previous to their study (early 1990's) was most marked over the northern continents in winter and spring, Shindell et al (Shindell *et al.*, 1999) add that northern latitude winter warming has been the most notable global trend in climate change. The forcing of climate by a combination of anthropogenic and natural factors was addressed by Stott et al (2000) who summarised that more than 80% of observed multidecadal-scale global mean temperature variations and more than 60% of 10- to 50-year land temperature variations are due to changes in external forcing (both anthropogenic and natural). Stott et al (2000) also assert that under standard emissions scenarios, anthropogenic global warming is predicted to continue at a rate similar to that observed in recent decades. Complications arise when trying to ascertain the role of anthropogenic forcing on climate systems, as the majority of observed climate change has been through the forcing of natural climatic variables (Corti *et al.*, 1999). Corti et al (1999) do not attempt to conclude the role of anthropogenic forcing, as recent climate change can be interpreted in terms of changes in the frequency of occurrence of natural atmospheric circulation regimes and as such the definitive role of anthropogenic forcing is difficult to establish.

Sea level rise of approx. 1.8mm/year (1961-2003) has been observed and is a product mainly of thermal expansion, melting of glaciers, ice caps, and the Greenland and Antarctic ice sheets (IPCC, 2007). As a function of global increase in temperature, it is simple to observe relationships and potential feedbacks between ice melting, sea level rise, albedo and temperature and the consequences for precipitation regimes (Houghton, 2004).

From a UK perspective, specific changes have be noted to the UK climate, showing that temperatures have increased across the whole of the UK, but not equally. The central England temperature record has shown an increase of approximately 1°C since the 1970's and 0.8°C in Scotland since 1980 (Jenkins *et al.*, 2008). Both of these figures suggest a rapidly changing climate across the UK, and precipitation data suggests that more winter precipitation is being received through storm events over the last 45 years, in combination with a reduction in summer rainfall in all areas except Scotland and NE England (Jenkins *et al.*, 2008). This is especially relevant for considering the role of changing precipitation patterns and the potential interaction with temperature in UK ecosystems.

1.5.2 Implications for terrestrial systems

Baring in mind the modelled predictions of temperature increase in the order of 1-3.5°C over the course of the 21st century (Shaver *et al.*, 2000), and that northern latitude systems are likely to see greatest increases (IPCC, 2007), it is of great importance to quantify the potential response of terrestrial systems to climate change. The regulation of many biogeochemical cycles (partly) by temperature indicates that cycling of material and general metabolic activity within terrestrial systems may become enhanced under increased mean temperatures. The implications of temperature increase will depend much upon the initial conditions of a system, and this is nowhere more notable than in the arctic and boreal systems (Schlesinger & Andrews, 2000) where soil temperatures are at or below freezing for a considerable portion of the year (Schimel & Mikan, 2005).

The most notable obstacle when considering climate change implications is the possible interactive effects (Norby & Luo, 2004, Panikov, 1999) and feedbacks that may occur (Shaver *et al.*, 2000). These feedbacks may be positive and act to accelerate climate change (Cox, 2000) especially when considering the turnover of carbon. Linking in the potential feedbacks

associated with carbon turnover and climate change, Cox et al (2000) establish that the terrestrial biosphere will act as a net source of carbon by 2050 (under 'business as usual' modelled predictions) and this is a broad modelled response from a set of highly complex and sensitive processes. The transformation of carbon in soil via initial increase in ecosystem productivity followed by increased heterotrophic respiration (and consequent reduction in net ecosystem productivity) tend to show most models in agreement that terrestrial systems will be net sources of carbon by the middle of the 21st century (Cox, 2000, Cramer *et al.*, 2001, Jones, 1998).

Scaling these predictions down to the ecosystem or even the plot scale must involve the integration of high resolution environmental manipulation experiments to add clarity and accuracy to any prediction as there are often high incidences of variability when comparing habitat-scale models (Thuiller, 2004) With this in mind, the sensitivity of ecosystem types and ultimately soil types, must be studied in detail (Sutherland, 2006) and integrated into models to provide habitat specific predictions and accurate climate change-system feedbacks.

1.6 Experimental approaches to measure and model soil C.

1.6.1 Field

Experimental field monitoring is inherently difficult due to the heterogenic nature of ecological systems. This issue is often overcome by appropriate levels of replication and resolution of sampling. Within this strategy, assumptions have to be made about the sensitivity of a system to the manipulation and the response of the measured environmental processes. To this end, field manipulations involve fully replicated treatments with comparison control plots.

Due to the nature of climate change experiments, any treatment will focus on modification of prevailing conditions, rather than necessarily adding a novel variable. This means the regulations of climatic variables such as rainfall, ambient temperature, periodicity of precipitation, length of seasons etc. In order to maintain such treatments and ensure accurate and consistent application, heavily engineered approaches are often required.

One such approach is utilised as part of a European wide project, Vulcan. Vulcan aims to assess the response of European shrub lands to climate change by modifying the amount of summer rainfall and the ambient night time temperature of the ecosystem, in line with climatic predictions of late 21st century conditions. The treatments use retractable roof technology to draw out a curtain over the manipulation plot. Curtains used to increase night time warming roll out during the onset of dark conditions and utilising a highly IR reflective aluminium based material, reflect 96% of direct radiation and 97% of diffuse radiation (Beier et al, 2004). Curtains used to induce experimental drought are constructed out of transparent polyethylene plastic and are capable of fully excluding incoming precipitation, without significantly interfering with radiative behaviour. The passive approach to warming ecosystems has been employed under a variety of other methods (such as open top chambers) with success (Bergner *et al.*, 2004, Godfree *et al.*, 2011, Munier *et al.*, 2010, Sierra-Almeida & Cavieres, 2010).

Soil heating cables are also regularly employed in a range of ecosystems (Bergh & Linder, 1999, Bronson & Gower, 2010, Hagedorn *et al.*, 2010, McHale *et al.*, 1998, Schindlbacher *et al.*, 2009). However, as this approach focuses warming on the bulk soil and roots, the similarity to actual climate warming is poor. Using passive warming approaches allows for entire ecosystem warming to take place which is likely to more closely mimic that of climate change. Expecting soil warming to occur at specific depths without seeing a comparative (or greater) degree of warming in above ground compartments is unlikely. Soil heating techniques offer advantages in that the in-situ monitoring of specific soil temperature effects can be allowed, and that the process-based response can be more tightly controlled.

1.6.2 Laboratory

Manipulation under controlled conditions allows for a precise focus on the functional process response. In particular, substrate addition experiments tend to be carried out under laboratory conditions (Boddy *et al.*, 2007, Jones & Murphy, 2007). Manipulations of temperature and the implications for temperature sensitivity have also been conducted in the laboratory (Bol *et al.*, 2003, Feng & Simpson, 2008), as well as moisture status (Catherine Eimers *et al.*, 2003, Paul *et al.*, 2003). Whilst these practices allow for a tight control of experimental conditions, the transferability of findings to in-situ conditions can be problematic due to the inherent disturbance associated with such approaches. Typical techniques for maintaining environmental conditions in the laboratory include the use of growth chambers (Loya *et al.*, 2004), or the manipulation of cores in mesocosm experiments (Blodau *et al.*, 2004, Briones *et al.*, 2009, Knorr & Blodau, 2009). Laboratory approaches also take advantage of the potential for using high-end equipment to interrogate samples during incubations, and therefore make qualitative inferences about the contribution of certain physical components to the observed functional response (Andersen & White, 2006, Poirier *et al.*, 2005).

The analysis of soils from national surveys tends to be carried out under such laboratory conditions, and the link between the capability of large surveys and the standardisation of methods under laboratory approaches is potentially powerful. Repeated sampling of soils over time provides a robust method for the monitoring of change. Soils surveys are rare when considered on a national scale, and two such recent approaches (Bellamy *et al.*, 2005, Emmett *et al.*, 2010) have provided major comments on the state of soils in England, Wales and Scotland, even sparking controversy (Bellamy *et al.*, 2005, Smith *et al.*, 2007).

1.6.3 Modelling turnover of SOC using Radiocarbon

In light of climate and land use change, understanding long-turnover SOC is central to gauging the resilience of terrestrial systems to change. Whilst most current studies focus on short-term exchanges of C between soils and the atmosphere, a number of approaches allow for estimation of the components of SOC that reside in soil for decades and longer. Radiocarbon (^{14}C) exists naturally in terrestrial systems due to uptake of $^{14}CO_2$ by plants and subsequent incorporation into biomass and soil. Natural abundance of ^{14}C is small (~.0000000001% of total C) and due to its radioactive decay (half life of ~5730 years) can be used as a dating tool on a millennial timescale. The production of 'bomb carbon' due to atmospheric weapons testing during the late 1950s and early 1960s caused a pulse in atmospheric $^{14}CO_2$ content which peaked at roughly twice the pre-bomb levels. This produced a near-conservative tracer within terrestrial systems. Due to the availability of high-resolution atmospheric data, bomb-^{14}C can be used to estimate the incorporation and loss of C from soil, and therefore turnover of Soil Organic Carbon (SOC) can be estimated on a decadal timescale.

This approach has been employed to consider the residence time of C in a number of studies, but these generally focussed attention on a small number of locations, or a single site (Bol *et al.*, 1999, Chiti *et al.*, 2009, Evans *et al.*, 2007, Ladyman & Harkness, 1980, O'Brien, 1984). This has been extended to consider a comparison across a wider spatial scale, specifically UK woodlands (Tipping *et al.*, 2010). Generally, these approaches assume soil to contain C in pools of varying residence times, utilising pools with fixed turnover times (Amundson, 2001) allows an expression of the relative dominance of specific pools over another. Linking defined pools with physical or chemical properties of soil has received some attention, and there have been significant relationships found between residence times and recalcitrance indices (Baisden *et al.*, 2002b, Trumbore & Zheng, 1996). Linking to field measurements of soil respiration, radiocarbon efflux has given some indication as to the relative contribution of these components to respired fluxes (Trumbore, 2000).

1.7 Aims

Using an established climate manipulation field site (Emmett *et al.*, 2004), the sensitivity of soil respiration to predicted climate change in an upland heath community was investigated. A year-round ecosystem warming and summer throughfall exclusion manipulation allowed for an assessment of the driving factors of temperature and soil moisture, and linked in ecosystem response to predicted climatic change in UK uplands*. It is hypothesised that summer drought and year-round warming will increase the rate of soil respiration, with a greater overall impact of drought due to the natural excess of soil-water.*

Trace gas loss from the same site was compared to that of a similar upland heathland in an area historically more polluted by reactive N and S species due to acid deposition. The loss of N and feedbacks to climate are of particular relevance, and understanding some of the spatial variation between similar ecosystems is key to this. *It is hypothesised that a greater loss of N_2O via denitrification will be observed under higher deposition due to greater input of reactive N.*

Up-scaling of C storage and turnover to national scales allows for estimations to be made of the stock of C and the resilience of said stock. Using a mineralisation study of a national soil survey (Emmett *et al.*, 2010) allowed for an assessment of the larger-scale drivers of soil respiration and the possible influence of broad vegetation types on observed differences. *It is hypothesised that C mineralisation will vary with vegetation as a function of organic matter, such that a greater flux will be observed under higher SOM. It is also hypothesised that mineralisation will be constrained by soil pH and N content.*

Using radiocarbon modelling of SOC turnover, an investigation was made into the national scale drivers of turnover on the decadel-millenial timescale. Linking observations to vegetation and soil types allows for an assessment of the likely resilience of C to land use change, and when viewed in the context

of findings at other scales, can inform the response of SOC to climate change. *It is hypothesised that SOM turnover will be controlled mainly by edaphic factors that typically constrain soil respiration (pH, BD, SOM content, N content).*

Overall, this project aims to identify links between the drivers of C mineralisation and storage across a range of spatial scales in an attempt to provide insight into the similarity of response of short and long term processes to change.

Chapter 2. The effect of year-round night time ecosystem warming on soil respiration in an upland heathland system.

2.1 Introduction

Accumulation of carbon in upland organic soils is a key factor in terrestrial C turnover and storage. It is well documented that organic soils in northern latitude regions contain vast quantities of Soil Organic Carbon (SOC) (Rinnan *et al.*, 2008), brought about by the prevalence of cool, wet conditions, low pH and low nutrient availability limiting decomposition. UK upland soils tend to contain an appreciable amount of SOC, found either as peat or as highly organo-mineral enriched soils. Countryside Survey (CS) 2007 estimated GB topsoil C stocks in organo-mineral soils(LOI 30 – 60%) to be in the order of 99.7 tC/ha, and peat soils (LOI >60%) 84.9 tC/ha (Emmett *et al.*, 2010). This carbon is often relatively stable in the soil due a wide range of protection mechanisms and chemical recalcitrance, but fundamentally, the decomposition pathways involved in eventual mineralisation of SOC are limited by prevailing conditions.

Temperature is a universal rate modifier for biochemical processes, and given this, there will undoubtedly be a fundamental dependence of soil respiration on temperature. This subject has been central to the understanding of soil respiration dynamics for a considerable time (Witkamp, 1969), and basic explanations and mathematical equations for predicting and explaining the response of soil respiration to temperature have been thoroughly investigated (Lloyd & Taylor, 1994). Despite this length of investigation, there remains a considerable amount of uncertainty of the nature of the respiration-temperature relationship. This is especially evident when identifying the degree to which temperature modifies respiration in the presence of confounding factors. Recently, the debate has focussed primarily on the relative temperature sensitivities of certain components and substrates within soil (Davidson & Janssens, 2006, Fang, 2001, Giardina & Ryan, 2000, Trumbore, 2006), and attempts have been made to ascertain differing temperature sensitivities to substrates with an assigned degree of recalcitrance.

The long-term impacts of warming on soil respiration remain relatively unclear. Some studies have shown that over time, the response to continued soil warming results in a gradual decrease of extra-respiration such that efflux may fall to pre-manipulation levels. This was observed by a number of authors (Bradford *et al.*, 2008, Luo *et al.*, 2001, Melillo *et al.*, 2002) and resulted in the view that the stimulation of warming might not produce a significant net elevation of soil respiration. Bradford et al (2008) described three types of thermal acclimation which can be identified by the temperature sensitivity of warmed versus control soils. Type one acclimation suggests a suppression of temperature sensitivity in warmed soils as temperature increases, despite a common sensitivity at lower temperatures. Type two sees a generally higher rate under control soils across all temperature ranges, whilst Q_{10} could essentially remain similar. Due to an alteration in thermal optimum of soil respiration, type-three acclimation sees a reduced respiration rate at intermediate temperatures whilst a common rate may exist at temperature extremes. Explanations for these observations have been through hypothesis surrounding either microbial community change (Zhang *et al.*, 2005) or through the depletion of substrate due to enhanced decomposition (Luo *et al.*, 2001). The latter however assumes that enhanced decomposition losses would fail to be met by comparable (or greater) increases in NPP due to plant stimulation. Most of these studies are confined to mineral soils, and work on highly organic soils is rare. In this respect, the observation that warming has maintained a consistent stimulation of soil respiration above control levels after 10 years of experimental warming (Sowerby, personal communication, 2010) suggests that acclimation (if present) may be much slower to materialise in organic soils.

Field manipulations generally involve warming the system in one of two main ways; either by passive ecosystem warming (Beier *et al.*, 2004, Munier *et al.*, 2010), by infrared lamps (Bokhorst *et al.*, 2011), or by more invasive techniques involving the use of heating cables (Bergh & Linder, 1999, McHale *et al.*, 1998, Schindlbacher *et al.*, 2009). Manipulations of soil and plant warming have found respiration response to vary substantially.

Generally, the response has been for soil respiration to increase with ecosystem and soil warming (Rustad *et al.*, 2001, Wu *et al.*, 2011). The meta analysis carried out by Rustad (2001) showed that the mean change was an increase of 20% in respiration rates to experimental warming. Numerous studies have found soil temperature to be a major component of soil respiration (Davidson *et al.*, 1998b, Dorrepaal *et al.*, 2009, Grogan & Chapin III, 2000, Peterjohn *et al.*, 1994, Updegraff *et al.*, 2001), but temperature often behaves interactively with other controlling factors (Davidson *et al.*, 1998b) to create a highly complex system in field conditions. The positive response of respiration to temperature will depend much on the baseline conditions, and analysis of warming across multiple climatic zones has shown variable response (Emmett *et al.*, 2004), with the stronger response tending to be noted in systems which are generally more temperature limited. However, the magnitude of the temperature increase has significant impact on observed response, with only small increases (<1°C) shown to have little effect on decomposition in southern Atlantic Antarctic islands (Bokhorst *et al.*, 2007) and in Northern Sweden (Rinnan *et al.*, 2008). A greater magnitude effect was noted with increased temperature treatment, supporting the concept that baseline conditions strongly dictate the observable response. The response to warming will not only originate from the soil decomposer communities, but also the autotrophic components, and unravelling the contribution from each is a point of difficulty. Attempts have been made, and the issue causes considerable research effort (Schindlbacher *et al.*, 2009).

This study aims to assess the current state of passive night-time warming on an upland heathland which has been under experimental treatment since 2000. Specifically, this study considers the temporal trends in observations and investigates the seasonal variation in rates and the temperature sensitivity of soil respiration. It is hypothesised that soil respiration will be greater in warming than under control, and as the treatment is year round, the treatment effect will also be. It is also hypothesised that warming treatment will increase the temperature sensitivity of soil respiration as

warming stimulates greater production and therefore reduces the possible limitation by substrate availability.

2.1 Methods

2.2.1 Site description

The site is a *Calluna vulgaris* - *Vaccinium myrtilus* (NVC H12 community) heathland located in Denbighshire, North Wales (53° 3'N 3° 28'W). The site occupies a NE facing slope at an altitude of 410m ASL. The soil is characterised as being a shallow (~15cm depth) well drained organo-ferric podzol with a pH of 3.87 overlying gritstones in the Denbigh grit sequence. Site mean annual temperature is 7.6°C and annual rainfall is 1584 mm.

2.2.2 Experimental approach and plot layout

Nine 4.0 m x 5.0 m plots were established at the site during 1998 and treatments of summer drought, year-round night-time warming and control plots were established in a randomised block design. Warming treatment consisted of a retractable roof constructed from reflective aluminium foil interwoven with plastic line for strength (Figure 2.2.1). Roofs were extended over the plot during the onset of night (as detected by a light sensor) using a simple motor positioned at one end of the plot. The roof moved across the plot along supportive scaffold runners, and was kept taught by a spring at one end. The warming treatment remained on throughout the duration of night, throughout the year, unless either the wind speed reached 12 m/s (strong enough to damage the roof material) or a precipitation event occurred. The latter was implemented so as to avoid a reduction in soil moisture under warming treatments associated with drought. Roofs were re-extended over the plots when wind speed dropped, or when a precipitation event ceased.

Figure 2.2.1 Photograph showing general plot layout with control plot in the foreground, and an extended roof shown for demonstration over a plot.

2.2.2 Plot layout and sampling strategy.

Three soil respiration sampling points were located within each experimental plot. At each sampling point, a PVC soil respiration collar of 10cm diameter and 4.4 cm depth was cut into the soil surface to a depth of 2.5 cm in 1998. This collar represents total soil respiration, as the depth of the insertion was within the upper layers of the soil organic horizon, and would allow ingress of roots and mycorrhizae after initial insertion. During the course of the sampling period, any plant growth (notably *Vaccinium myrtillus*) within the collars was removed by cutting with sharp scissors. Mosses however were not removed, as the point at which live moss material can be differentiated from dead material is often difficult. Also, as the moss presents a significant input of litter material to the SOM, it was deemed far more detrimental to remove this input than the possible implications of having biomass within the collar. Normal litter fall from higher plants was not removed.

2.2.3 Data collection

Soil respiration measurements were made at fortnightly or monthly intervals throughout the period Oct 2006 – December 2009. Building on an existing measurement programme in place since 1998, measurements were made between 10 am and midday on each occasion. A PP-Systems EGM-4 and a Li-COR 8100 IRGA were used during the study period to collect soil respiration measurements. Simultaneous measurements of soil temperature were made at each respiration sampling point using the temperature probe supplied with the IRGA, or a standard electronic thermometer in cases where the on-board probe did not function. Soil moisture measurements were made using a Delta-T theta probe (Model ML-2, Delta-T Services, UK) adjacent to the soil respiration collar from Oct 2006 – Dec 2008, after which concerns about the suitability of theta probe measurements caused a cessation in manual moisture measurements. Intact cores were taken in place of theta probe measurements and soil moisture determined gravimetrically.

2.2.4 Data analysis and presentation

Soil respiration data was analysed for significant treatment effect over time using a repeated measures ANOVA after log transformation. Between groups comparisons of other data were carried out using ANOVA and T-tests where appropriate. All data was visually inspected for normality prior to any analysis using quantile-quantile plotting, and log transformations were carried out when needed to comply with ANOVA assumptions. Statistical analysis was carried out using R statistics version 2.11.1 (R, 2010) Linear and exponential regression fits between soil temperature and respiration were fitted using Sigmaplot version 11 (Systat, 2009). Figures were also produced in Sigmaplot version 11 or in R statistics.

2.3 Results

2.3.1 Treatment effect on soil moisture and soil temperature

Soil temperature at the time of sampling for soil respiration is shown in Figure 2.3.1. The data followed an expected seasonal pattern, however the shape of this seasonal dynamic was variable between the three sampling years. At this resolution, there was no significant effect of treatment on soil temperature despite the average temperature being 0.1°C higher in warming than control. By considering the higher resolution logged data (not available for the entire duration of the experimental period), there is a more recognisable effect on soil temperature. Figure 2.3.2 shows hourly sampling of soil temperature, and visual assessment of this figure suggested higher maximum temperature under warming than control. Figure 2.3.3 takes the difference between the two treatments, and as shown, warming soil temperature is elevated above control. The mean difference (for June 2009 only) amounts to 0.5 °C higher soil temperature in warming, with a higher reading being taken 89% of the time.

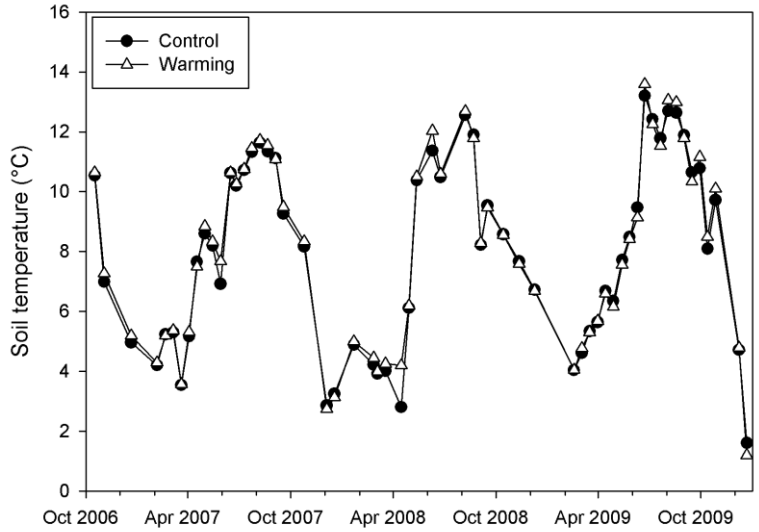


Figure 2.3.1 Soil temperature at 5 cm depth for both control and warming plots at time of soil respiration sampling.

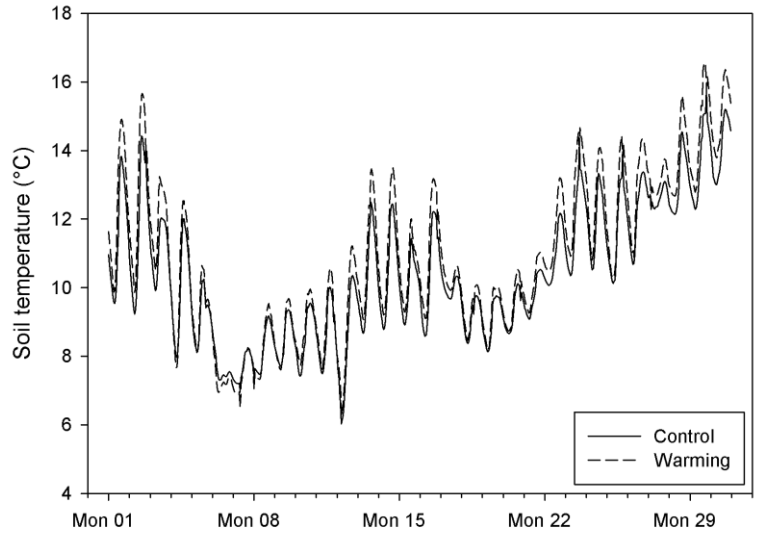


Figure 2.3.2 Hourly logged soil temperature at 5 cm depth for control and warming plots during June 2009.

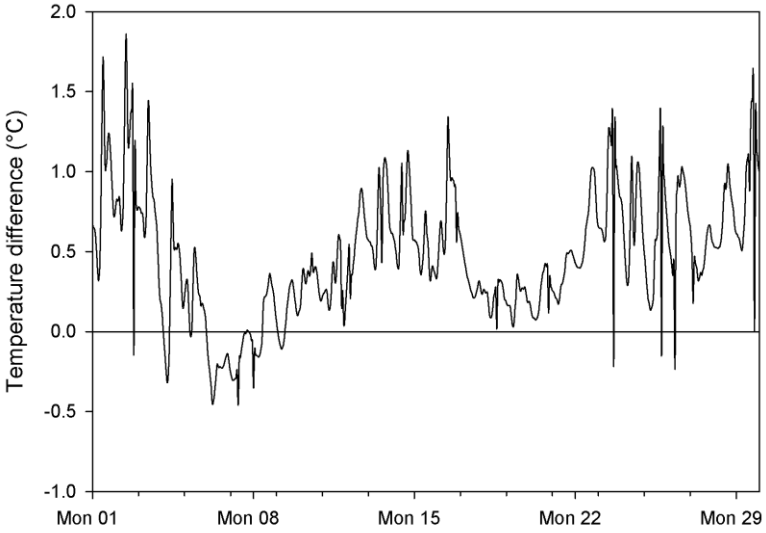
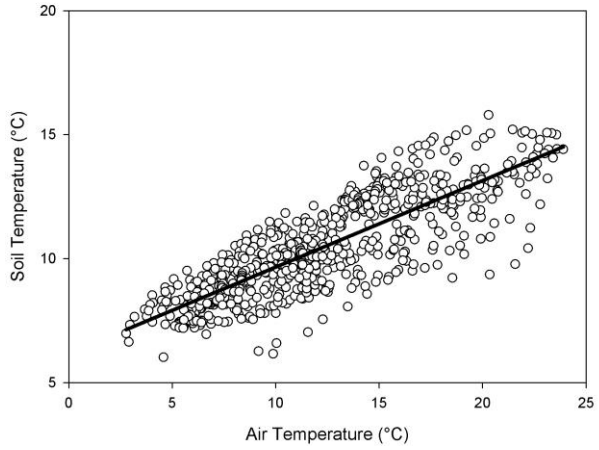
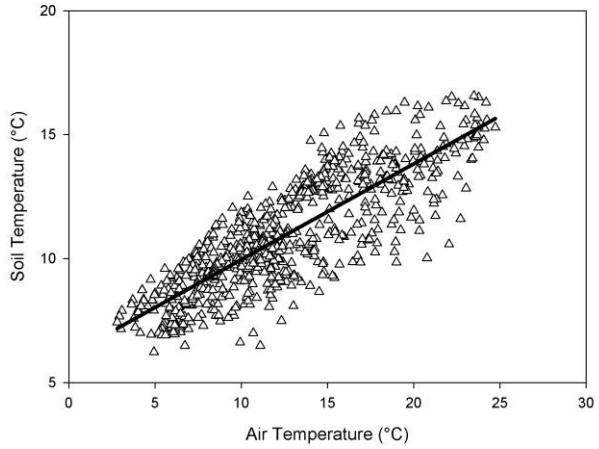


Figure 2.3.3 Difference in hourly soil temperature between control and warming plots for June 2009. A positive value indicates soil temperature in warming plots to be greater than control.



(a)



(b)

Figure 2.3.4 air temperature and soil temperature from control (a) and warming (b) plots. Control linear regression $r^2 = 0.69$, $p < 0.001$. Warming linear regression $r^2 = 0.69$, $P < 0.001$.

Using the slope of the linear regressions between air temperature and soil temperature in both control and warming suggests warming soil temperature to be more responsive to changes in air temperature (Figure 2.3.4). Control soil temperature increases by 0.35 °C per 1°C rise in air temperature, whereas warming soil temperature increases by 0.39°C over the same air temperature increase.

Figure 2.3.5 shows the mean daily time course of temperature increase in warming relative to control for selected months during 2009. There is a general elevation of soil temperature, but it is most notable that the effect is

more pronounced during the day (when treatment is not operational). The variation during the day is also dependent upon the time of year, with September showing the greatest range during the day.

Warming had no consistent effect on soil moisture, with treatment means being comparable throughout the dataset as shown in Figure 2.3.6.

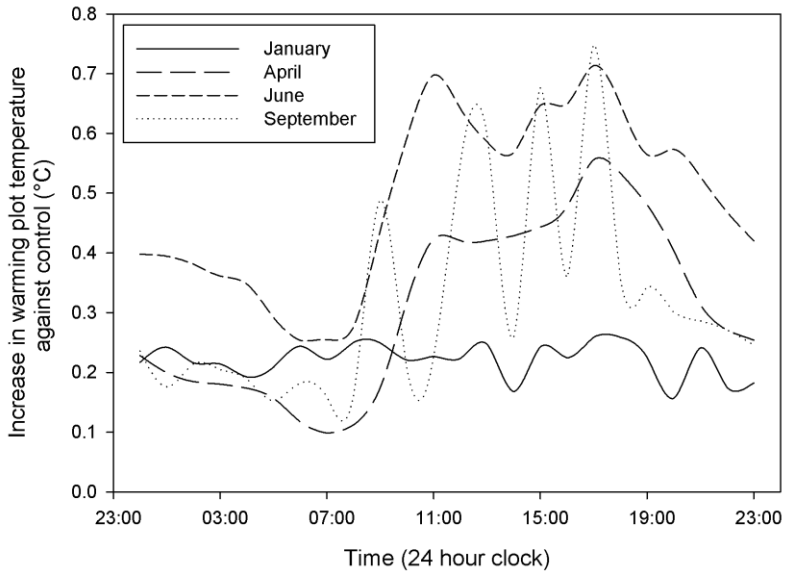


Figure 2.3.5 increase in soil temperature under warming plots relative to control. Values are mean for each hour of each day during the labelled months during 2009.

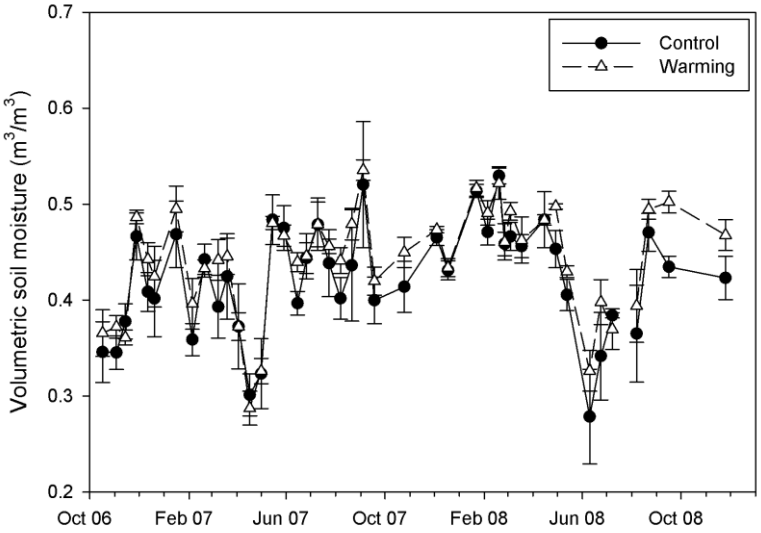


Fig 2.3.6 Volumetric soil moisture in control and warming treatments at 5 cm depth measured at time of soil respiration sampling.

2.3.2 Treatment effect on soil respiration

To identify periods of significant treatment effect, repeated measures ANOVA was carried out over the entire data set using month and year as factors, with plot as an error term. Over the entire dataset, warming is non-significant (p= 0.058), however there are clearly periods where the rate under warming is considerably higher than control (Figure 2.3.6 and 2.3.7). Investigating this using the predefined seasons (see methods) gave only winter to be significant (p= 0.049), with spring, summer and autumn failing significance (p= 0.11, 0.10, 0.12 respectively) despite there being apparent differences in rates over spring, summer and autumn (Figure 2.3.9). Analysis by month-pairs allowed for a greater scrutiny of the dataset, and this revealed that the two pairs April – May and May – June were significant (p= 0.033, 0.031 respectively) suggesting a significant late spring and early summer stimulation of respiration by warming treatment. The winter period was significant when restricted to November – December (p=0.047). There was also evidence of some marginal treatment effect during September – October (p= 0.052) and December – January (p= 0.058).

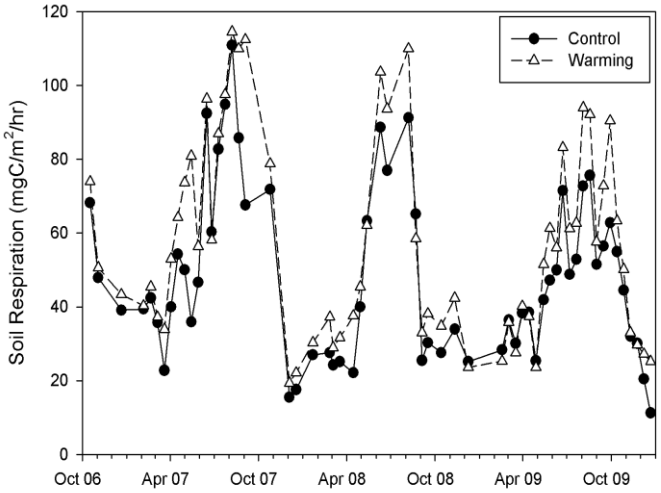


Fig. 2.3.7 Soil respiration for control and warming treatments October 2006 – December 2009.

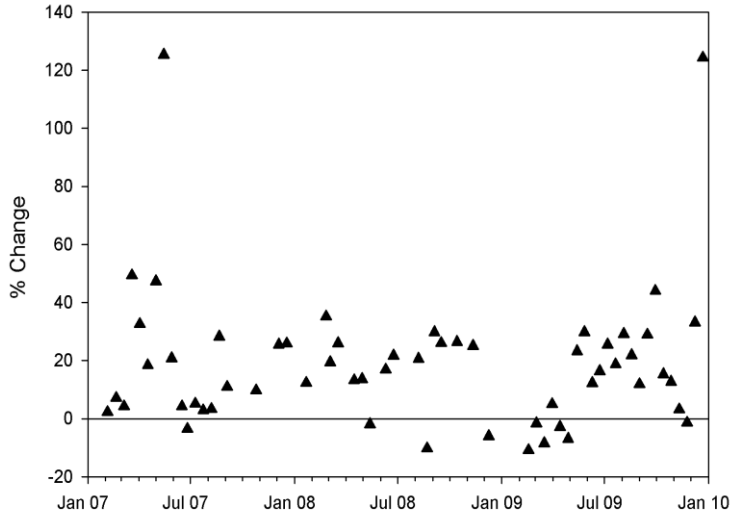


Figure 2.3.8 Percentage difference between control and warming soil respiration for January 2007 – December 2009. A positive value indicates a greater (in percentage terms) respiration flux in warming than control.

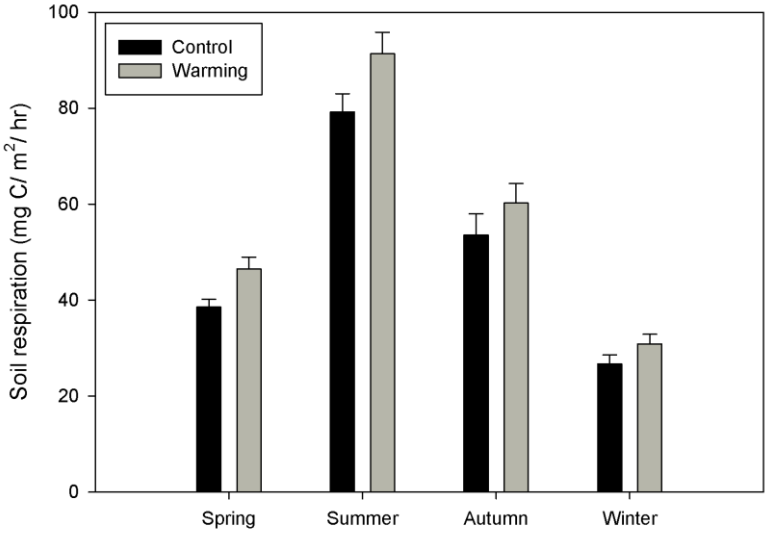


Figure 2.3.9 Mean soil respiration rates grouped by season for warming and control treatments. Bars are standard error of the mean.

2.3.3 Temperature sensitivity

Temperature sensitivity of soil respiration for the entire sampling period showed warming to have a higher Q_{10} than control when using both linear and exponential regression approaches (Figure 2.3.10 and 2.3.11). The size of the Q_{10} value was notably different between the two approaches (Table 2.3.1), however both had comparable r^2 and P statistics.

The yearly datasets suggested the temperature sensitivity to be different between years, but also the magnitude of the treatment difference varied. The r^2 value for the regressions was lowest during 2008, and when visually assessing Figure 2.3.12, there appeared to be very low temperature sensitivity in the 2 – 9 °C range for much of the year, this being poorly represented by the regression.

Seasonal sensitivities were constructed, and again, warming was more sensitive than control in each month (Figures 2.3.13-2.3.16). The Q_{10} varied between seasons in the order autumn > spring > winter > summer (Figure 2.3.17), however when considering the r^2 and p statistics for each

regression, clearly only spring provided a reliable relationship between respiration and soil temperature.

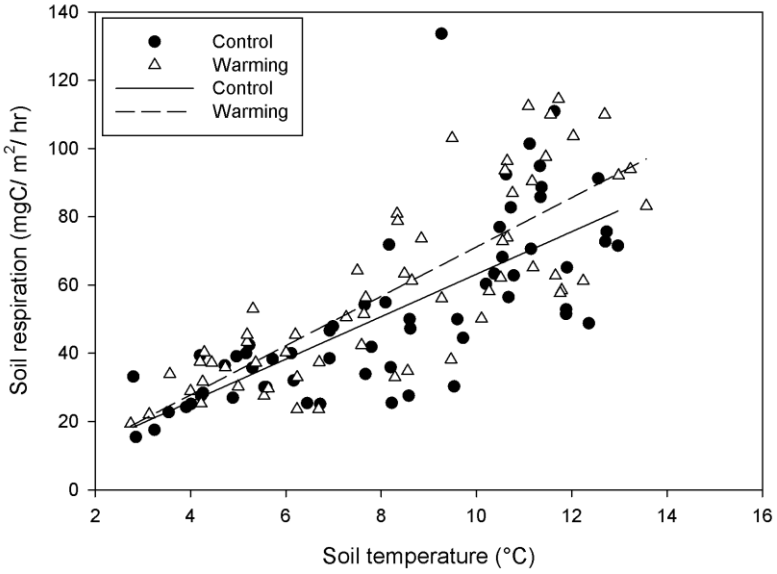


Figure 2.3.10 Temperature sensitivity of soil respiration in control and warming plots for October 2006 – December 2009. Linear regression parameters and output are found in Table 2.3.1.

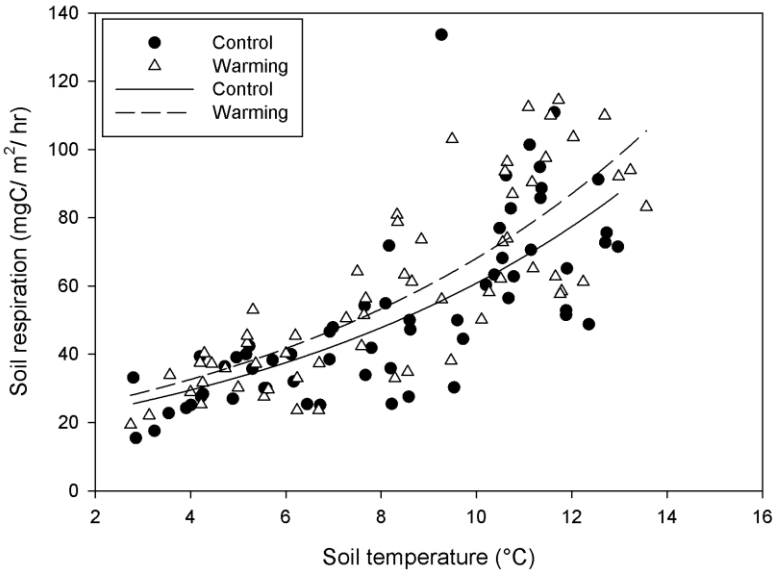
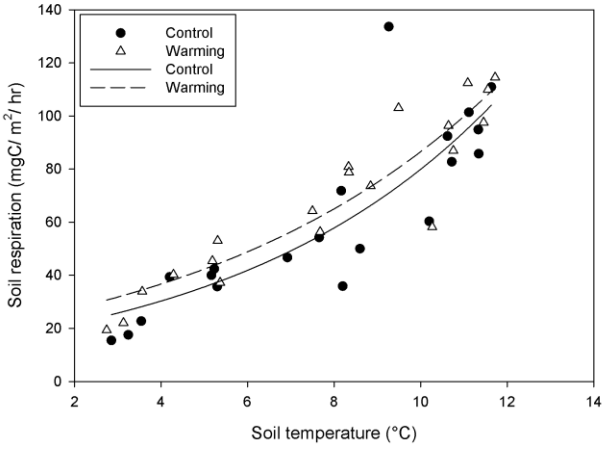
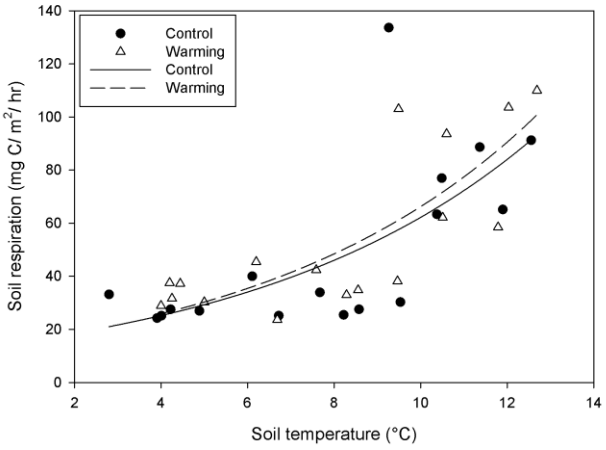


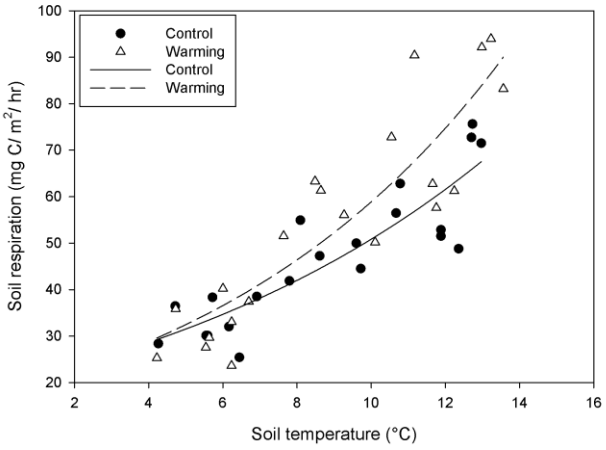
Figure 2.3.11 Temperature sensitivity of soil respiration in control and warming plots for October 2006 – December 2009. Exponential regression parameters and output are found in Table 2.3.1



2007



2008



2009

Figure 2.3.12 Temperature sensitivity of soil respiration in both control and warming for 2007, 2008 and 2009. Exponential regression parameters and output are found in Table 2.3.1

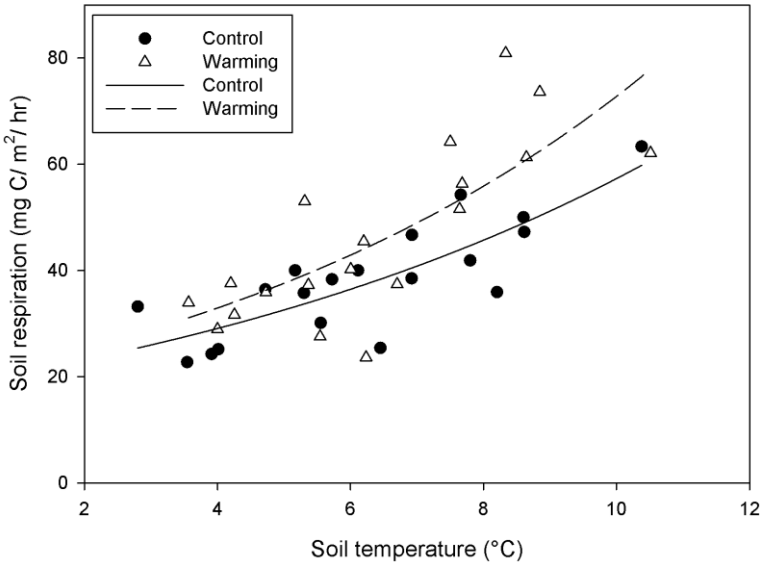


Figure 2.3.13 Temperature sensitivity of soil respiration in both control and warming for spring months (Mar - May) 2007, 2008 and 2009. Exponential regression parameters and output are found in Table 2.3.1.

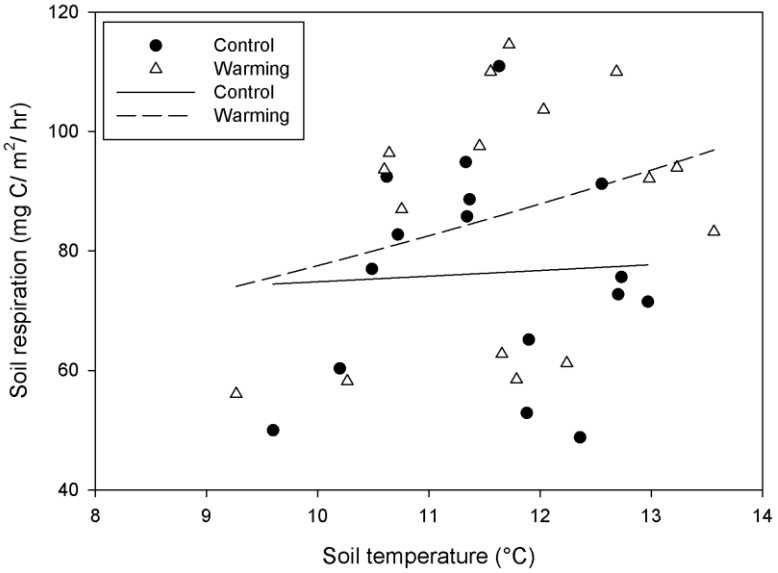


Figure 2.3.14 Temperature sensitivity of soil respiration in both control and warming for Summer months (June - Aug) 2007, 2008 and 2009. Exponential regression parameters and output are found in Table 2.3.1.

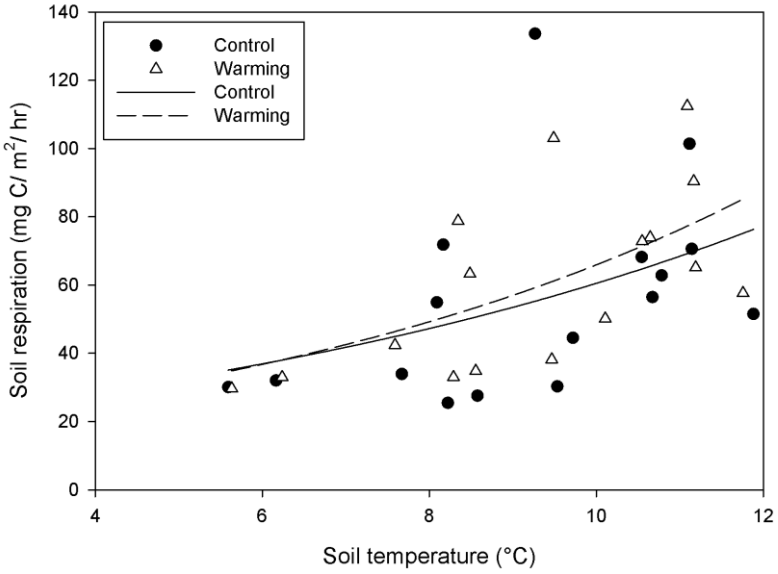


Figure 2.3.15 Temperature sensitivity of soil respiration in both control and warming for autumn months (Sep - Nov) 2007, 2008 and 2009. Exponential regression parameters and output are found in Table 2.3.1.

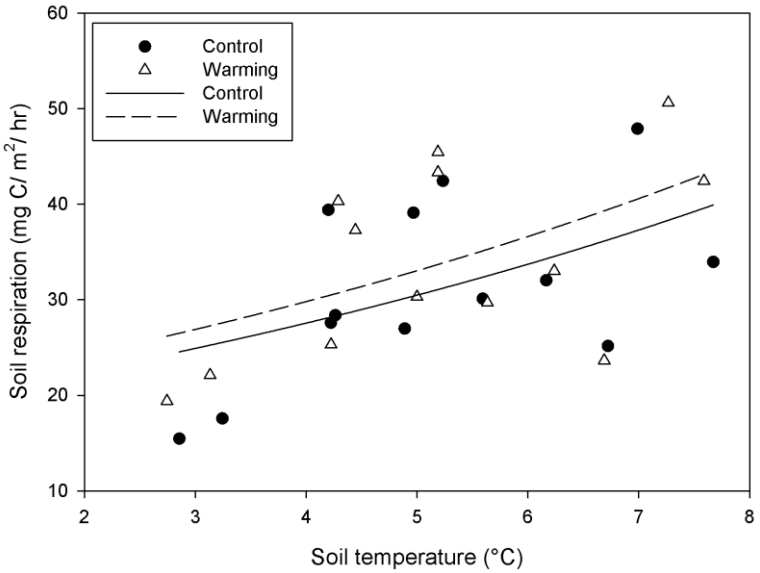


Figure 2.3.16 Temperature sensitivity of soil respiration in both control and warming for winter months (Dec – Feb) 2007, 2008 and 2009. Exponential regression parameters and output are found in Table 2.3.1.

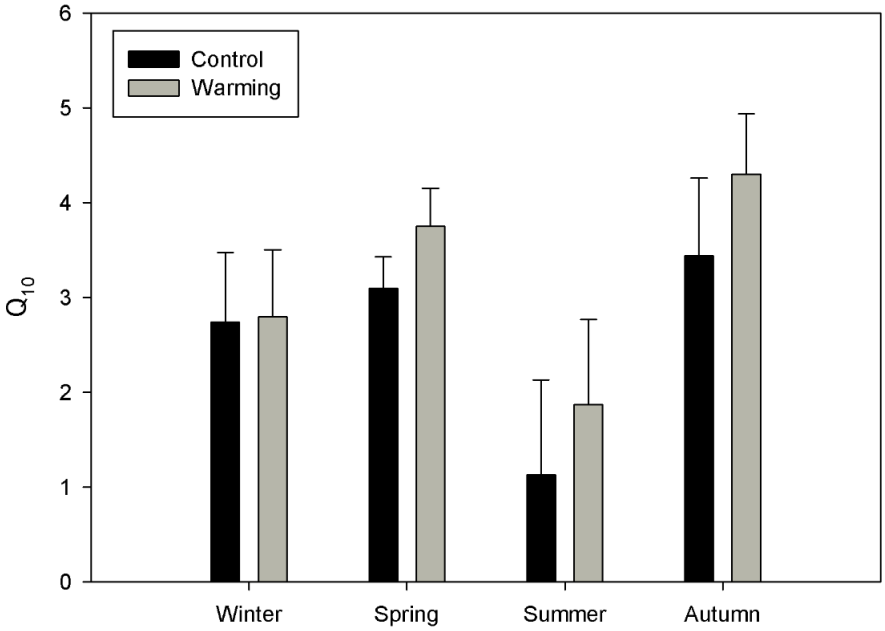


Figure 2.3.17 Q_{10} of soil respiration from Control and warming plots by season. Values are taken from the exponential regressions in Table 2.3.1. Error bars represent 1 – r^2 value, thus indicating the explanatory power of the fitted regression such that a shorter bar is equal to a higher r^2.

Table 2.3.1. Regression parameters and calculated Q_{10} values for temperature sensitivities shown in Figures 2.3.10 – 2.3.16.

Treatment	Period	y0	a	b	r^2	p	Q_{10}
Control	*Oct 2006 - Dec '09*	0.9414	6.2251	-	0.54	< 0.001	5.65
Warming	*Oct 2006 – Dec '09*	-1.115	7.2273	-	0.65	< 0.001	6.42
Control	*Oct 2006 - Dec '09*	-	18.2318	0.1205	0.53	< 0.001	3.34
Warming	*Oct 2006 - Dec '09*	-	19.9984	0.1226	0.64	< 0.001	3.41
Control	*2007*	-	15.8838	0.1616	0.71	< 0.001	5.03
Warming	*2007*	-	20.7189	0.143	0.86	< 0.001	4.18
Control	*2008*	-	13.8154	0.1505	0.46	0.003	4.50
Warming	*2008*	-	13.8834	0.1563	0.64	< 0.001	4.77
Control	*2009*	-	19.5326	0.0957	0.78	< 0.001	2.60
Warming	*2009*	-	17.8898	0.1191	0.79	< 0.001	3.29
Control	*Winter*	-	18.4027	0.1009	0.27	0.069	2.74
Warming	*Winter*	-	19.7527	0.1028	0.29	0.059	2.80
Control	*Spring*	-	18.5018	0.1131	0.67	< 0.001	3.10
Warming	*Spring*	-	19.4084	0.1322	0.60	< 0.001	3.75
Control	*Summer*	-	66.0758	0.0124	0.00	0.836	1.13
Warming	*Summer*	-	41.4923	0.0625	0.10	0.234	1.87
Control	*Autumn*	-	17.6026	0.1235	0.18	0.100	3.44
Warming	*Autumn*	-	15.3348	0.1458	0.36	0.014	4.30

2.4 Discussion

Passive night time warming of experimental plots has shown to have a notable effect on soil respiration rates. Such that, on average across the three year study period, 14.6% more CO_2 efflux through soil respiration was measured under warming plots than control. The general picture of warming causing an increase in soil respiration has been noted in a number of key papers (Davidson *et al.*, 2000, Melillo *et al.*, 2002, Updegraff *et al.*, 2001) as well as more complex results with no clear outcome (Wan *et al.*, 2007). A review of warming effects by Rustad (2001) demonstrated that field experiments with similar duration and treatment approach as the current study, observed increases in respiration rates in the region of 20% above control levels. A more recent meta-analysis of terrestrial system response to warming (Wu *et al.*, 2011) reinforced the link between warming and increased ecosystem respiration across a wide range of ecosystems. These repeated conclusions place the current study well within the general trend of observations from both the Rustad paper (2001) and meta-analysis by Wu et al (2011).

Based on the manual temperature readings made at the time of sample, the warming treatment appeared to have little effect on soil temperature (see Figure 2.3.1). However, when the high-resolution logged data was investigated, the temperature dynamic was more revealing. Analysis investigating the shorter term effects suggested a high degree of variability on a diurnal and monthly basis, which then extrapolates up to the coarser measured seasonal and yearly variation. Within this, there is evidence for an elevation of soil temperature by warming treatment, specifically in the peak temperature reached during the day (Figure 2.3.2). As moisture was shown not to vary between treatments (Figure 2.3.6), the temperature enhancement during the day under warming cannot be explained by a drier soil. It is therefore only reasonable that by retaining heat during the night, the response-time of surface soil temperature to increased air temperature in enhanced due to the initially higher starting temperatures under warming. This is supported by the slightly stronger driving of soil temperature by air

temperature under warming as shown in Figure 2.3.4. Also, as the relationship between air and soil temperature is reasonably linear, it follows that control temperature rises as does warming, so the relative difference remains throughout the day. This would explain some of the plateaux-type behaviour observed in Figure 2.3.5 in the relative difference for April and June. Rainfall input during the day would dampen any treatment difference by cooling the surface layers or soil, and this might explain the fluctuations often seen during the day in the September profile.

The higher resolution data will be generally more reliable for giving an accurate measure of the treatment effect, but could also provide scope for modelling. The major drawback to this approach though is the low (relative) resolution of respiration data, with sampling only at the fortnightly or monthly scale. It would appear then the night warming retains warmth in the soil, but also allows for warming soil-temperature to exceed that of control temperature during the day, even when treatment is no longer in operation. Bearing this in mind, it is of interest that measured respiration rates were often taken below the daily temperature optimum, as the daily time-course work suggests the maximum soil temperature for the day often lies in mid to late afternoon, whereas the measurements were usually taken around midday. Modelling the variability in this daily maximum across the year and relating (via ascribed temperature sensitivities) the temperature course to respiration rates is sadly not possible on the current data due to the short period of time with accompanying high-detail soil temperature. Despite this, it can be said with some confidence that the measured flux rates, and the estimated values for total treatment-induced (extra) respiration are likely to be an underestimate.

2.4.1 Seasonality

Seasonality was evident in the data of both warming and control plots, with the general rise in rates coinciding with expected seasonal changes in the main growing season months. However, the more interesting outcome of the

seasonal rates exploration was the difference in treatment effect over season. Warming appeared to cause a noticeable pulse in spring respiration relative to control, this tending to appear in the May-June period, and is most evident in 2007 and 2009. This observation from Figures 2.3.7 and 2.3.8 is reinforced by the repeated measures ANOVA which concluded significant treatment effect on soil respiration such that the pairs April – May and May – June were significantly higher under warming ($p= 0.033$ and 0.031 respectively).

Observing a warming-induced pulse in spring/early summer respiration rates could be explained by a number of factors. If it is assumed that the majority of early-season respiration is plant derived, then it would seem likely that the observed pulse is a consequence of phenological change induced by warming (Bloor *et al.*, 2010). In this respect, earlier bud-burst, root growth and general metabolism would increase the CO_2 flux by plant respiration, and likely by the stimulation of rhizosphere respiration by root-derived C (exudates, sloughed cells from exploratory roots etc.). Earlier bud-burst in response to warming of black pine was observed by Bronson et al (2009) who found warming caused bud-burst 9-11 days earlier than unheated control. In a later study using the same system, Bronson and Gower (2010) failed to observe any significant alteration to photosynthesis or autotrophic respiration following warming, although they did not measure soil respiration. Warming has been shown to increase rates of photosynthesis and autotrophic respiration in other studies (Bergh & Linder, 1999, Zhou *et al.*, 2007), but most treatment effect tends to occur in spring, and be less noticeable during summer periods (Zhou *et al.*, 2007). Davidson et al (2006) noted a spring time burst in above ground respiration (no treatment) under forests, with soil respiration lagging somewhat. The authors suggest this is due to the delay in soil warming, and the slower rate at which root-derived respiration responds to seasonal changes. This is a comparable situation to that observed here, however, as this study focuses on soil respiration, it may be that the measured pulse may come after an aboveground response which could be revealed by future measurements of NEE.

Plant litter of a reasonably fresh nature (perhaps residual from previous years litter fall) will be decomposed during spring as soil temperatures rise and permit increased mineralisation rates. Warming earlier in the season could stimulate this decomposition pathway (van Meeteren *et al.*, 2008), but could also then indirectly stimulate the turnover of native SOC by the priming effect (Kuzyakov, 2002a) as simple decomposition products and nutrients are released through litter turnover (Tian *et al.*, 1992). It would be difficult to quantify the contribution of either of these processes, but it is expected that they would both further explain the observed warming-induced pulse. This pulse is then followed by rapid 'catch up' of the control rate, leading to fairly similar flux rates between the treatment and control. This would support the notion that warming has lengthened the growing season and the period of favourable decomposition conditions.

Stimulation of soil respiration by warming (mean daily temperature increase 1.2°C) of a subarctic heath was seen confined to early growing season in a study by Rinnan et al (2009) who found warming respiration to be significantly different from control during June, but not towards the end of the growing season. This was observed in the current study, with July – September failing to show any significant effect of warming treatment. Enhanced heterotrophic respiration due to warming appeared to be more related to soil properties than to plant traits in a study by Grogan and Chapin (2000), particularly, in control plots, respiration rate was related to plant traits, suggesting warming enhanced total respiration by stimulating SOC turnover rather than plant respiration. The photosynthetic overcompensation suggested by Wan et al (2009) as a result of warming includes an increase in drawdown of photosynthate during the night, it is sensible to suspect that this mechanism (if widely applicable) could increase respiration potential by elevating exudation rates (as previously mentioned) or increasing the below-ground allocation of C which could be decomposed later during root senescence.

Winter effect seems to be variable between years, and is perhaps most noticeable in the latter part of 2009, when air temperatures remained very

low for a considerable part of the winter. Overall, winter was the only season which came out as significant (p= 0.049), and when scrutinised in the month-pairs, it was the November – December pair that came out (p=0.047). This is a significant finding, and given the low-rate of plant activity likely to occur during winter coupled with the relative rate increase given by a modest warming, enhanced winter-time efflux of soil-C could become a major source of C loss from these heathland systems.

The seasonal data suggests a number of key issues. Firstly, the magnitude of the treatment response varies at key times of the year, mostly at times when temperature limitation plays a central role in controlling the decomposition dynamics. Secondly, there may be some intrinsic thermal energy threshold required to observe an effect. This can be explained by noticing that the times which should be naturally temperature limited (save the periods already mentioned), i.e. the winter, are less so. This may be because there just isn't the heat energy in the system to start with, so passive night-time warming (which aims to retain ecosystem heat) fails to demonstrate a heat gain at this point. Other factors, more to do with technical issues might be that the system is more prone to malfunction and breakdown during the winter, and that a persistent treatment cannot be guaranteed during the winter months. Finally, the seasonality of soil respiration (and the treatment effect) varies markedly between years, such that although fairly broad comments can be made about the temperature effects on respiration, other driving variables are likely to interplay to such an extent that it would be unwise to suggest a specific seasonal trend would be the norm. Despite these cautions, there is clear evidence that warming affects the intra and inter yearly flux rates with explainable patterns, and modest warming could act to modify key decomposition processes that may ultimately influence the sink-strength of upland soils.

2.4.2 Temperature sensitivity

Temperature sensitivity was calculated by expressing the Q_{10} value from regression equations plotted for respiration against temperature. Exploration was made here as to the usefulness of exponential and linear equations for the prediction of temperature sensitivity. As exponential-type equations tend to predict the soil respiration well within the range of data, they are often chosen, however, the linear regression performed just as well as the exponential function. Despite the reasonable fit of both tested functions, it is clear from the r^2 values, and from visual assessment, that temperature is certainly not the sole driver of respiration. There is considerable variation about the regression lines, and the relationship appears to be less pronounced at more elevated temperatures. This is of course sensible, as temperature is more limiting at lower temperatures, so it follows that the rate will be more temperature sensitive under these conditions. Even though the exponential function describes the range of data well, there are obvious concerns about extending beyond the range of data, whereas the linear function could be more reliable. Despite these concerns, whilst considering within the range data, the exponential approach was used. The calculated Q_{10} values were reasonably different between the two methods, with the exponential function giving a higher Q_{10} value across the total range of data.

Evaluating figures 2.3.13 – 2.3.16 it is clear that there are seasonal effects to the sensitivity. These effects are explored when categorising the data by season, as previously carried out with raw fluxes and percentage change data.

Spring sensitivity was by far the most reliable, with significant ($p < 0.001$) regression fits and high r^2 values (> 0.6). This follows given the turnover of residual litter from previous litter fall coinciding with the flush of respiration associated with the phenological events of spring. Summer showed a poor relationship, and this is not surprising given the generally high temperatures found during this period, coupled with the likelihood that respiration is limited not by temperature, but perhaps by nutrient, moisture, substrate supply or an

interaction of factors. Winter rates were also non-significant, and came with very low r^2 values (<0.3), and although treatment was observed to have an effect on soil respiration, the sensitivity estimate is likely to be confounded by the low general variability in soil temperature. The most intriguing case however was Autumn. Here, control showed a non-significant (p= 0.1) fit, whereas warming maintained a significant (p= 0.014) driving of soil respiration, explaining 36% of the variation in respiration data. Autumn respiration represents post-growing season efflux, and it is reasonable to assume that a dominant substrate component during this period would be recent litter input. Connecting the warming stimulation of NPP to a greater litter input (in quantity terms) could explain a degree of the observed increased sensitivity, as here, substrate will be less limiting during a period where soil temperature is still reasonably high.

2.5 Conclusion

Soil respiration rates are significantly increased in an upland heathland system by passive night time warming of around 0.3°C. The increase is, on average 14.6% greater in warming than control, which, assuming thermal optimum is not reached before hand, a rise of 1°C would increase the rate of soil respiration by ~44% under a linear realtionship. Respiration is highly variable across time, whilst following an expected general seasonal pattern, the dynamics of the flux pattern is variable between years, and shows considerable seasonality. The effect of treatment appears to be pronounced at key phenological and metabolic points in the year, with respiration bursts being enhanced by warming at points most likely to coincide with early plant growth, and decomposition of SOC and root-derived C. Temperature sensitivity appears to be only slightly increased by warming treatment, although there is a degree of seasonality to the sensitivity estimates.

The extra respiration cannot, at this point, be totally attributed as a loss of SOC, as it is expected that any increase in NPP would be translated to increases in biomass (which has not yet been observed (A.Sowerby, personal communication, 2011)). Even if this is the case, there is sufficient evidence to suspect that onset of earlier spring, and possible extension to the growing season will stimulate enhanced turnover of native SOC as well as extra recent C from NPP increases. Given the current state of debate within the literature on warming stimulating loss of SOC from distinct pools (Conant *et al.*, 2008, Davidson & Janssens, 2006, Giardina & Ryan, 2000), it is tenuous to suggest one mode of loss over another. But it is possible that C will be mineralised from both labile (due to increased plant biomass production and exudate input) and more recalcitrant SOC pools (due to energetic favourability to decompose more chemically recalcitrant substrate), as the whole ecosystem is likely to respond to the treatment rather than just the soil decomposer communities. Given the continued stimulation of respiration by warming after 10 years, the acclimation to warming observed in a number of comparable studies (Bradford *et al.*, 2008, Luo *et al.*, 2001) appears not to be found here. If acclimation occurs as a result of microbial

community change, this might be delayed (or avoided) in organic soils due to the physico-chemical conditions which restrict the microbial community to specialists in low pH soils. Depletion of substrate requires a loss of SOC (which has not been measured at this site) and by definition implies that decomposition will be preferentially stimulated over NPP. Given these observations, it is probable that the majority of extra respiration caused by warming will be autotrophic in origin, and the extra decomposition of SOC may currently be balanced by increased litter input, perhaps in belowground compartments. The longevity of this theorised resilience though is unknown and requires urgent investigation.

Chapter 3. The effect of summer time throughfall exclusion on soil respiration in an upland heathland system.

3.1 Introduction

Soil respiration is heavily dependent upon the amount and availability of soil moisture (Orchard & Cook, 1983). The response of soil respiration to modification in soil moisture content will depend both on the pre-existing conditions, and the direction of the moisture fluctuation (Davidson *et al*, 2000). Moisture status change by either a naturally-induced change in rainfall, an experimentally imposed regime, or a water-table change can act to substantially alter the rate of soil respiration by a number of factors. These include affecting the motility of soil organisms, altering O_2 concentration, altering solubility and availability of nutrients and substrate, changing root activity and by simply reducing the availability of water for metabolic processes. Davidson *et al* (1998) considered the relative effects of drought on soils with inherently different drainage characteristics in a forest system. In this study, drought caused a rapid decline in respiration rates in all but the most poorly drained site, which experienced a much slower decline in rates.

Under reduced soil moisture conditions, there can be substantial negative impacts on rates of respiration. This negative effect has been observed in systems which would normally be reasonably drought tolerant, and imposed reductions showed a marked fall in respiration rates (Huang & Fu, 2000). Systems which tend to be limited by a water excess have shown the opposite trend, with an increase in respiration following a reduction in moisture excess. Water-table drawdown is the main method by which wetlands tend to experience natural soil moisture variation, and this has been reported to have substantial effects on gaseous losses of carbon (Alm *et al.*, 1999). Very small changes in water table drawdown (1 cm) resulted in a response in CO_2 production in a Finnish bog, with the small change increasing respiration rates by 7mg CO_2/ m^2/ hr (Silvola *et al.*, 1996). Jungkunst et al (2008) extended this to show extensive drawdown (to 40 cm) caused an exceptional flux of CO_2 (129-172 mg CO_2-C/ m^2/ hr), and that this extra flux fell as groundwater level was raised towards the surface (47-65 mg CO_2-C/ m^2/ hr). The same authors also noted that the response time to the

drawdown was rapid, suggesting the biology of these soils was adapted to periodic water level changes. However, C-loss (in absolute terms) will persist during water logging of organic soils, as CH_4, DOC and small amounts of anaerobically produced CO_2 have been reported (Blodau *et al.*, 2004). Organic soils which do not experience water table effects, but are generally high in soil moisture will also experience an increase in decomposition and respiration given a reduction in soil moisture content. This was shown by Sowerby et al (2008) where summer drought caused a significant increase in the rates of soil respiration relative to control plots in a mesic upland heathland.

Considering moisture excess and limitation can be detrimental to decomposition, there likely exist optimum soil moisture levels for respiration and decomposition. Ilstedt et al (2000) found that optimum soil water conditions for microbial activity were variable among soil types, but crucially, that more organic soils were potentially more resilient to a variable water regime. This suggests that organic soils may have a wider optimum 'plateaux' than more mineral soils, which may exhibit a more 'peaky' optimum soil moisture. In studying the effects of drought on soil respiration in Amazonian rainforests, Sotta et al (2007) identified soil moisture (soil matric potential) optima and demonstrated by means of throughfall exclusion and ambient sampling, moisture shortage and excess limiting respiration rates.

The fluctuation of soil moisture levels often caused by periods of excessive rainfall followed by a relative drought will cause a degree of stress on microbial activity and will influence the dynamics of decomposition. The reduction in decomposition followed by a flush upon re-wetting has been observed in numerous studies (Birch, 1958, Fierer, 2002, Miller *et al.*, 2005, Wu & Brookes, 2005). The initial observations made by Birch (1958) highlighted the possible mechanisms by which decomposition can be altered by drying changing the physical properties of the soil (substrate release from clay lattices in this example). This situation has become more clear over subsequent studies, especially when considering the role of drying on

changing the nature of organic materials in soils, especially peats (Oleszczuk & Brandyk, 2008).

As soil moisture and soil temperature both act to control respiration rates, soil moisture limitation, if altered, will change the responsiveness to temperature change (Davidson *et al.*, 1998a). The complexity of this situation was demonstrated by Huang et al (2005) who found that the moisture dependence of root respiration was significantly modified by soil temperature. In their study, Huang et al (2005) showed that drying only affected respiration rates significantly when soil temperature was above 10°C. This suggests the interaction of limiting factors varies as one factor becomes less limiting. Water table manipulations in the study by Silvola et al (1996) linked Q_{10} to water table height, such that near-surface water table levels (0-20 cm) had a Q_{10} of 4.9, and draw down (>20 gave a Q_{10} of 1.3).

The relative response to drought appears then to be mainly influenced by the mode of moisture change and the relative extent of moisture limitation, be it by excess or shortage. The interaction of drainage characteristics and soil types has been shown to have a significant interactive effect on the drought response, and in particular, the further interaction with other rate modifiers such as soil temperature (Davidson *et al.*, 1998a).

This study aims to identify the impact of an imposed summer drought (by means of throughfall exclusion) on the rate of soil respiration in a mesic upland shrubland system in the U.K. Investigating the temporal element of the treatment effect, and any implications for soil moisture reduction on the temperature sensitivity of soil respiration are also central to this study.

As the site typically experiences excess soil-moisture limitation of soil respiration (Emmett *et al.*, 2004, Sowerby *et al.*, 2008), it is hypothesised that a reduction in throughfall will cause an increase in the rate of soil respiration in drought plots. Due to the interaction of soil moisture and temperature (Davidson *et al.*, 1998a), it is also hypothesised that reduction in soil

moisture will reduce the controlling effect of water-excess, and therefore increase the temperature sensitivity of soil respiration.

3.2 Methods

3.2.1 Site description

The Climoor research site is a *Calluna vulgaris - Vaccinium myrtilus* (NVC H12 community) heathland located in Denbighshire, North Wales (53° 3'N 3° 28'W). The site occupies a NE facing slope at an altitude of 490 m ASL. The soil is characterised as being a shallow (~15cm depth) well drained organo-ferric podzol with a pH of 3.8 overlying gritstones in the Denbigh grit sequence Site mean annual temperature is 7.6°C and annual rainfall is 1584 mm.

3.2.2 Experimental design and plot layout

The Climoor/Vulcan warming and drought experiment was set up at the field site during 1998 and includes nine 4*5 m plots with 3 plots each allocated to the warming, drought and control treatments in a randomised block design. Plots are delimited by tubular steel frames which allow for access without trampling vegetation, but also support the housing of the roof technology which provides the two manipulations treatments. Detail of the treatment design and structure can be obtained from Chapter 2 and Beier et al (2004). The photograph in figure 3.2.1 shows an example of a plot in the field and the vegetation type is clearly visible.

The drought treatment involved the use of retractable plastic roofs which was automatically rolled out over the plot after the detection of a rain event greater than 2 ml. Roofs remained out over the plot area until the end of the rain event, but retracted if wind speed exceeded 12 m/s to reduce damage to the roof material. The treatment was a summer-only treatment, and the timings of the drought period are shown in table 3.3.6

Figure 3.2.1 Photograph of a drought plot with roof extended over the plot.

3.2.3 Data collection

Soil respiration measurements were made at fortnightly or monthly intervals throughout the period Oct 2006 – December 2009, with measurement being made between 10 am and midday on each occasion. Three soil collars were installed previously into each plot by cutting a 10 cm PVC collar ~2 cm into the soil. A PP-Systems EGM-4 and a Li-COR 8100 IRGA were used during the study period to collect soil respiration measurements. Simultaneous measurements of soil temperature were made at each respiration sampling point using the temperature probe supplied with the IRGA, or a standard electronic thermometer in cases where the on-board probe failed to function. Soil moisture measurements were made using a Delta-T theta probe (Model ML-2, Delta-T Services, UK) adjacent to the soil respiration collar from Oct-2006 – Dec 2008, after which concerns about the suitability of theta probe measurements caused a cessation in manual moisture measurements.

Throughfall values were obtained by sampling two throughfall containers situated in each plot at fortnightly intervals. Data was obtained from A. Sowerby (unpublished data) and represent bulked monthly values.

3.2.4 Hydrophobicity tests

The Water Drop Penetration Time (WDPT) test and the Molarity of Ethanol Drop test (MED) were carried out on Climoor soils (Douglas *et al.*, 2007, Zhao *et al.*, 2007). Soils were collected during July 2007 from each of the control and drought plots. Soils were returned to the lab where the upper (litter) and lower (organic) layers were separated using a sharp knife. Representative slices of each layer were then prepared and air-dried for 48 hours at 20°C. The WDPT test involved dropping five 1ml drops of deionised water onto each soil layer from a height of one centimetre. Timing the period between the drop application and the infiltration of the drop was then carried out, and a mean value for infiltration of the five drops was then used for each slice. The MED test involved placing drops of ethanol onto the surface layers starting with a low concentration, and building up to more concentrated solution. The concentration at which five drops infiltrated within a set time period was recorded as the threshold concentration for this test.

3.2.5 Data analysis and presentation

Soil respiration data was analysed for significant treatment effect over time using a repeated measures ANOVA after log transformation. Between groups comparisons of other data were carried out using ANOVA and T-tests where appropriate. All data was visually inspected for normality prior to analysis using quantile-quantile plotting, and log transformations were carried out when needed to comply with ANOVA assumptions. Statistical analysis was carried out using R statistics version 2.11.1 (R, 2010) Linear and exponential regression fits between soil temperature and respiration were fitted using Sigmaplot version 11 (Systat, 2009).

3.3 Results

3.3.1 Treatment effect on soil moisture and soil temperature

Alteration to throughfall amounts (i.e. the effectiveness of the treatment) is shown in Figure 3.3.1, and the percentage difference is extracted from this and shown overlaid with the periods of drought treatment in Figure 3.3.2. In both of these figures there is shown a definite reduction in the amount of throughfall entering the drought plots. This is backed up by ANOVA analysis which gave no significant difference between drought and control throughfall during non-treatment periods ($p= 0.969$), but a significant difference during the treatment ($p= 0.014$).

To investigate the impact of throughfall reduction on soil moisture, volumetric soil moisture is shown for control and drought plots in Figure 3.3.3. There was no detectable treatment effect on soil moisture, apart from three sampling points during the 2008 drought treatment period. To identify any evidence for cyclical behaviour in the temporal variation of soil moisture, analysis for autocorrelation was carried out. Figure 3.3.2 shows the output from autocorrelation analysis, and suggests that although there is some small cyclical behaviour at the start, there is no significant relationship between lag data points. This concludes that although there might be some general variation in the soil moisture data, there is no strong cyclic behaviour (therefore no seasonal variation) across the time period shown.

Soil temperature variation is shown in Figure 3.3.5, and there is a notable temporal variation in the data. Autocorrelation for both control and drought (Figure 3.3.6) show a strong cyclical nature to the data, following seasonal patterns.

Analysis of variance was conducted to identify effect of treatment period on soil moisture and soil temperature, using treatment and drought ‘on or off’ as factors. There was no significant difference between control and drought

measures of soil moisture ($p= 0.999$) and soil temperature ($p= 0.999$) during drought treatment periods. In drought plots, although soil temperature was shown to differ significantly ($p< 0.001$) between treatment and non-treatment periods, this is likely to be merely a seasonal variation rather than a treatment effect, especially as there was no difference between drought and control plots.

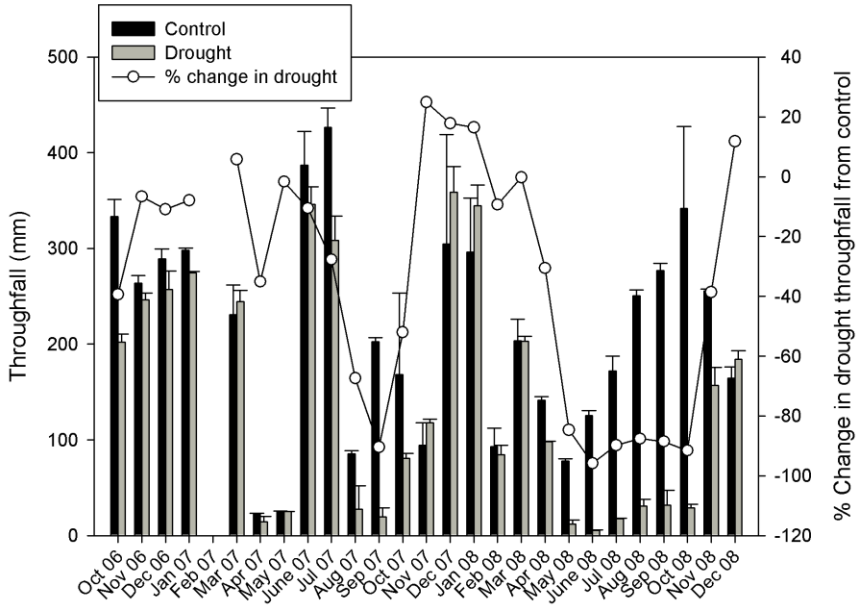


Figure 3.3.1 Monthly cumulative throughfall for drought and control (Oct 2006 – Dec 2008) with percentage change in drought relative to control.

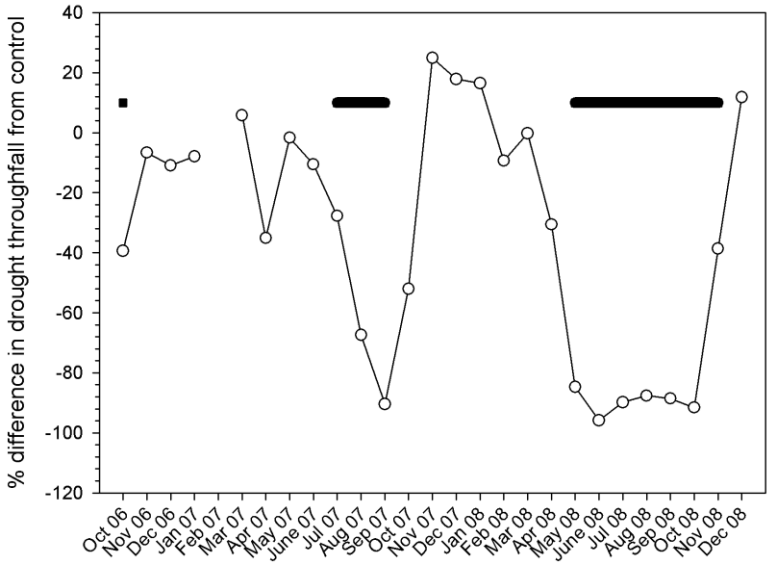


Figure 3.3.2 Percentage difference between drought and control throughfall with drought period overlaid.

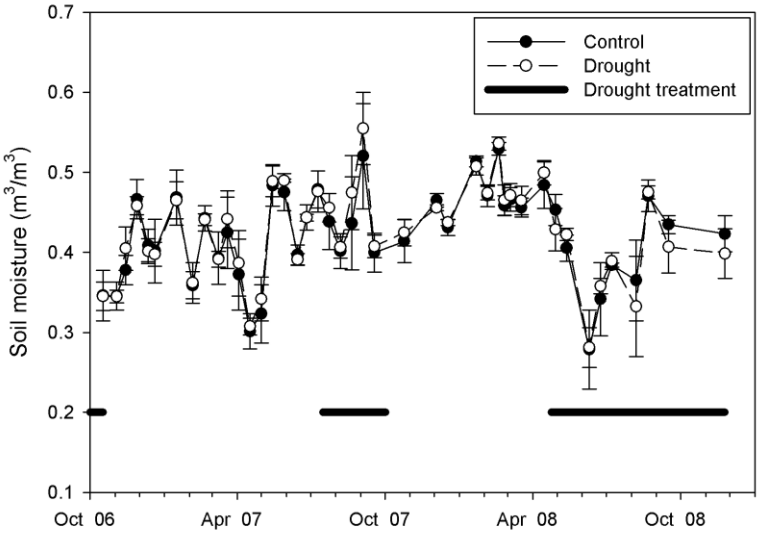


Figure 3.3.3 Volumetric soil moisture from control and drought plots measured at 5cm depth at time of sampling for soil respiration (Oct 2006 – Dec 2008). Bars are standard error of the mean. Solid black lines indicate timing of drought treatment.

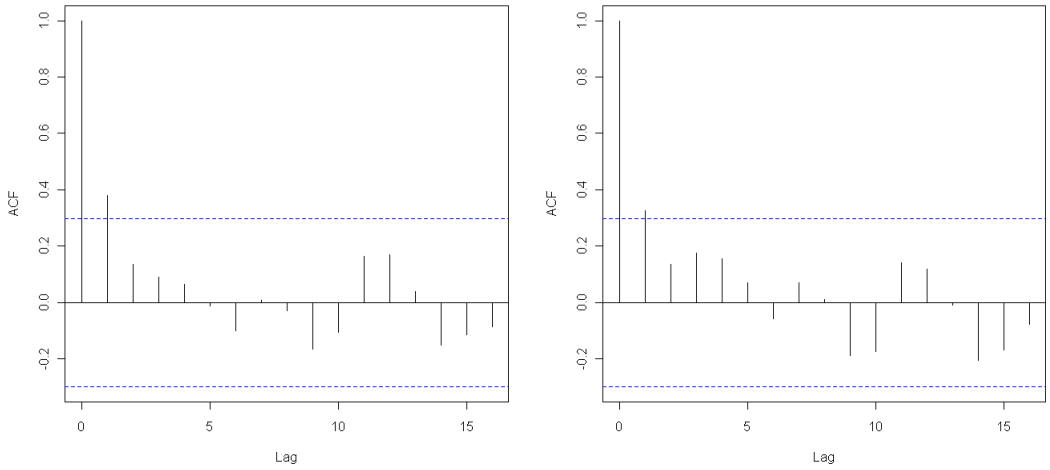


Figure 3.3.4 Autocorrelation plot for soil moisture in control (left) and drought (right) plots. Significant lags in cyclical behaviour are shown by the line reaching beyond the horizontal dash.

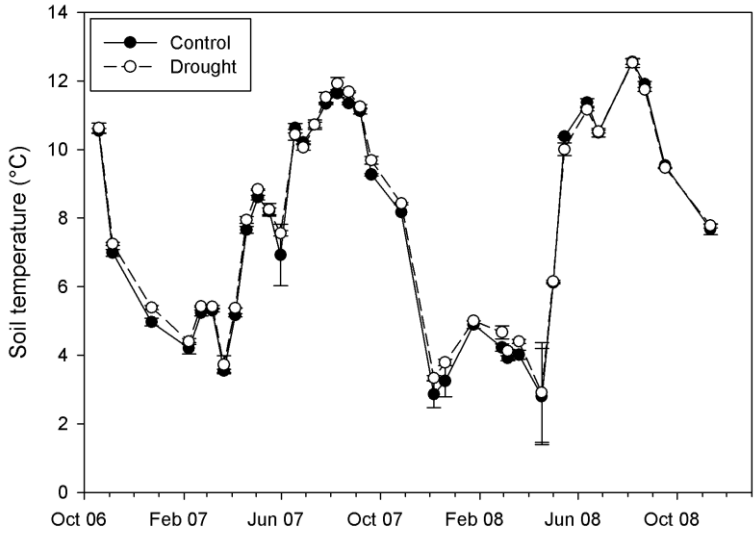


Figure 3.3.5 Soil temperature measured at 5cm depth in both control and drought plots at time of respiration sampling. Points are treatment means with standard errors of the mean.

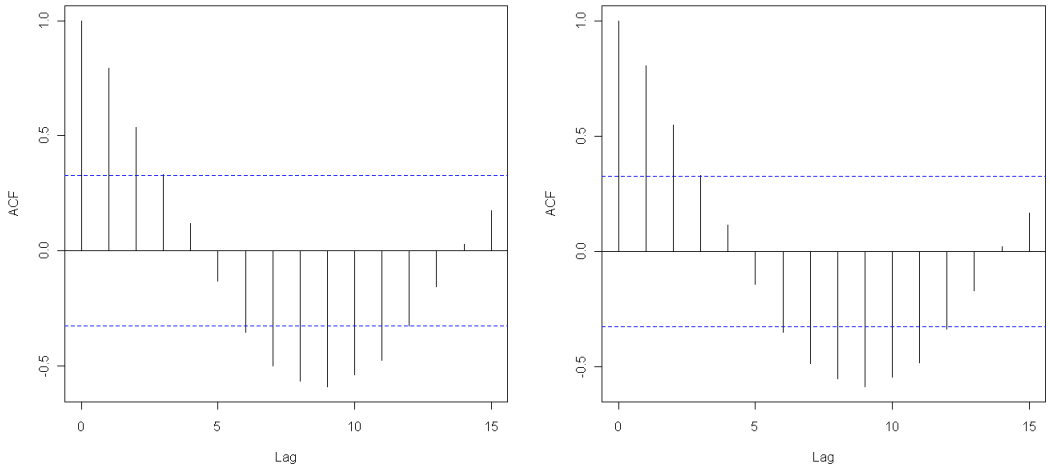


Figure 3.3.6 Autocorrelation plot for soil temperature in control (left) and drought (right) plots. Significant lags in cyclical behaviour are shown by the line reaching beyond the horizontal dash.

3.3.2 Treatment effect on soil respiration.

Respiration rates follow a seasonal trend, with a low, basal level during winter and a rapid increase during spring to a peak summer level. Decline during autumn tended to be very rapid. Figure 3.3.7 shows the inter-year variability in peak and trough of rates, as well as there being an observable difference between drought and control. To identify the possibility of seasonal variation in treatment effect, relative respiration rate means were calculated for the four ascribed seasons (Figure 3.3.8). The treatment effect seemed to be most noticeable during the summer period in this figure, and this is backed up by repeated measures ANOVA which showed only a significant difference during May-August (inclusive) ($p= 0.02$).

The percentage change figure (Figure 3.3.9) shows 2009 data to have respiration under drought treatment more continually above that of control than would be apparent in previous years. Figure 3.3.10 gives a simpler overview of the flux dynamics, and it is clearer here that the winter-time fluxes were similar during 2008 and 2009, but much higher during 2007. Differences in peak fluxes are also evident, and the similarity in peak control fluxes for 2007 and 2008 contrasts with the difference in drought peak fluxes. The 2009 data is clearly (as with Figure 3.3.7) markedly different from the previous two years.

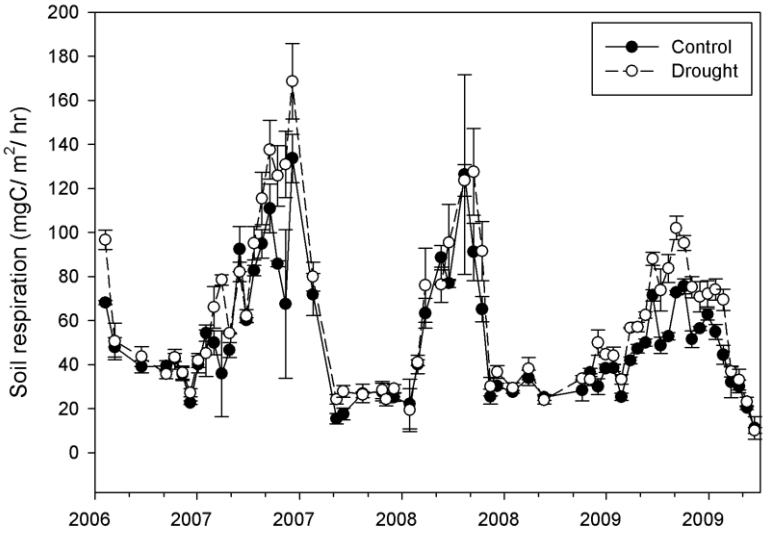


Figure 3.3.7 Soil respiration rates in control and drought plots for the period Oct 2006 – Dec 2009. Data points are treatment means with standard error of the mean.

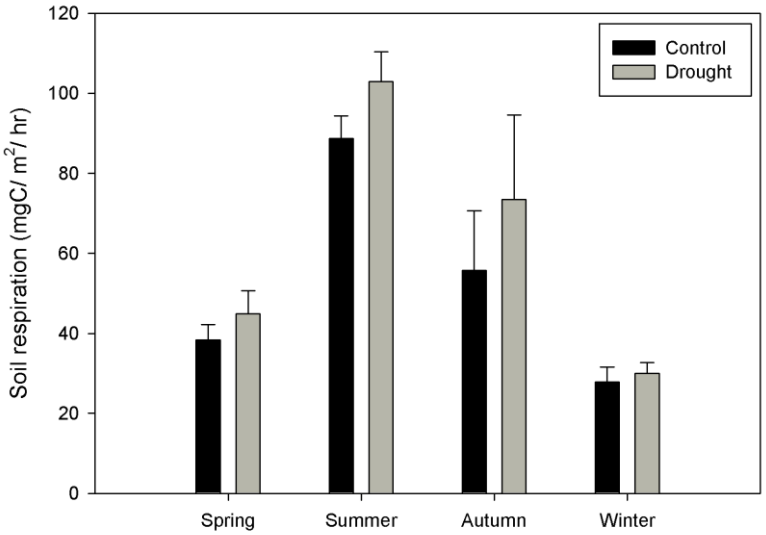


Figure 3.3.8 Mean soil respiration rates grouped by season for drought and control treatments. Bars are standard error of the mean.

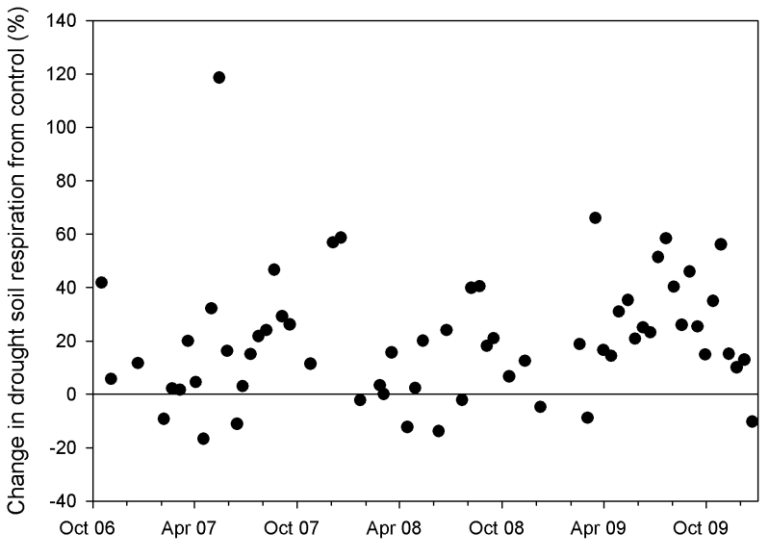


Figure 3.3.9 Percentage change in soil respiration from drought plots relative to control for the period Oct 2006 – Dec 2009

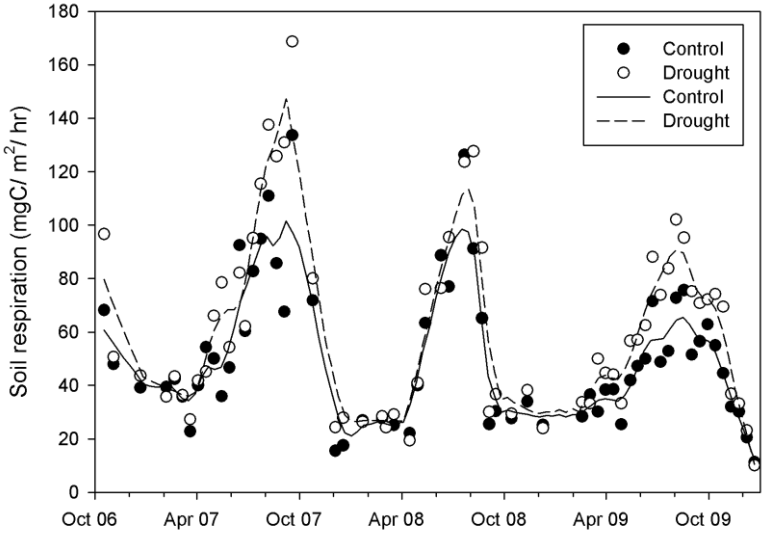


Figure 3.3.10 mean values for soil respiration under drought and control. Smooth lines are fitted to the data using a bisquare weighting with polynomial regression.

The magnitude of the treatment effect on soil respiration is shown in Figure 3.3.7. Here, the percentage difference in the drought throughfall relative to control suggested that more extreme treatment causes less treatment-induced respiration. The plot on the left shows data only from the current study period, whereas the importance of investigating a wider time frame is demonstrated by the plot on the right which includes data from four previous treatment years.

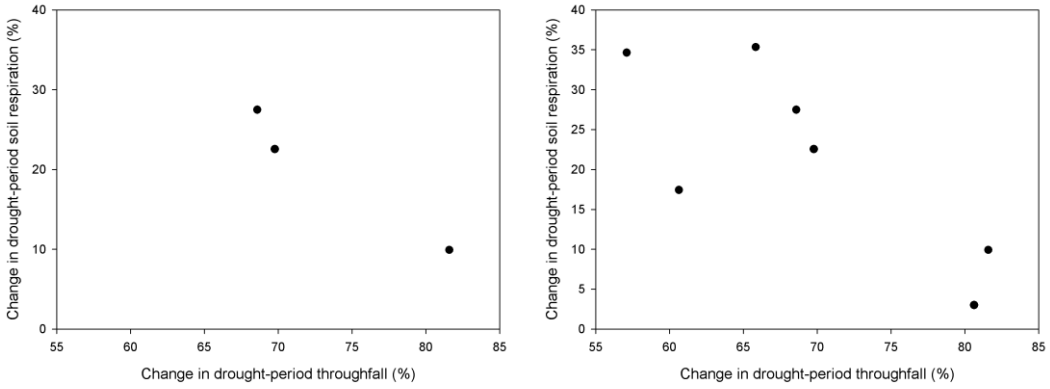


Figure 3.3.11 Drought period throughfall as % change from control against drought period respiration as % change from control. Data from 2007-2009 (left) and 2002-2009 (right). Data for 2005 not included due to large amount of missing data.

3.3.3 Temperature response of soil respiration

Temperature sensitivity of soil respiration was calculated using the Q_{10} function. The regressions used to calculate this value are shown in Figure 3.3.11 and 3.3.12. The exponential and linear fits gave different Q_{10} values (as can be seen in the accompanying tables), and the regression equations both give comparable r^2 values, although the linear regression fits were marginally better. Either way, both approaches showed a high sensitivity to temperature, with drought giving a greater degree of sensitivity than control.

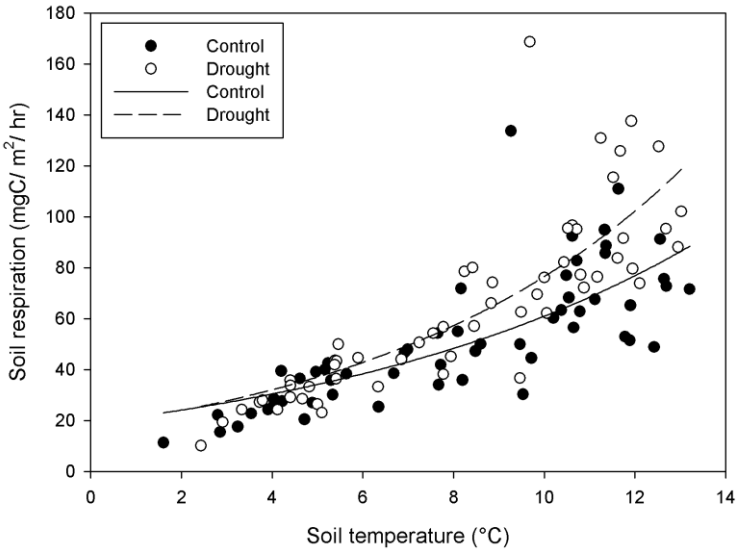


Figure 3.3.12 Temperature response of soil respiration for control and drought treatment (Oct 2006 – Dec 2009). Regressions are single exponential, 2 parameter regressions. Parameters and output are found in Table 3.3.2

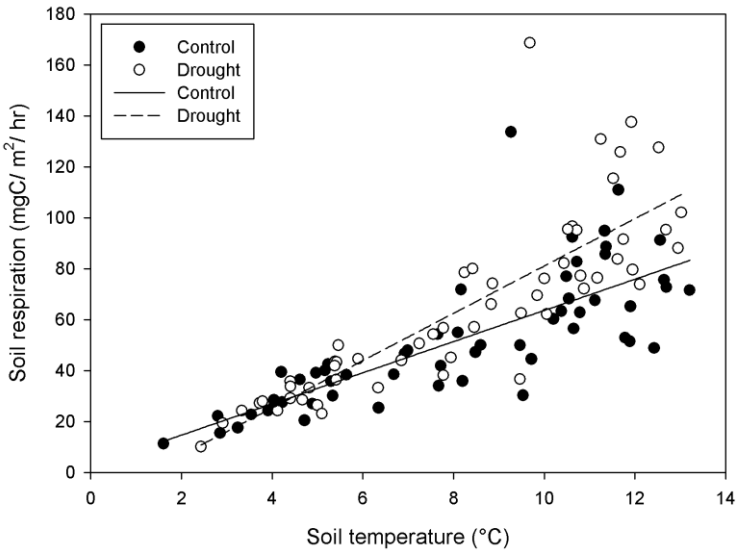


Figure 3.3.13 Temperature response of soil respiration for control and drought treatment (Oct 2006 – Dec 2009). Regression lines are linear regressions. Parameters and output can be found in Table 3.3.3

Table 3.3.2 Model parameters and output for regressions used in Figure 3.3.12.

2006-2009	*Parameters*		*Output*		
Treatment	a	b	r^2	p	Q_{10}
Control	19.1193	0.116	0.56	< 0.001	3.19
Drought	17.9544	0.1449	0.67	< 0.001	4.26

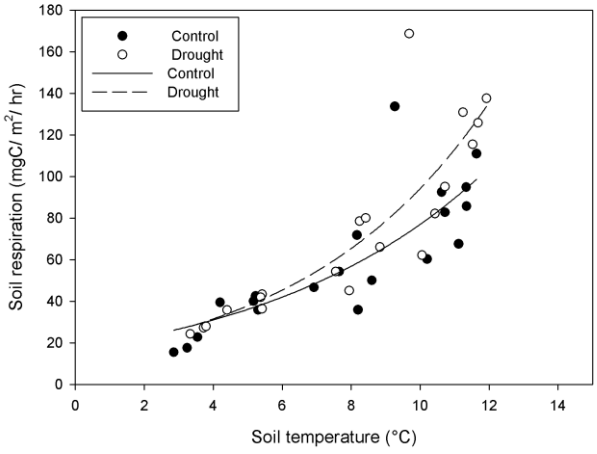
Table 3.3.3 model parameters and output for regressions in Figure 3.3.13.

2006 - 2009	*Parameters*		*Output*		
Treatment	y0	a	r^2	p	Q_{10}
Control	2.4102	6.1221	0.59	<0.001	2.12
Drought	11.8154	9.2898	0.69	<0.001	3.68

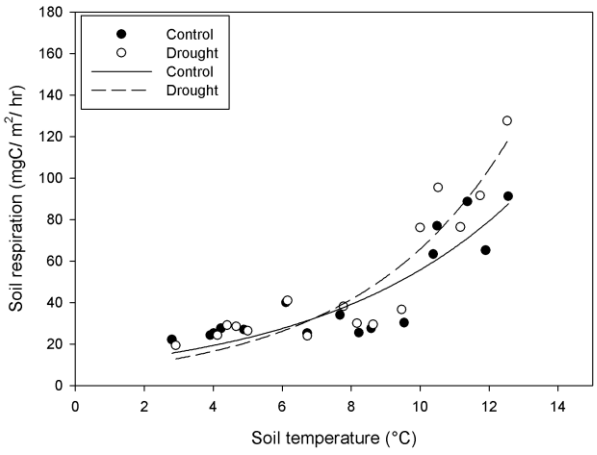
The inter-year variability in the Q_{10} estimate is shown in Figure 3.3.13 and Table 3.3.4. Here the yearly sensitivity is shown to vary distinctly across the three treatment years. The r^2 values for each regression fit were high, and the Q_{10}s ranged from 2.83 – 9.99. The drought treatment remained much more sensitive than the control across all years. The magnitude of the annual temperature sensitivity estimate is related to the mean annual soil temperature average such that a higher soil temperature average reduced the temperature sensitivity in both control and drought. The slope of the linear regressions indicate that the relationship may be more pronounced in the drought than the control.

Table 3.3.4 Regression parameters and model output from exponential temperature sensitivities in Figure 3.3.13.

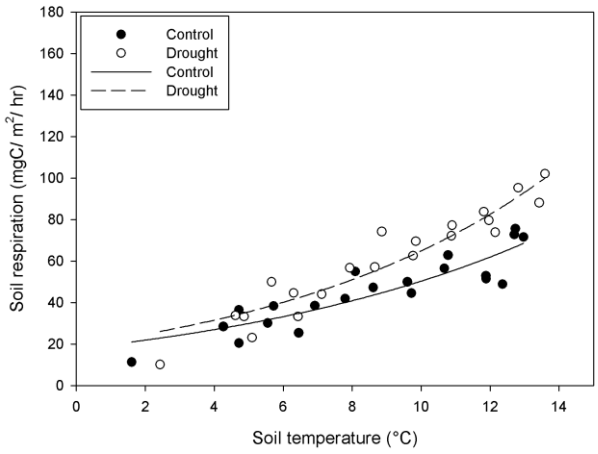
		Parameters		*Output*		
Year	Treatment	a	b	r^2	p	Q_{10}
2007	Control	16.9151	0.1515	0.66	< 0.001	4.55
2007	Drought	15.1842	0.1825	0.73	< 0.001	6.20
2008	Control	9.5384	0.1765	0.77	< 0.001	5.84
2008	Drought	6.5852	0.2302	0.85	< 0.001	9.99
2009	Control	17.7934	0.104	0.79	< 0.001	2.83
2009	Drought	19.4812	0.1204	0.89	< 0.001	3.33



(a)



(b)



(c)

Figure 3.3.14. Temperature response of soil respiration for control and drought treatments by year 2007, 2008, 2009 (a, b, c respectively). Regression lines are single exponential, 2 parameter regressions. Model parameters and output can be found in Table 3.3.4.

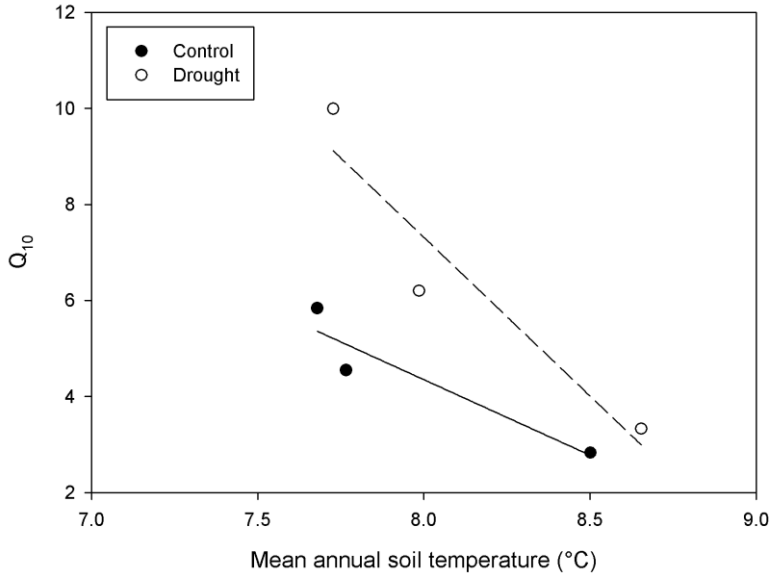


Figure 3.3.15 mean annual soil temperature and Q_{10} of soil respiration for control and drought plots for the years 2007, 2008 and 2009.

3.3.4 Seasonal temperature sensitivity

Seasonal temperature sensitivity estimates are calculated using the linear or exponential (or both) regressions shown in Figures 3.3.19-3.3.22. The regression output in Table 3.3.5 suggested that the regressions for summer and autumn are not highly significant, whereas the spring and winter relationships were highly significant. Q_{10} values for winter were variable and much dependent upon the choice of regression equation. Despite the issues regarding significance of fit and regression choice, drought treatment was consistently more temperature sensitive across all seasons. The relationship between seasonal mean soil temperature and the Q_{10} estimate is shown in Figure 3.3.23. The control plots showed a decrease in the Q_{10} estimate with increasing soil temperature, however the drought treatment has modified this and the response does not suggest a Q_{10} dependency on mean seasonal temperature in the drought treatment.

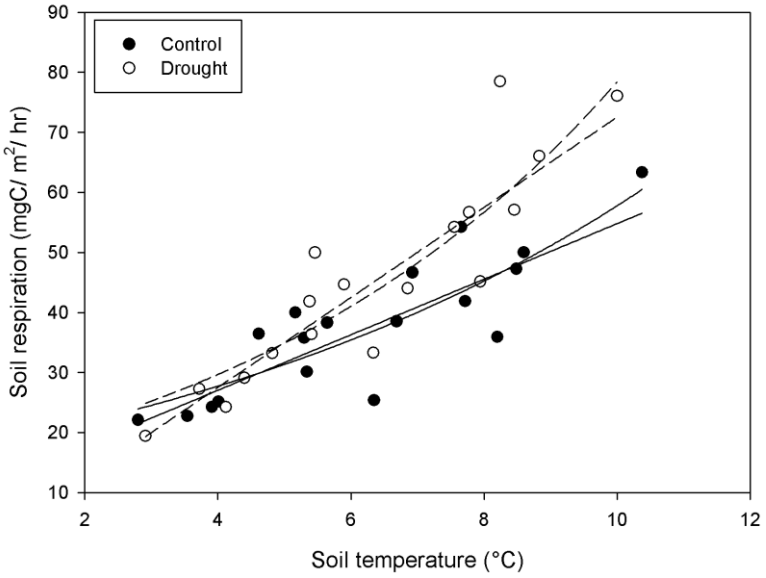


Figure 3.3.16 temperature dependence of soil respiration during Spring in control (black dots, solid lines) and drought (white dots and dashed lines) plots with linear and exponential regressions.

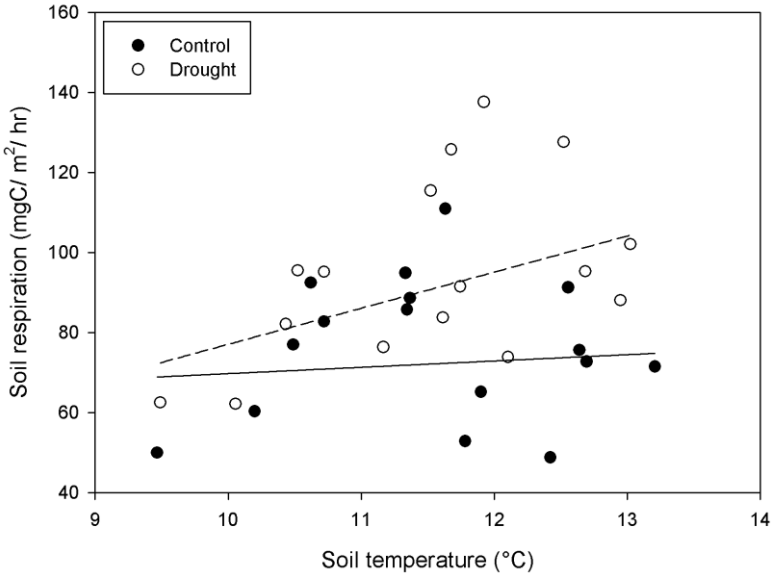


Figure 3.3.17 temperature dependence of soil respiration during Summer in control (black dots, solid line) and drought (white dots and dashed line) with linear regressions.

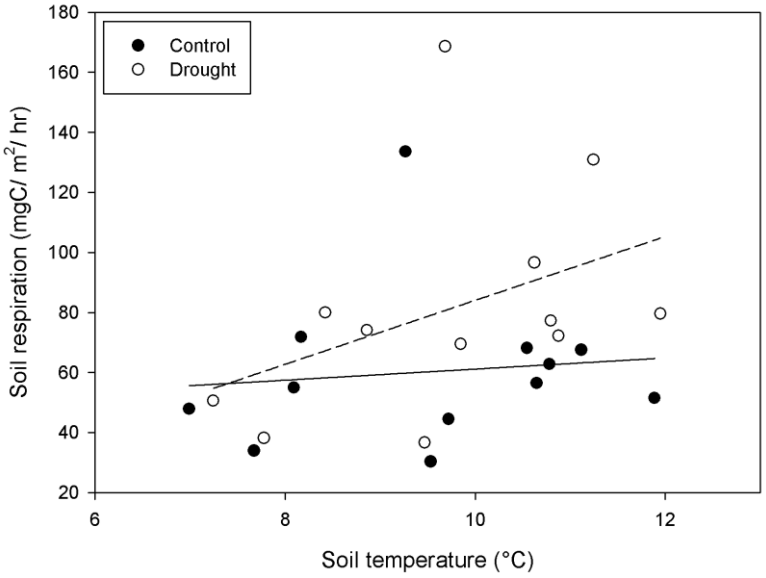


Figure 3.3.18 temperature dependence of soil respiration during Autumn in control (black dots, solid line) and drought (white dots and dashed line) with linear regressions.

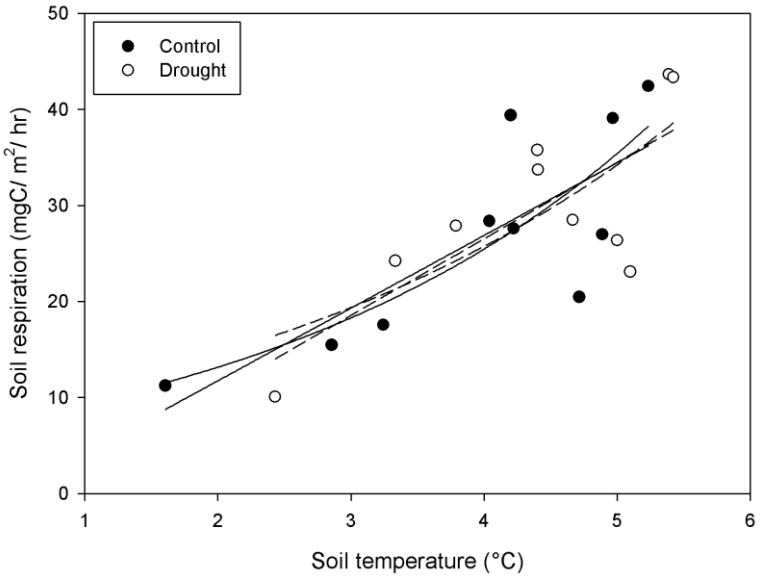


Figure 3.3.19 temperature dependence of soil respiration during Winter in control (black dots, solid lines) and drought (white dots and dashed lines) plots with linear and exponential regressions.

Table 3.3.5 Regression parameters and output from seasonal temperature sensitivity estimates.

			Parameters			*Output*			
Season	**Treatment**	**Regression**	**y0**	**a**	**b**	**p**	**Q_{10}**	**r^2**	**Adj. R^2**
Spring	Control	Linear	8.5326	4.6272	-	< 0.001	2.46	0.67	0.66
Spring	Control	Exponential	-	16.9997	0.1223	< 0.001	3.39	0.69	0.68
Spring	Drought	Linear	-2.5231	7.5065	-	< 0.001	3.14	0.78	0.77
Spring	Drought	Exponential	-	15.5287	0.1619	< 0.001	5.05	0.78	0.77
Summer	Control	Linear	53.9481	1.5784	-	0.66	1.25	0.01	0
Summer	Control	Exponential	-	-	-	-	-	-	-
Summer	Drought	Linear	13.1977	9.0239	-	0.02	3.83	0.24	0.2
Summer	Drought	Exponential	-	-	-	-	-	-	-
Autumn	Control	Linear	42.6706	1.8484	-	0.74	1.35	0.01	< 0.001
Autumn	Control	Exponential	-	-	-	-	-	-	-
Autumn	Drought	Linear	22.3932	10.6428	-	0.18	4.45	0.17	0.09
Autumn	Drought	Exponential	-	-	-	-	-	-	-
Winter	Control	Linear	-3.3849	7.5651	-	0.006	3.19	0.62	0.58
Winter	Control	Exponential	-	6.8051	0.3298	0.006	27.05	0.63	0.58
Winter	Drought	Linear	-5.3391	7.9652	-	0.01	3.31	0.58	0.53
Winter	Drought	Exponential	-	8.2511	0.2844	0.013	17.18	0.56	0.5

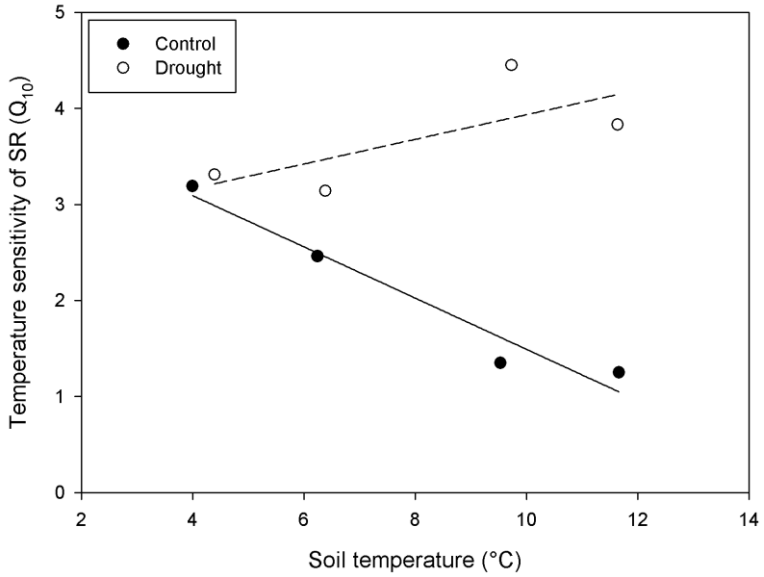


Figure 3.3.20 Seasonal soil temperature and Q_{10} of soil respiration for drought and control plots

3.3.5 Timing of treatment and flux response

Investigating the response time of soil respiration to the start and end of drought treatments for each year was carried out and is shown in Figure 3.3.24. The timing of the treatment commencement and cessation is summarised in Table 3.3.6. The treatment effect appears to be associated with the start and end of the treatment during 2007, although it is clear that there was a difference between treatments slightly before the start of the treatment. Data for 2008 shows treatment timing to have no apparent relationship with any treatment effect, indeed when considering the yearly dynamic, it is not until the middle of summer before treatment effect was noticeable. 2009 treatment start comes at a point where a notable treatment effect is already in place, and the treatment appeared not to change the magnitude of rate differences. Treatment cessation does however show a strong impact, with drought rates falling to nearly match the control within two weeks of treatment cessation.

Table 3.3.6 Treatment diary for drought 2007 – 2009.

Year	Treatment on	Treatment off
2007	16/07/2007	02/10/2007
2008	24/04/2008	25/11/2008
2009	21/05/2009	22/10/2009

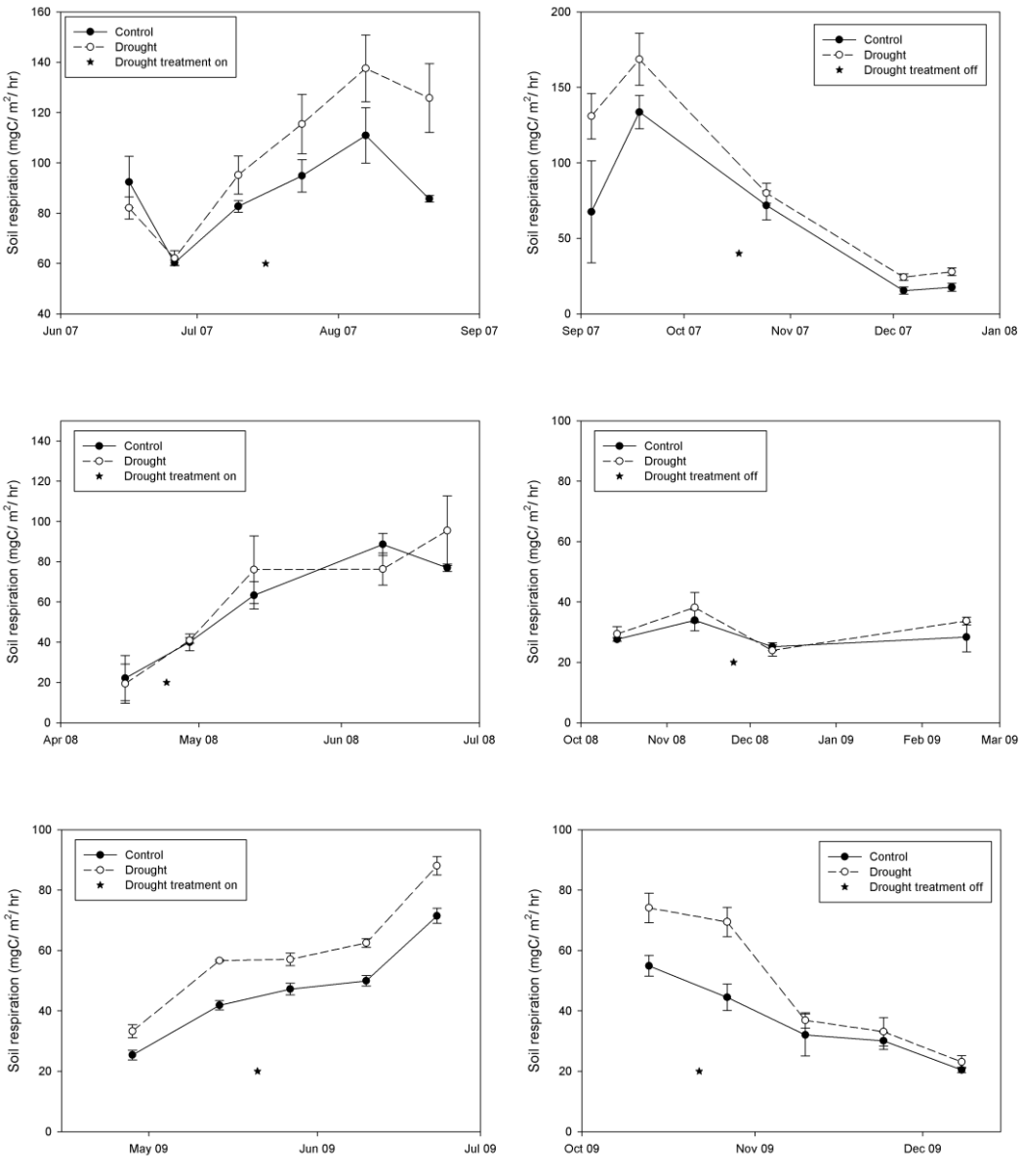


Figure 3.3.21 Respiration rates under drought and control around the treatment activation and cessation (indicated by the star symbol) for years 2007 (a), 2008 (b) and 2009 (c).

3.3.6 Hydrophobicity.

WDPT and MED tests (Figures 3.3.25 and 3.3.26) showed no difference between litter layer response between treatments. There was a difference between the peat layers. With drought having a longer mean WDPT and a higher MED concentration, however statistical analysis showed the difference to be non-significant.

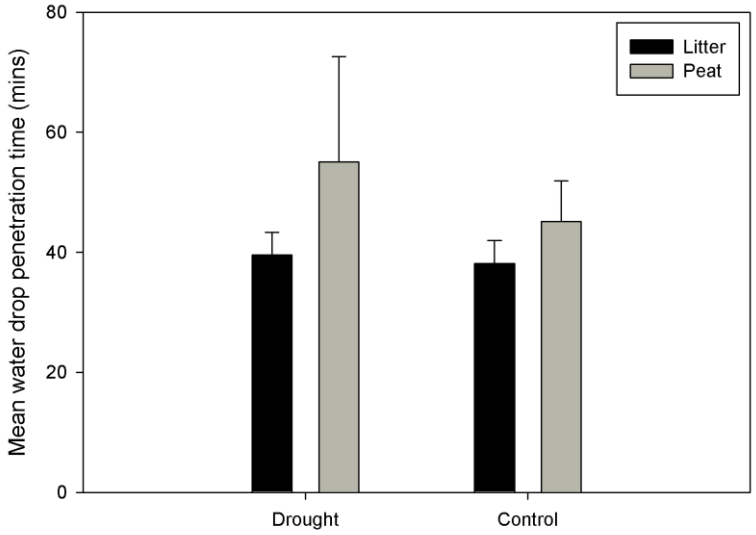


Figure 3.3.22 Mean time (minutes) for water drop penetration from control and drought soils for both litter and peat layers. Bars are standard error of the mean.

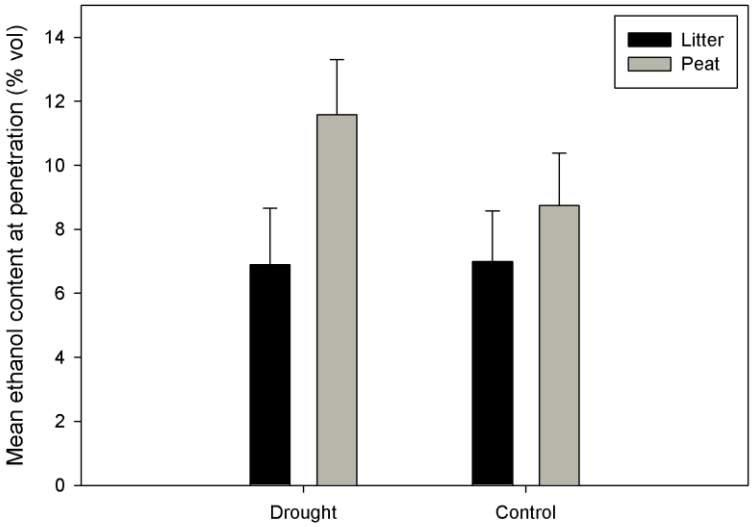


Figure 3.3.23 Mean ethanol concentration of drops penetrating in under a minute in soil litter and peat layers from control and drought plots. Bars are standard error of the mean.

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3.4 Discussion

3.4.1 Treatment effect on driving variables

Summer drought treatment was shown to have a significant effect on the amount of throughfall entering the system. This amount varied between years, and although the maximum change in 2007 and 2008 was similar (~90% less throughfall than control plots), the duration, and therefore severity of the treatment, was different across the studied period. Despite this degree of throughfall modification, soil moisture measurements appeared to be unaffected in the drought plots, and there were no significant differences recorded during the drought. As the theta probe measurement is made at a fixed depth (10 cm) and is averaged over that depth, it is entirely feasible that the method failed to pick up any treatment effect due to the bias of lower-soil moisture characteristics. This would require that the treatment affected only one component of the soil, either the surface layers (due to reduced throughfall and a lack of recharge via capillary action from depth), or the peat (minimal throughfall and constant drainage leads to drying of the peat, and any incoming water is not sufficient to moisten at depth). Both of these situations are plausible, but there is no way of determining this from the current data set. One remaining situation exists which is equally, if not more compelling, which is that there has been a physical change to the soil which masks the relative difference in soil moisture content. Volumetric water content can be compared to gravimetric content by factoring in the bulk density of a soil, so assuming a common bulk density, volumetric measurements made on two soil types would be comparable as would the gravimetric measures. However, a difference in bulk density which is not factored in to the volumetric measurement, would yield inaccurate data. The very low bulk density of soils at Climoor (~0.09 g/cm^3 for upper 6 cm) would need to be altered by only a very small amount to notably change the value of water content when expressed in volumetric terms. The theta probe measurement is set up to a standard for all the plots, and is therefore not

sensitive to small changes in the physical conditions that exist between treatments.

Laboratory soil moisture measurement made on Climoor soils showed that there was a difference between gravimetric measurements of soil moisture in drought and control plots, despite the field measurements showing no such change (data not shown). A change in the bulk density by 0.001g/cm^3 was also shown in this work, and by simple calculation with the set of actual volumetric measures from 2007, assuming a common bulk density gives non-significant treatment effect ($p= 0.63$), but altering drought by 0.001 g/cm^3 gives a significant effect ($p= 0.03$). So, small alterations to bulk density under drought conditions are a tangible source of error in the field measurements of volumetric water content. Reasons for this change in bulk density are possible from two sources. Peat soils are known to swell and shrink in response to changing soil moisture regimes, specifically here, shrinkage may occur under drying (Oleszczuk & Brandyk, 2008). This shrinkage will be accompanied (inevitably) by a change in the bulk density of the soil due to the change in volume despite no change in mass. This would result in an increase in bulk density under drying. This effect could be long-term, despite the input of rainwater during the non-treatment period. This may be due to hysteresis effects which govern the degree of wettability of the peat after a period of drying (see hydrophobicity discussion below). The second possibility is that the bulk density has increased in the litter layer due to an increase in the density of root biomass under drought.

Soil temperature classically acts as the other major climatic driver of soil respiration, and it is shown in this study to have a predictable cyclical behaviour which varies in accordance with seasonal changes. Treatment had no significant effect on the soil temperature in control and drought plots, however the indirect role of treatment on the response of soil respiration to temperature will be discussed later.

3.4.2 Drought effect on soil respiration

Plots of soil respiration from control and drought treatments (Figure 3.3.14) show rates to be generally elevated in drought relative to control. Respiration rates generally show variation throughout the year, this usually follows a predictable seasonal trend (Gaumont-Guay *et al.*, 2006). Departure from this trend has been noted in some studies, and a much closer link instead to fundamental soil conditions such as moisture content, is seen (Vanhala, 2002). The expression of the flux rates as a function of percentage change from control (Figure 3.3.13) show a fairly consistent elevation in drought levels. However, as these rates are relative rather than absolute, the differences can become misleading (i.e. a small change in a small number can appear as big as a large change in a large number). In this data there appears to be some difference across the course of each year, where the difference may be more pronounced during the summer months. This is shown well in Figure 3.3.14 and the range of seasonal peaks and troughs associated with each year can be clearly observed.

To identify the significance of absolute differences in respiration rates, repeated measures ANOVA was carried out using month and year as factors, and plot as an error term in the ANOVA. Over the course of the entire year, the respiration rates were not significantly different ($p= 0.06$), however, selection of month associated with the spring-summer growing season (May-August inclusive) gave a significant difference ($p= 0.02$). Outside of this period, the difference remained non-significant. This suggests that the drought elevation of soil respiration is confined to the summer growing period.

It can be theorised then that the treatment response was either mainly due to enhanced SOC decomposition (as period of elevated effect was during the actual treatment), or that the autotrophic component responds more so to the drought treatment. Defining what constitutes ‘the autotrophic component’ is difficult, and assigning particular observed trends to likely source components is tenuous Previous work by Cisneros-Dozal et al (2006)

suggests that the majority of the seasonal variation (especially the spring burst) is associated with the switch from structural component turnover, to turnover of recent photosynthate. Whilst the majority of respiration was derived from the turnover of recent photosynthate, it is not possible to determine whether this is directly respired by the plant, or by rhizosphere heterotrophy respiration. In the current study, it would appear than much of the drought response appears during the peak plant growing period, but the possible interaction by temperature causes difficulty in proposing a strict response by plants. Attempts to partition response to soil moisture has given varying results, with almost equal stimulation observed by Millard et al (2008) when irrigating dry savannah soils in Texas. Given the possible drivers of metabolic activity related to plant growth such as air temperature and Photosynthetically Active Radiation (PAR) (Larsen *et al.*, 2007), it is likely that explaining seasonal changes in soil respiration would require a more complex multivariate model.

When considering the general flux dynamics over time, it is clear that there is a degree of inter-annual variability, and as year was a significant component of the repeated measures this comment is statistically sound. Figure 3.3.14 shows the general trend in rates for both drought and control, and as well as the treatment effect being clearly observable, there is also a marked difference in the peak fluxes for each year, and the shape of the flux dynamic. Interestingly, although the absolute values for 2009 suggest a generally lower overall flux in both control and drought, but the percentage change figure shows a strong treatment effect, and an observable seasonal pattern. This suggests that under conditions whereby background levels of respiration are generally low, the drought enhancement of the rate is (percentage-wise) much greater. This may be due to other variables (temperature, nutrient supply etc.) being relatively limiting, so the drought effect becomes a more prominent controller of respiration flux. This supports the role of soil moisture content as an interacting variable, as demonstrated by Davidson *et al* (1998).

The response of soil respiration to the timing of the drought treatment was also investigated, and it is clear that there is a large amount of variation between each year. The lack of a response in a reasonable temporal proximity during 2008 is especially compelling, although when considering the two other years, if there were any trend, it would be that the cessation has a more noticeable effect. This could be explained such that at the start of the year, most of the respiration is primarily due to soil warming and due to autotrophic metabolism increases (i.e. is mostly temperature sensitive), whereas by the autumn, the majority of respiration could be turnover of litter and SOC (combination of bulk SOC and root litter) which may be more sensitive to drought. This is possibly even more likely given the fact that favourable temperature for respiration tends to continue into the autumn months, whereas the respiration rate falls rapidly. So there may be not only a general interaction of driving variables, but also a seasonal shift in the dominance of particular variables.

3.4.3 Drought effect on temperature sensitivity

The temperature sensitivity of soil respiration is explored in detail in this study, and it is clear initially that overall, the drought treatment modifies the already strong temperature sensitivity found in the control. The increase in sensitivity as measured by the calculated Q_{10} value is highly data-set dependant. This is first demonstrated by the difference in Q_{10} when looking at the two year, or the three-year dataset. The two-year set running from Oct 2006 – Dec 2008 gives a strong response with values of 4.16 and 6.05 for control and drought respectively. By adding in the third year, the values both fall to 3.19 and 4.26. The second figure also sees a slight fall in the r^2 value of the exponential regressions. Interestingly, the exponential regressions seem to not provide a very good fit to the respiration rates associated with the lower soil temperatures, and by applying a linear fit across the data, not only is the total r^2 improved, but the representation of the lower temperatures seems resolved. Q_{10} values associated with the linear regression are also slightly lower (2.12 and 3.68 for control and drought respectively) than the

exponential. Although the decision to choose linear over exponential regressions has been discussed in detail in the literature (Lloyd & Taylor, 1994), for the purposes of considering relationships within the data set (rather than for extrapolation), it is sensible here to consider the role of linear regression in accurately describing the observed flux relationship to temperature.

A single value for temperature sensitivity for the year has the potential to be misleading. Although the single value arguably captures the entire datasets sensitivity, the value is a composite of data from periods of very high temperature sensitivity and data from low sensitivity. Also, this expression assumes there are no other important variables which may vary simultaneously with temperature (Janssens & Pilegaard, 2003). The different components of soil respiration are also likely to have differential sensitivities to temperature (Heinemeyer *et al.*, 2007a), and the relative activity of those components during the year (i.e. autotrophic dormancy during winter) will mean a single annual Q_{10} will not reflect the inherent variability found in these systems.

Given the issues of using the entire year to derive a single Q_{10} value, and the ANOVA results highlighting the treatment effect during summer months only, it is the seasonal sensitivity estimates which may yield more informative results. Sticking with the three-month seasons, soil respiration and temperature was allocated to a season. Temperature sensitivity estimates as Q_{10} functions were calculated from either a linear and exponential regression, or a linear only (when exponential was not possible). Immediately clear is the difference across the seasons in the Q_{10} estimate, however, care must be taken in interpreting the values obtained for summer and Autumn given the exceptionally low r^2 and p values for the regressions. Spring estimates suggested drought to be substantially more temperature sensitive than control, and the magnitude of the difference was notable between the two regression equations. Interpretation of the winter-time Q_{10}s relies completely on the choice of regression equation, as the linear function suggests a modest (and highly similar) Q_{10} for both control and drought

(3.19, 3.31) whereas the exponential gives estimates of 27.05 and 17.18 for control and drought respectively. Clearly these larger Q_{10} values are over-estimates, as a 27 times increase in winter flux rates for control (~26 mgC/ m^2/ hr) would imply summer rates of 725 mg C/ m^2/ hr, which is around ten-times higher than the actual value. Fundamentally, these seasonal estimates rely on the assumption (as does the annual set) that the ascribed temperature sensitivity is continuously exponential (or linear) across the data set and into the predictive realms of higher temperature. This is not the case, and is demonstrated clearly by the lack of fit between temperature and respiration during the height of summer and into autumn. Here the temperature approaches optimum (given the other constraining variables in effect) for respiration, and the sensitivity relationship falls apart (summer and autumn r^2 values all <0.25).

If, we assume the r^2 values to be unimportant to an extent, and that the calculated Q_{10} is a sensible estimation of the temperature sensitivity (which in summer and autumn it is despite the low r^2, as the Q_{10} is reasonable), the relationship between the average temperature at a given time and the temperature sensitivity can be made. Classically, the Q_{10} will decrease as temperature increases (Janssens & Pilegaard, 2003, Wang *et al.*, 2010, Xu & Qi, 2001), although this is not always the case, and some inter-annual variability has been shown (Chen *et al.*, 2010a). This classic relationship is expected due to the lower constraining effect of temperature on metabolic activity. This is shown well in figure 3.3.23 to be the case for the control plots, however, drought appears to have altered this relationship, and the sensitivity to temperature remains throughout the summer and into the autumn. This would suggest that the drought reduced the soil-moisture stress on respiration and creates a new upper optimum for which remains sensitive to changes in temperature. When investigating seasonal temperature sensitivity in a Beech forest, Janssens and Pilegaard (2003) identified a strong seasonal shift in temperature sensitivity similar to that observed here in the control plots. The same authors suggested caution with interpreting whole-year Q_{10}s and added that whilst exceptionally high (winter

time) Q_{10}s may appear unrealistic, they are demonstrative of the degree of temperature limitation that exists at these periods.

3.4.4 Hydrophobicity as a consequence of drought.

The rewetting of soils during the cessation of the drought was shown by Sowerby et al (2008) to be inhibited in some way such that soil moisture failed to return to pre-drought levels (or comparable with control). Although this is not seen directly in this data set, for reasons associated with the measurement of volumetric water content, it can be assumed that the situation observed by Sowerby et al (2008) remains. A possible reason for this reduced water holding capacity could be an increase in hydrophobicity associated with drought soils, and this is suggested in the same paper by Sowerby et al to be a probable major issue. To investigate this, soil cores were taken during the height of the drought in 2007 and subjected to two analysis procedures that investigate the degree and severity of hydrophobicity. By looking at the distinct soil layers found within the surface 15 cm, identification of any particularly hydrophobic areas could be made. Both of these tests suggested that although there was a large difference in the hydrophobic properties of the distinct soil layers, there was no treatment effect on these values. Peat soils appeared to have a marginally longer penetration time and a higher molarity of ethanol needed for penetration when viewed simply as mean values. However, these differences were no significant, but hinted that any difference that may be developing was more likely to occur in the peat layer. This is in agreement with possible issues surrounding drought-induced shrinkage of peat material and the increase in hydrophobicity of organic material under drying. Hydrophobicity can be a highly isolated phenomenon though, and the heterogeneity of soils studies here may mask any differences in hydrophobic properties.

3.5 Conclusion

Summer-drought treatment was shown to have a significant effect on the throughfall entering treatment plots. Despite this, no change in soil moisture was observed to coincide with the treatment. It has been discussed that this may be due to a methodological approach issue, or due to a physical change in the soil bulk density under drought which adversely affects measurement accuracy. Even though the soil moisture data remains comparable, there is an observable response in soil respiration rates to the drought treatment. Rates are elevated above that of control for each of the three years, and the difference is significant during the summer months (May-August). This difference suggests a seasonal pattern in the drought response and indicates autotrophic-mediated (either direct root respiration, or rhizo-stimulation) components might be more drought sensitive than free-living microbes in bulk soil.

Temperature sensitivity was shown to have a strong seasonal element, and treatment interacted with this to give a varying degree of extra temperature sensitivity across the year. Overall though, drought caused a substantial increase in the temperature sensitivity of respiration and this is expected to be due to the interactive effect of reduced water stress on the temperature-dependant rate. Drought seems to have altered (through these mechanisms) the classically observed reduction in Q_{10} with increasing temperature, such that drought plots remain sensitive in the otherwise limited summer months. It is possible that this may be due to an increased substrate supply to rhizopshere respiration (due to increased photosynthate production) as photosynthesis and plant respiration are increased under the more favourable, drier conditions.

These modifications to upland systems are potentially significant, as if a substantial portion of the extra respiration is due to loss of native SOC, there could be a long-term trend of C-loss from these systems. Even if the majority of drought-induced respiration is autotrophic, there could still be priming of native SOC loss, but the increased rate of respiration could be

balanced by increased above and below ground biomass as autotrophic metabolism and growth are stimulated by more favourable conditions. Given the likely climate-change implications of drought coinciding with increasing temperature, the higher temperature sensitivity of drier soils could multiply any predicted respiration rates such that SOC loss is actually greater than would be otherwise under a single variable change.

Chapter 4. In-situ root exclusion in an upland heath system as method for compartmentalising soil respiration.

4.1 Introduction

Soil respiration combines the measurement of CO_2 flux from a number of components which can be broadly split into autotrophic and heterotrophic sources. This approach relies on the assumption that the total heterotrophic component is physically separate from, and therefore not reliant upon, the autotrophic component. Of course, this is not the complete picture, and although there will inevitably be a portion of the heterotrophic component which relies on bulk SOC for substrate, the contribution of rhizosphere microbes to total respired-C is great. Due to the intimate proximity, splitting further into source components at the rhizosphere level is difficult. The components of soil respiration can therefore be summarised in a simple relationship:

Eqn. 1. *Soil Respiration (SR) = autotrophic respiration + rhizosphere respiration + SOM respiration*

Given the understanding that rhizosphere respiration is complex, and the source components are potentially inseparable (i.e. rhizosphere microbes, by definition, cannot function adequately in the absence of the root), a broad picture of dependence can be formed, such that total soil respiration will be root dependent, or root independent. This allows a simplification of equation1 to:

Eqn. 2. *SR = Root dependent respiration (R_{rd}) + Root independent respiration (R_{ri})*

This approach avoids having to make a differentiation between autotrophic and heterotrophic contribution, more it recognises the role of roots in both directly contributing to respiration, but also stimulating a portion of heterotrophic respiration. To argue that the R_{ri} fraction is completely root independent would be flawed, as ultimately all soil biology is interdependent in some extraneous form or another. However, in reasonably short timescales R_{ri} can probably be seen as independent.

Various attempts have been made to investigate and separate the source components of soil respiration, both in the field and in the laboratory. However the results remain variable, with estimates ranging from 12-93% of the total respiration being R_{rd} (Raich & Tufekciogul, 2000). This variation will be partly due to the large number of theoretical and technical issues surrounding the estimates (Baggs, 2006), but also there will be an inevitable degree of variation between ecosystems

In terms of in-situ approaches, two physical methods aim to isolate the components of respiration:

1. Root exclusion.
2. Girdling (stopping the downward transport of photosynthate).

The first method requires the physical removal of plant roots, or the cutting and subsequent decomposition (in-situ) of the excised material. This then leads (over time) to a stable, steady basal rate of R_{ri} consisting of SOM and microbial biomass turnover. This method is described well by Heinemeyer *et al* (2007b). Using this method, Heinemeyer (2007) could estimate root contributions from a pine forest system to be ~15% of the total, with the remainder being split ~60% to heterotrophs, and 25% to ectomycorrhiza.

Trenching, whereby physical barriers are placed in the soils to prevent growth of roots (similar to that used by Heinemeyer *et al* (2007)) was employed by Li et al (2004) who showed root exclusion accounted for 70 and 56% of the total respiration in two forest systems. In the study by Li *et al* (2004), the difference in contribution was dependent upon the maturation of the ecosystem, with the higher impact being seen in the secondary forest, over the lower impacted plantation woodland. Buchman (2000) used a similar trenching approach, but to selectively remove fine roots only. This study found that microbial mineralisation was the dominant source of CO_2 efflux, contributing around 70% of total respiration. The girdling approach allows the soil to remain intact, with roots not physically disturbed, but essentially cut the transport of fresh photosynthate material to the roots.

This approach differs from trenching due to the disturbance element, but also in that the rhizosphere microbes, whilst being starved of their major substrate source, remain in the soil. This allows for partitioning of the actual root-derived substrate dependent respiration from the SOM respiration. This approach is confined to plants that can physically allow this process (trees), and so is generally restricted to woodland systems as in a number of studies (BhupinderpalSingh *et al.*, 2003, Binkley *et al.*, 2006, Frey *et al.*, 2006, Hogberg *et al.*, 2001). Results from girdling were similarly variable as trenching, with reports of decreases in respiration of 16-54% from the above mentioned studies. The speed at which girdling interrupts the respiration is fast, indeed Hogberg *et al* (2001) found a reduction of 37% within five days. This demonstrating that rapid mineralisation of fresh photosynthate is a key component of soil respiration in forest systems. The impact on community biomass has also be found following girdling, with a general reduction in both bacterial and fungal biomass (Subke *et al.*, 2004) suggesting a strong interdependence for total decomposition on the input of photosynthate. These differences (given they are all in woodlands) emphasise not only the shear degree of variability that can be obtained with this fairly common approach, but also serves to highlight the dominance of forest-based studies in the literature. Most non-forest based approaches tend to be laboratory based using quick-growing grass species.

The accumulation of humus material and recognisable plant litter in organic upland soils suggests decomposition of organic material is more restricted than NPP, and this is explained by the suite of well-described constraining factors which often prevail in these soils (low pH, high moisture content, input of recalcitrant litter, low available nutrients). Given this situation, it would be assumed that R_{rd} might be less limited by these conditions, and indeed contribute the majority of total respired C. Also, as the two major source components of soil respiration are likely to be differentially controlled (albeit subtly) by prevailing conditions, the response of separated components to changes in such conditions would be offset. The importance in understanding the component response of climate change is central to explaining the results so-far observed at the Climoor research site. The

greater soil respiration in both warming and drought treatments (chapters two and three) could be due to stimulation of either R_{rd} or R_{ri}, or indeed both. The links between this stimulation and the consequences for SOC storage are obvious, i.e. stimulation of R_{rd} would suggest C loss be balanced by increased NPP, whereas stimulation of R_{ri} would lead to net loss of SOC. Therefore it is important that attempts be made to unravel the difference between these compartments. Isotopic techniques using ^{14}C (Trumbore, 2000) or ^{13}C as a tracer (Heinemeyer *et al.*, 2006, Johnson *et al.*, 2002) can also be used to differentiate between components of soil respiration, but are not considered here as ^{14}C has previously been used as a tracer at this field site.

In an attempt to investigate this under field conditions, root-free cores were installed into the established manipulation plots at the Climoor field site and the soil respiration flux was monitored at both the root-free (R_{ri}), and the existing rooted (SR) cores simultaneously. It was hypothesised that the two components would have different respiration fluxes, with the rooted component having a greater flux rate based on the assumption that NPP (and therefore root-dependent respiration) is less restricted by prevailing conditions than the R_{ri}. It was also expected that the flux dynamic would differ such that SR would be more seasonally responsive, and R_{ri} would respond more to prevailing soil conditions.

4.2 Methods

4.2.1 Site description

The Climoor research site is a *Calluna vulgaris* - *Vaccinium myrtilus* (NVC H12 community) heathland located in Denbighshire, North Wales (53° 3'N 3° 28'W). The site occupies a NE facing slope at an altitude of 490 m ASL. The soil is a shallow (~15 cm depth), well drained organo-ferric podzol with a pH of 3.8 overlying gritstones from the Denbigh grit sequence. Site mean annual temperature is ~7-8°C and annual rainfall is ~1500 mm.

4.2.2 Experimental design

This study uses the Climoor/Vulcan warming and drought experiment as in previous chapters. Plots are delimited by tubular steel frames which allow for access without trampling vegetation, but also support the housing of the roof technology which provides the two manipulations treatments (drought and warming). Detail of the treatment design and structure can be obtained from Beier *et al* (2004). Within each plot, three locations are used for soil respiration measurements, and three are used for root-free respiration measurement. Rooted respiration is measured on the shallow (~2 cm) collars which were inserted before the current study by cutting into the soil with a sharp knife to 2 cm and pushing the collar firmly into the soil. The root-free cores were constructed of 15 cm deep PVC cylinders with the same diameter (10 cm) as the shallow collars. These were similarly cut into the soil and pushed until they were at full depth, or they had reached parent material which was too resilient to insert further. This depth was deemed sensible to bypass roots, as previous laboratory observations had concluded that intact root material was seldom found in the mineral layer of soil, which typically is around this depth. The bottom of the core was open to allow drainage.

4.2.3 Soil respiration measurement

Soil respiration was measured in both rooted and root-free collars during the same measurement session either fortnightly or monthly. Measurement was carried out using both a PP-Systems EGM-4 IRGA fitted with a SRC-1 10 cm survey chamber, and a Li-COR 8100 IRGA also with a 10 cm survey chamber. Flux rates were automatically calculated by each machine based on headspace accumulation of CO_2 over a 60-second enclosure using either a default (linear) fit in the case of the EGM-4, or selection by machine of linear or quadratic fit in the case of the Li-COR 8100.

4.2.4 Environmental variables

Soil moisture measurements were made using a Delta-T theta probe (Model ML-2, Delta-T Services, UK) adjacent to the soil respiration collar until December 2008, after which concerns about the suitability of theta probe measurements caused a cessation in manual moisture measurements (this is discussed further in chapter 3). Throughfall values were obtained by sampling two throughfall containers situated in each plot at fortnightly intervals. Data was obtained from Alwyn Sowerby (unpublished data) and is bulked monthly values. Soil temperature values were obtained from manual temperature probes inserted into the soil to a depth of 5 cm immediately adjacent to the respiration collar.

4.2.5 Root and soil examination

At the end of the study period, a single root-free core form each plot was removed for analysis. To compare with the plot cores, three cores of a similar size were taken from pristine areas outside the plots. These were collected by cutting in three of the 15 x 10 cm cores and removal of the intact sample within each core. All samples were collected on the same day and returned to CEH Bangor for subsequent analysis. Each core was weighed and measured before being split into an upper organic layer and a lower

mineral layer (if present). Each sample was homogenised by hand and split into bulk soil, dead wood material and obvious roots. A sub-sample of the roots were taken for estimation of metabolic activity (data not directly discussed here). Soil moisture and LOI was determined on all samples by drying at 105°C overnight for moisture, and then at 375°C overnight for LOI. Bulk density was also determined on each sample.

4.2.6 Data analysis

Rooted and root-free data was analysed for significant difference in respiration rates using a repeated measures ANOVA after log transformation. This was carried out within each treatment to identify differences in rooted and root-free respiration estimates. All data was visually inspected for normality prior to any analysis using quantile-quantile plotting, and log transformations were carried out when needed to comply with ANOVA assumptions. Statistical analysis was carried out using R statistics version 2.11.1 (R, 2010) Linear and exponential (single, 2 parameter exponential) regression fits between soil temperature and respiration were fitted using Sigmaplot version 11 (Systat, 2009). Figures were also produced in Sigmaplot version 11 or in R statistics.

4.3 Results

4.3.1 Respiration data

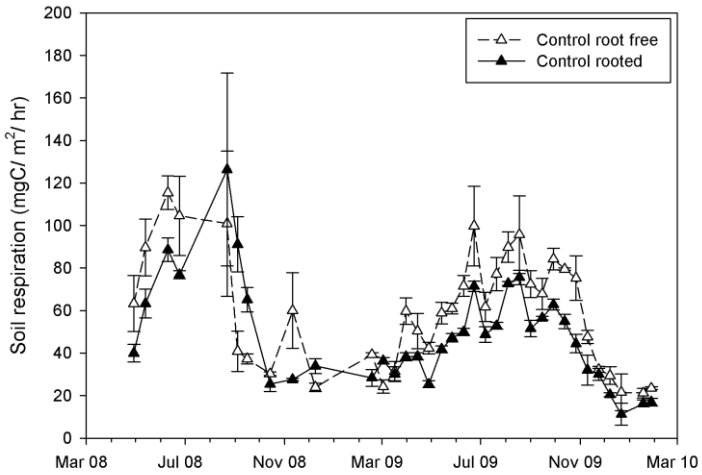
Root-free respiration rates (Figure 4.3.1) followed the trends observed in rooted respiration over the course of the study period. Control treatments showed an initial dominance of root-free in the months immediately after cutting, but this fell away during the autumn. This first pattern was not observed in the drought and warming, but the rooted pulse during the autumn is more pronounced. Considering 2009 as a complete growing-year, statistical analysis (repeated measures ANOVA) was carried out on the difference in respiration rates. Although control root free appeared to be consistently greater than rooted, the whole year difference was not significant at the $p < 0.05$ level ($p = 0.08$). However, the period April – November gave a significant difference between the rooted and root free ($p = 0.015$), with other months being non-significant. Drought treatment was significantly different when considering the whole year ($p = 0.048$), but when including month as a factor, only the November-December period gave a significant difference between rooted and root-free ($p = 0.01$). Warming treatment provided no significant difference across the time period ($p = 0.5$), or in any month class investigated.

4.3.2 Difference expressions

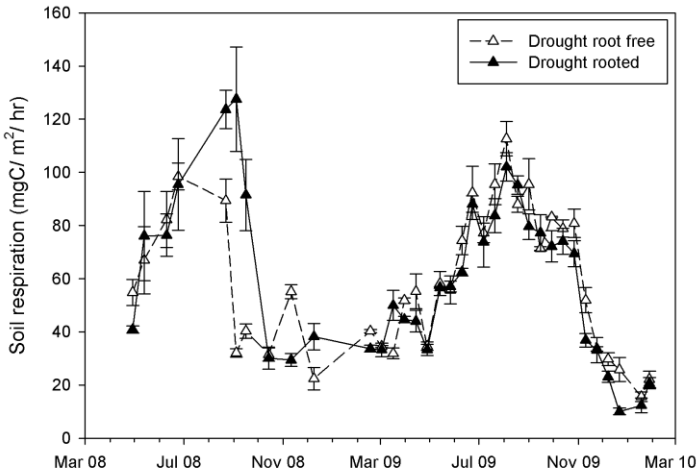
The differences between rooted and root-free under each treatment are explored in Figures 4.3.2 and 4.3.3. The higher contribution by root-free declined after the initial excision exercise, and the rate fell to around half that which was produced by rooted soils. The contribution then shifted rapidly during autumn to give ~50-125 % more respiration from root-free during November. During 2009, the contribution was less variable, but there were some notable between-treatment differences. Control plots saw a persistent dominance of root-free soils, with the greatest overall contribution as a percentage. Drought and warming had almost identical contributions by root-

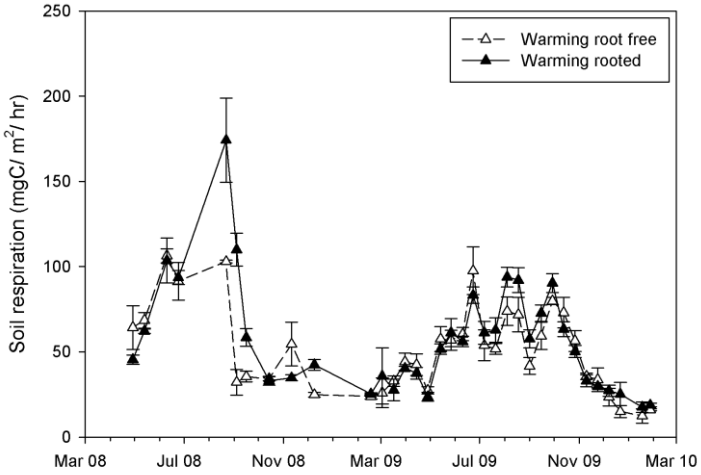
free during the spring months of 2009, but during the summer, the warming treatment fell such that rooted cores contribute more until October. A brief rise in autumn 2009 in warming plots precedes a fall back to summer levels. Drought continued to see marginally more respiration from root-free, with a notable pulse during December 2009 before falling back to autumn levels.

Figure 4.3.4 shows the relative mean flux rate for 2009 of rooted and root-free cores. It is immediately clear that under control, root-free was substantially greater than rooted ($p= 0.007$), and as in Figure 4.3.3, this decreased in the order drought>warming such that warming in fact showed an actual (but not significant) greater flux from rooted than root free.



(a)





(b)

(c)

Figure 4.3.1 Soil respiration from rooted and root-free cores under control (a), drought (b), and warming (c) treatments. Bars are ± SEM.

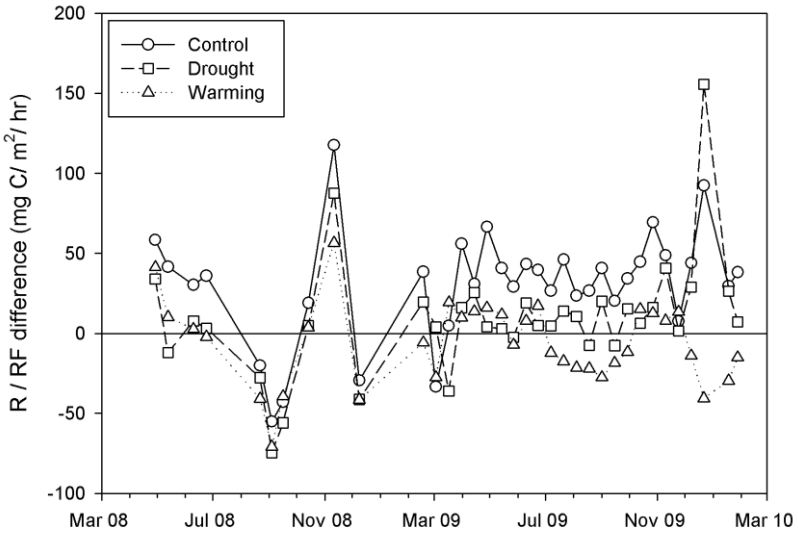


Figure 4.3.2 Difference between rooted and root-free respiration rates under control, drought and warming treatments. Values are the root-free rates minus the rooted rate, so a positive value indicates a greater contribution from the root-free core.

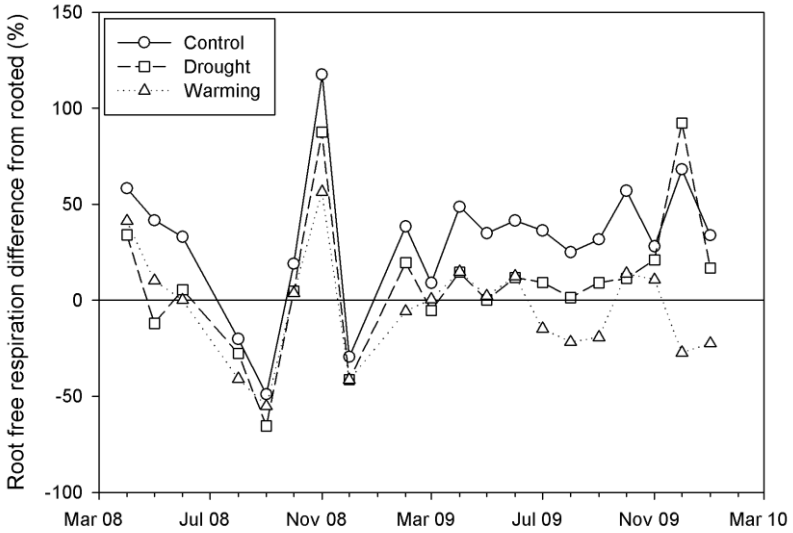


Figure 4.3.3 Monthly mean root-free respiration as a percentage difference from rooted respiration under control, drought and warming treatments.

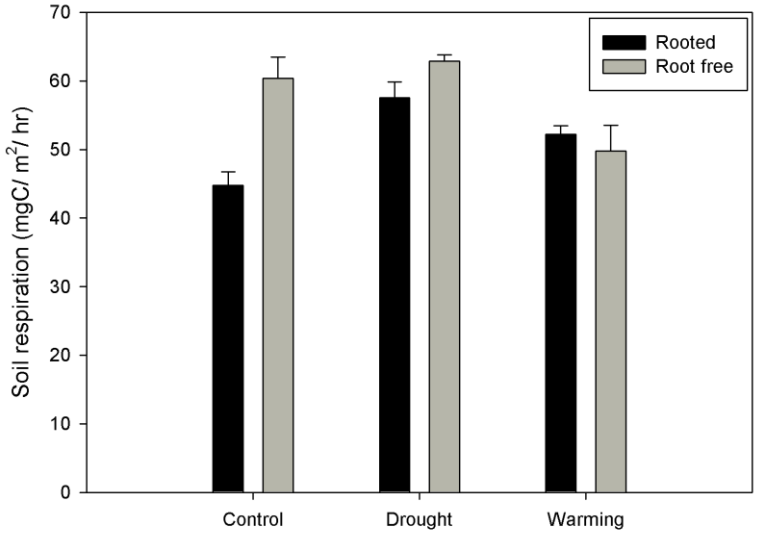


Figure 4.3.4 Mean (± SEM) respiration rate form rooted and root-free cores for 2009 under control, drought and Warming treatments.

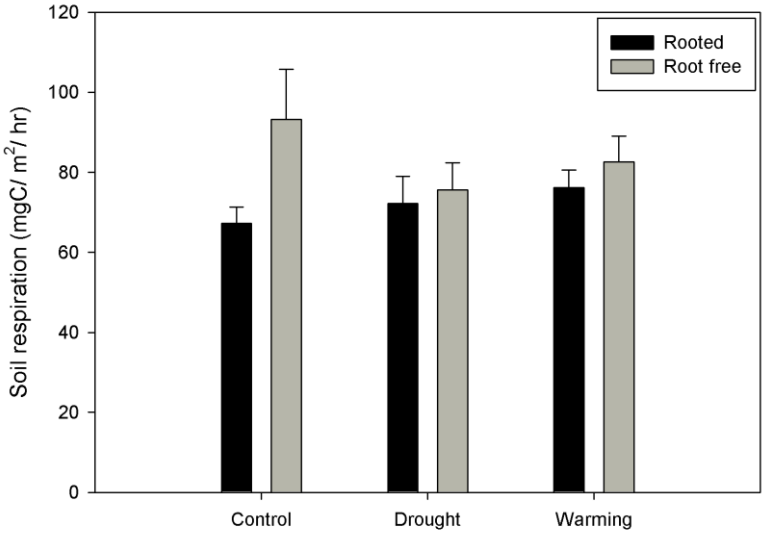


Figure 4.3.5 Mean (± SEM) respiration rate form rooted and root-free cores for the first two months after root-free core installation (2008) under control, drought and Warming treatments.

4.3.3 Soil temperature, moisture and throughfall

The trend in soil temperature data followed an expected seasonal pattern, and is shown in Figure 4.3.5. Throughfall data (Figure 4.3.6) gives an indication that there is little seasonal variation. The effect of drought treatment on incoming rainfall is shown clearly in this figure by the reduction in levels seen during the summer months.

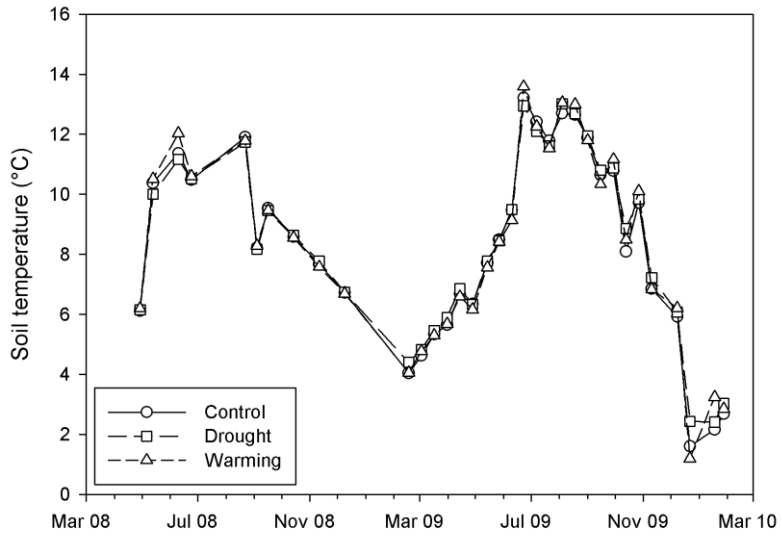


Figure 4.3.5 Soil temperature at 5 cm depth under control, drought and warming treatments.

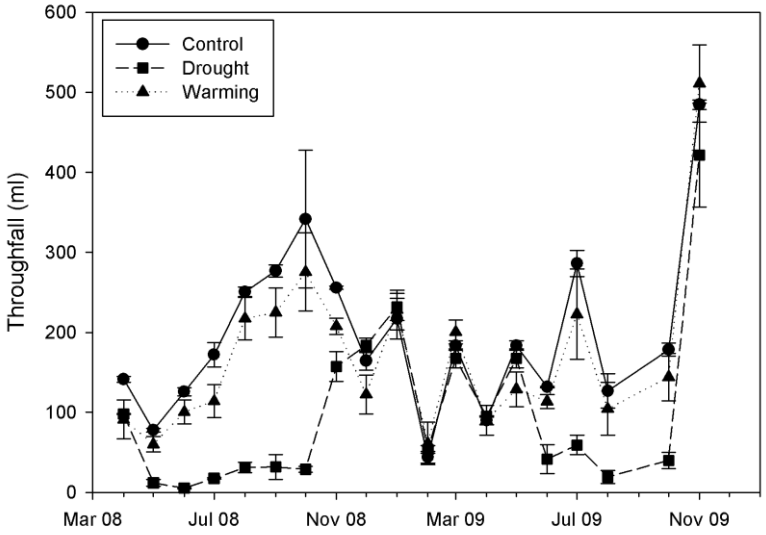
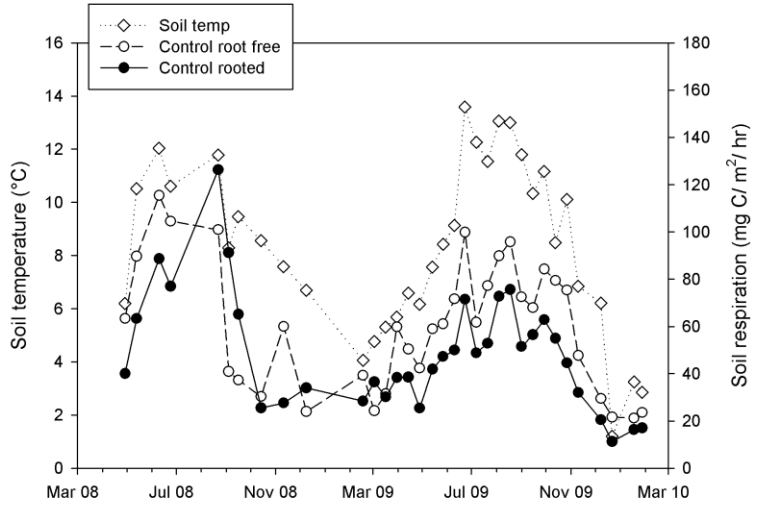


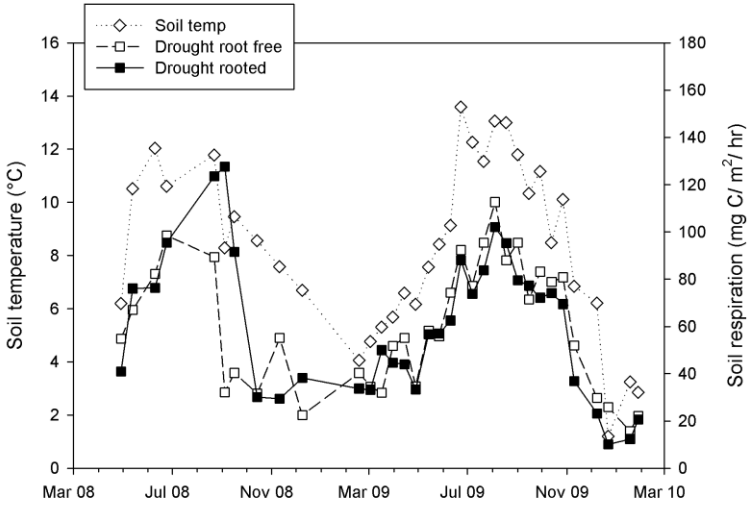
Figure 4.3.6 Mean (± SEM) monthly throughfall for control, drought and warming treatments April 2008 – Dec 2009.

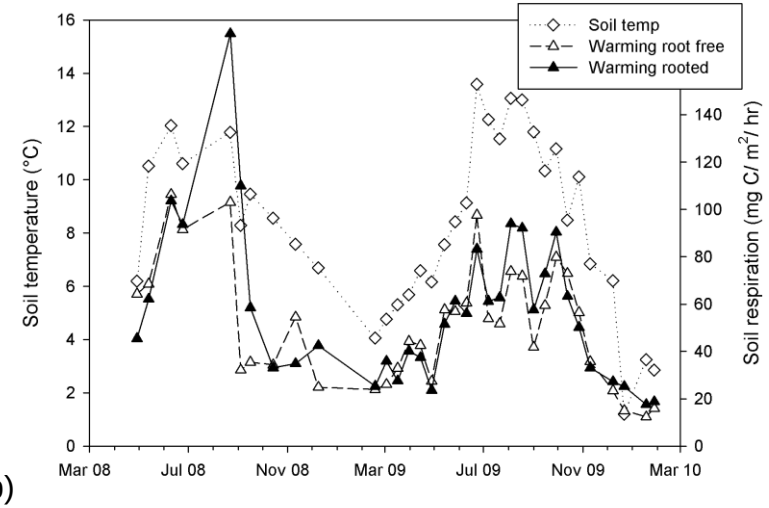
Observing the seasonal dynamic between respiration rates and soil temperature (Figure 4.3.9) suggests a reasonably tight relationship between soil temperature and respiration, most notable during 2009. The slow decline in autumn 2008 is miss-matched by the respiration rate though, with a rapid fall to basal winter levels in rate, whilst the soil temperature fell slowly. The summer fluctuations in temperature were mirrored in the fluctuations in rate, although this is possibly more pronounced in the warming and control than in the drought.

To assess the dependence of soil respiration on soil temperature, linear and single, 2-parameter exponential regressions were fitted to both rooted and root-free respiration, and are shown in Figure 4.3.8. Q_{10} values were calculated based on the output from these regressions (Table 4.3.1, Figure 4.3.10). The choice of regression equation has an impact on the calculated Q_{10}, with exponential regression tending to give a higher estimate than linear. The difference between rooted and non-rooted was treatment (and equation) dependent, with control plots being generally less temperature sensitive than the treatment plots. The conclusion for drought depends entirely on the regression equation chosen, whereas the differences appear more marked in the warming treatment. Generally though, the temperature sensitivities are very similar across both rooted and non-rooted samples.



(a)





(b)

(c)

Figure 4.3.7 Rooted and root-free soil respiration and soil temperature for control (a), drought (b) and warming (c) treatments. Standard error bars are not shown in this figure for purposes of clarity.

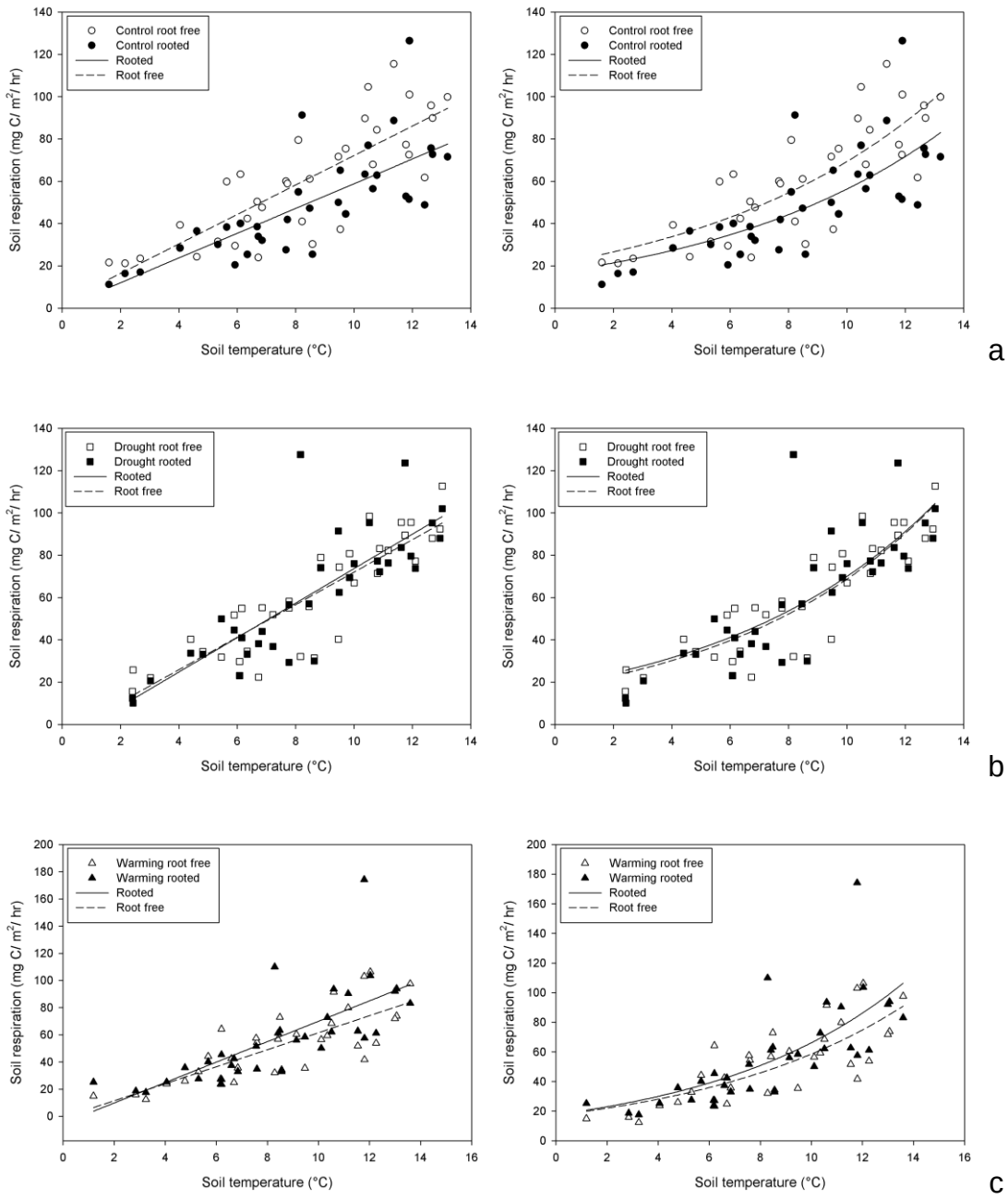


Figure 4.3.8 rooted and root-free soil respiration and soil temperature with linear (left) and exponential (right) regressions under control (a), drought (b) and warming(c) treatments. Q_{10} estimates of temperature sensitivity are found in Table 4.3.1.

Table 4.3.1 Output and calculated Q_{10} values from linear and exponential regressions shown in Figure 4.3.9.

Treatment	R/RF	Regression	y0	a	b	Q_{10}	r^2	p
Control	Rooted	Linear	0.3665	5.8466	-	2.98	0.56	< 0.001
Control	Root-free	Linear	2.521	6.9645	-	2.86	0.66	< 0.001
Control	Rooted	Exponential	-	16.8188	0.1209	3.35	0.55	< 0.001
Control	Root-free	Exponential	-	20.9503	0.1197	3.31	0.66	< 0.001
Drought	Rooted	Linear	7.8115	8.1487	-	3.47	0.66	< 0.001
Drought	Root-free	Linear	4.8495	7.6847	-	3.29	0.77	< 0.001
Drought	Rooted	Exponential	-	18.5797	0.1326	3.77	0.63	< 0.001
Drought	Root-free	Exponential	-	17.462	0.137	3.94	0.78	< 0.001
Warming	Rooted	Linear	5.1973	7.5164	-	3.32	0.53	< 0.001
Warming	Root-free	Linear	1.0725	6.2607	-	3.07	0.61	< 0.001
Warming	Rooted	Exponential	-	17.6739	0.1321	3.75	0.53	< 0.001
Warming	Root-free	Exponential	-	17.2326	0.1224	3.40	0.6	< 0.001

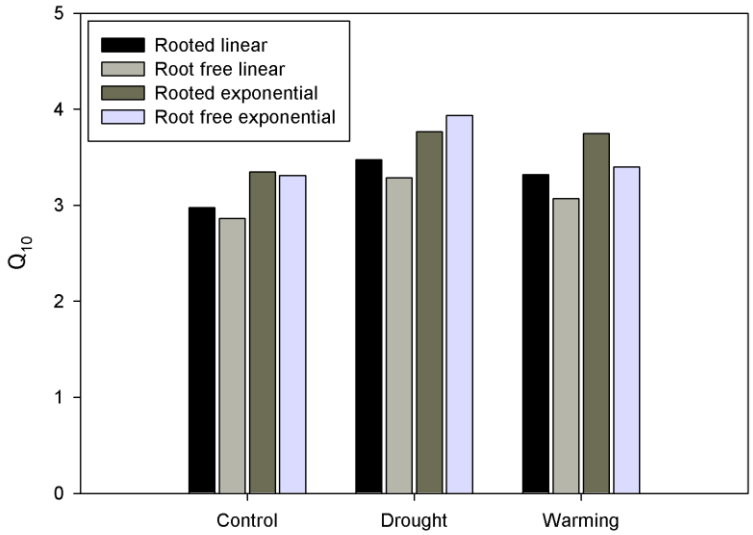


Figure 4.3.9 Q_{10} values for rooted and non-rooted soil respiration calculated from linear and exponential regressions.

4.3.4 State of decomposition in root-free cores

To identify whether the observed trends related in any way to decomposition within the root-free cores, comparison of root and wood mass between extruded cores from each plot and from pristine areas outside of experimental plots was carried out. As the upper organic layer was intact in all samples both within and outside the plots, and the mineral layer content was highly variable (and in some cases absent), comparisons were carried out only on the upper organic layer.

Initial investigation of bulk soil properties showed that bulk density values were not significantly different between any plot or between plot and outside pristine areas (p= 0.12). C content was different however, and as shown in Figure 4.3.11, the greater content in the outside pristine plots was significantly different from control, drought and warming plots (p= 0.01, 0.049, 0.038 respectively). There were no significant differences between

plots. The moisture status of these soils also appears to be unaffected by then root-exclusion technique, as soil moisture at time of sample was not significantly different between plots or between plots and pristine areas (p= 0.96).

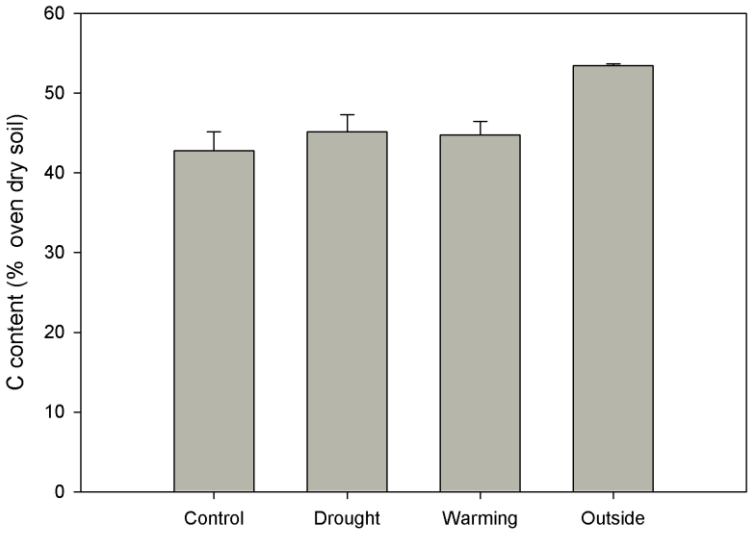


Figure 4.3.10 Carbon content (% air dry soil) of root-free plot cores and pristine area comparison sores. Bar values are means, ± SEM.

In terms of possible decomposition, on a mass-loss basis, comparison of root and wood mass (as a percentage of total dry soil mass) was made across the four sample sources (plots and outside pristine area). Figure 4.3.12 shows the root content, and although there appears to be differences between sample sources, none of the differences were significant. Dry wood mass (Figure 4.3.13) does however give significantly higher values for drought than warming and drought against the outside pristine areas (p= 0.019 and 0.009 respectively).

The ratio of wood mass : root mass allows for a combination of the two measured variables such that a higher wood : root mass ratio would indicate a greater proportion of dead biomass relative to live roots. Using this metric

(Figure 4.3.14), drought was significantly different from the outside pristine plots (p= 0.003) and the control plots (p= 0.038).

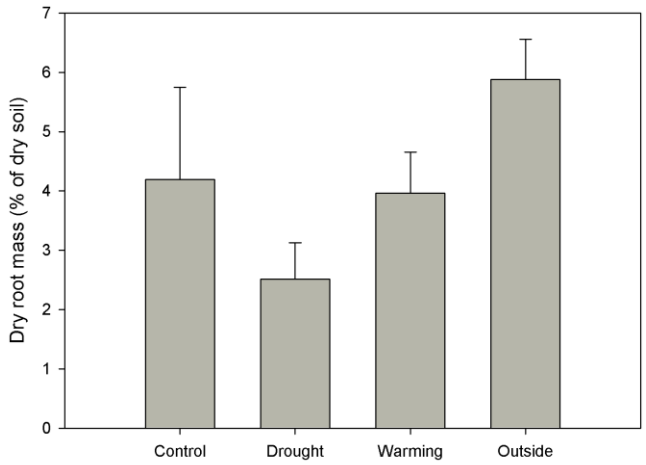


Figure 4.3.11 Dry root mass (% of oven dry soil) of root-free plot cores and outside pristine area cores. Bar values are means, ± SEM.

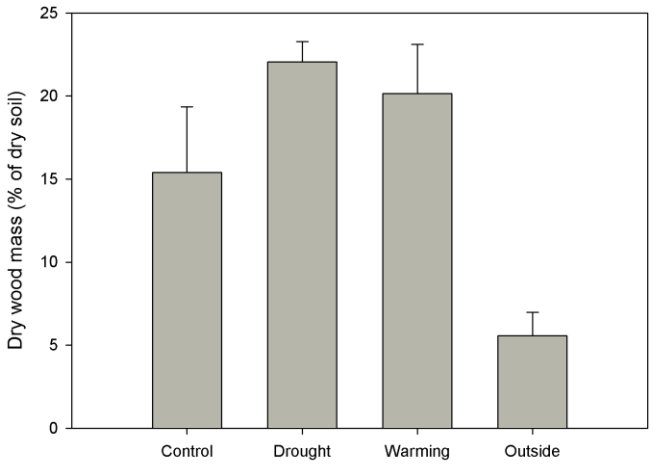


Figure 4.3.12 Dry wood mass (% of oven dry soil) of root-free plot cores and outside pristine area cores. Bar values are means, ± SEM.

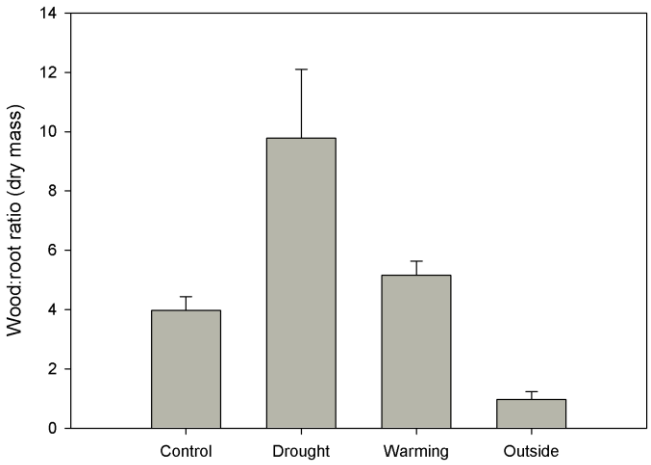


Figure 4.3.13 Dry wood : dry root ratio of root-free plot cores and outside pristine area cores. Bar values are means, ± SEM.

4.4 Discussion

The in-situ attempts to compartmentalise soil respiration at Climoor has produced some unexpected results. In a general sense, it would appear that the technique has failed to establish a true roots+SOM and a SOM only comparison, as there appears not to be a consistent lowering of root free respiration below that of intact. An initial response could be that SOM respiration may make up the vast majority of total respired CO_2, but given the consensus in the literature (where roots contribute between 12-93% of total respiration (Raich & Tufekciogul, 2000)) and the observation that root-free repeatedly gave higher rates than rooted, this response is almost definitely invalid. Even if the roots contributed only 12 % to the total respiration, based on the SOC pool (to 15cm depth) of ~14 kg C/ m^2, and the mean respiration efflux (1999-2010) of control plots being ~590 g C/ m^2/ yr, over 500g of SOC would be lost each year. Assuming a constant respiration rate and an input of 200 g C/ m^2/ yr to the SOC pool, the soil would have no residual SOC after 45 years. This is unlikely, and to even maintain SOC content under this scenario, roots must contribute ~50% to total respiration.

The observed flux rates of CO_2 show that the initial excision causes the root-free cores to be dominant in control, but not in drought and warming. This rapid decline in respiration rates under drought and warming versus the much slower decline in the control plots suggests that excision of roots has severed the major pathway of respiration under treatment plots, and in fact the ratio of root:SOM respiration might be higher in the treatment plots.

During the onset of winter months however, the root-free rate rises and falls sharply, and at a point is between 60-120% greater than rooted cores. Due to the time of year, it is probable that SOM respiration rates remain high relative to rooted, as the reasonably clement soil temperatures (between 6-8°C) and the likely abundance of nutrient (due to recent root excision) allow for continued SOM decomposition. As the soil temperatures will be common to both rooted and root-free, the role of fresh nutrients in the root-free cores could be a major explanation for the observed spike. Despite the possible

explanations given, this spike is only a transient phenomenon, and the return to lower fluxes is noted during the spring of 2009. The differential sensitivity of rooted and non-rooted cores to seasonal shifts in prevailing conditions could also explain these observations, and given the higher rates of root-free respiration during the winter period, it could be assumed that the rooted respiration is more sensitive to climatic variation than root-free. This was found in a study by Lavigne *et al* (2004) where the root-free respiration was less sensitive to water stress during spring and autumn than rooted respiration in a coniferous forest.

The rest of 2009 shows control root-free plots to continually respire more than the rooted plots, whereas the drought, and more so the warming plots, show a decline in the rate such that for the most part, warming plots actually see the rooted core contributing more than the root-free. This demonstrates two possible situations. Firstly, the treatment plots could initially be more dependent upon root-respiration, therefore seeing a more rapid decline in the relative rates after root exclusion. Secondly, the root-free respiration rate is assumed to be a measure of the basal SOM turnover, and if this is the case, the more rapid decline in root-free rates under treatment plots might point to a general reduction in the more labile components of SOM due to the continued drought and warming treatments applied to these plots. There appears little consensus on the prospect of greater root respiration under a warmer climate. Acclimation of respiration to increased temperature would suggest that the rate will, in the long term, not increase, but even decrease (Burton *et al.*, 2008). However, the acclimation to temperature often assumes there is little or no limitation by other variables, and it is clear that this is not the case at Climoor. In fact, moisture limitation has a greater overall impact on respiration than temperature, as seen by the ~20% increase in rates under the drought plots (chapter three and Sowerby *et al* (2008)). Despite this, it would appear (based on the soils removal exercise) that soil moisture was not affected by root excision treatment as there was no significant difference in soil moisture found (Section 4.3.4).

Temperature sensitivity of SOM decomposition has often been related to recalcitrance (Conant *et al.*, 2008, Plante *et al.*, 2010, Xu *et al.*, 2010), and in this respect, the second point made above could be supported if the sensitivity was much higher in root-free treatment plots than control. However, this was not the case, and although the rates were slightly higher in the treatment plots, this was true for both rooted and root-free, and indeed the difference between estimates using different regression equations was similar to the between-treatment difference. The similar temperature sensitivity between the rooted and root-free contrasts with that found in some studies showing higher rooted sensitivity (BhupinderpalSingh *et al.*, 2003, Boone, 1998, Hartley *et al.*, 2007) and higher SOM only sensitivity (Vicca *et al.*, 2010), but agrees with other studies which conclude a similarity in sensitivity (Jiang *et al.*, 2005)

The turnover of substrate input has been shown to be dominated by distinct microbial groups (Eilers *et al.*, 2010), such that bacteria tend to specialise in lower molecular weight substrate, and fungi the more complex material. Whether the presence or absence of roots has an impact here is intriguing, however, Paterson *et al* (2008) showed the presence of roots to have no effect on the rate or fate of substrate mineralisation. Assuming this relates to the soils studied here requires a relative absence of Low Molecular Weight (LMW) substrates under root-free, but due to the root excision, this might not be the case, and a leakage of LWW-substrate may well sustain the bacterial community for some time. The concept of a shift in community structure in response to changing substrate has been addressed (Eilers *et al.*, 2010, Griffiths *et al.*, 1999) finding that substrate loading can alter community structure, but also that the type of substrate addition can have subtle effects on diversity without having a direct impact on the amount of respired CO_2. Therefore the shift to more fungal dominance as the LMW sources subsides could occur in the root-free cores without altering the overall respiration rate. This was observed by Subke *et al* (2004) when girdling increased the fungal biomass in soil organic layers. As suggested by Subke *et al* (2004), this could mean not only a gross increase in fungal biomass, but also a shift towards more saprophytic fungi decomposing the excised woody root debris.

The effect of the exclusion approach on roots and decomposition processes was considered by the removal of a root-free core from each plot and comparison of the soil and root conditions. A reduction (relative to outside pristine cores) in total % C across all treatments suggests that the coring approach has led to a degree of decomposition. This difference was significant, and this can be assumed due to the decomposition of excised root material, and possibly also some primed decomposition of bulk SOM. The lower amount of roots (especially in the drought plots) relative to the pristine area, coupled with the higher amount of woody debris supports the turnover of fresh root material, and the accumulation of woody debris. The greater portion of woody debris will be a direct result of cutting, but also hints at the slow rate of decomposition of these woody materials.

The survival of roots in the root-free cores is a possible source of error. The principle assumption of this approach is that the excision would cause the senescence and subsequent decomposition of all excised roots, however if this were not the case, then it is entirely feasible that roots may continue to respire. As part of the soil investigation exercise, some of the roots which were included in the root-mass calculation were analysed for metabolic activity. This work was incomplete at the time of writing, but initial results suggest that at least in one case, a live root was found (Andy Smith, personal communication). The root in question belonged to *Vaccinium mrytilus*, which has also been known to sprout fresh green shoots from excised root material after storage of soil samples under refrigeration (authors own observation, and personal communication from Alwyn Sowerby, 2010). Given the life strategy of *Vaccinium mrytilus*, where vegetative propagation tends to be a common form of reproduction, it is likely that intact root material will contain considerable stores of energy sufficient to establish new photosynthetic biomass. In terms of the continuous respiration of these live roots (given all above-ground biomass was routinely clipped during the observation period) it may be that mycorrhizal associations could be maintaining the metabolic viability of the plant segment, or simply the energy stores are maintaining the activity. The contribution this may make to

the overall observed flux is unknown though, and even if every root within the excised core was still alive, it is doubtful this would cause the flux to remain as high as observed.

4.5 Conclusion

The technique to exclude roots used here follows from similar principles of physical, in-situ approaches used in forests. Although the soils analysis appears to show that roots have been successfully excised (at least in part) and have been turned over to a degree, there is such a large pool of highly recalcitrant woody debris left, that reaching a steady basal state is still far off. The respiration rates observed in the root-free were higher in control than the rooted, suggesting that the excision created a significant stimulation to the decomposer community which remained throughout the period of observation. This was less marked in the treatment soils, and given the slightly lower (yet not significant) mass of root material in the treatment soils, two possibilities are proposed. Either the treatment soils favoured a decomposer community that could rapidly mineralise fresh litter input, and as such saw a faster decline in root-free as root material was decomposed, or that the treatment soils were more dependent on root respiration initially, and excision had a greater net effect.

This study, although failing to achieve SOM-only respiration, highlights the role that fresh litter input might make to stimulating SOC turnover for notable lengths of time. Specifically, although C content had declined in the root-free soils, the mineralisation rate continued to be near, or above the rate of intact soils for the duration of the experiment. In the light of these findings, it is suggested that alternative approaches (e.g. isotope tracers, ^{14}C analysis of respired CO_2) be carried out in-situ to attempt estimation of the contribution of plant-dependent and plant-independent sources of soil respiration.

Chapter 5. Comparison of trace gas (CH_4 and N_2O) and CO_2 flux from two contrasting upland heathlands.

5.1 Introduction

Trace gases (N_2O, CH_4) and $CO_2$are heavily implicated in global climate change (IPCC, 2007), and the relative global warming potential of these three gases makes understanding their exchange with terrestrial systems a key research challenge. There is a considerable body of research focussing on the flux of CO_2 between soils and the atmosphere across a range of soil and ecosystem types, however, the remaining two gases tend to be more heavily researched in an agricultural context (Flessa *et al.*, 1998, Freney, 1995, Mosier *et al.*, 1991, Sanchez-Martin *et al.*, 2010). The large accumulation of C and N in natural and semi-natural organic soils means the potential for trace gas loss is potentially high, especially under disturbance or land use change (Regina *et al.*, 2004).

As the production of CH_4 and N_2O from soils is dominated by anaerobic processes (Bardgett, 2005) and the production of CO_2 by aerobic processes, the effect of driving variables on flux rates will vary considerably. Key environmental variables controlling flux rates include soil temperature (Holtan-Hartwig *et al.*, 2002, van Hulzen *et al.*, 1999, Yuste *et al.*, 2007), soil moisture (Orchard & Cook, 1983, Schaufler *et al.*, 2010), water table behaviour (Blodau *et al.*, 2004, Hughes *et al.*, 1999), climatic conditions (Ruehr *et al.*, 2010) and the interaction of these factors with the suite of soil physico-chemical conditions at a given site. Soil respiration (CO_2 flux) has been shown to be highly sensitive to soil temperature and soil moisture (Davidson *et al.*, 1998a), with a broad dependence on the amount and availability of mineralisable substrate (Grogan & Jonasson, 2005). Due to the complex range of decomposition pathways and respiration sources in then plant-soil system (i.e. microbial SOC decomposition, rhizosphere respiration, root respiration), controlling variables will exert differential control over these distinct components. Anaerobic processes involved in the production of CH_4 and N_2O also have been shown to respond to similar factors (Peterjohn *et al.*, 1994), however the relationships tends to be opposed to that of CO_2 due to the fundamental difference in metabolic pathways. The need for strict anaerobic conditions in the production

pathways of CH_4 and N_2O mean that wet soils are prime candidates for possible major efflux of these gases. However, most naturally wet soils will experience some degree of variability in water levels, and as such, there is also the potential for oxidative processes to take place (CO_2 production, methanotrophy).

Upland soils in the UK tend to be characterised by the accumulation of significant amounts of organic material either as peat, or as organo-mineral complexes. Excessive rainfall (>1500 mm) and generally mild temperatures (mean annual temperatures of 5-10 °C) coupled with low natural nutrient content reduce decomposition processes and lead to a soil with a high organic C and N content. These soils can become periodically saturated due to the high water holding capacity (WHC) of the soil and the high rainfall input. This dynamic environment which experiences periods of excessive soil moisture and periods of drier conditions will have potential to produce all three gases at varying degrees. The switch between aerobic and anaerobic conditions will mean the production and uptake, especially of CH_4 will be complex and variable. Due to the heterogeneity in structure of upland organic soils, even during relatively dry periods, there remains the potential for anaerobic processes due to the presence of microsites where anoxic conditions prevail. This spatial variability (both across site and vertically within the soil) creates a highly complex scenario for understanding the nature of trace gas flux.

Two research sites in the UK were included in this study (Figure 5.2.1). These sites are comparable in a broad sense in that they are both typical upland heathlands, but the subtle differences in vegetation type and soil conditions has a notable effect on the observed trace gas dynamics. The historic deposition of S and N is also markedly different between the two sites, and given the effect of sulphate on methane production, and the possible implications of excessive reactive-N deposition on denitrification, site comparisons on these grounds is also of interest.

This study therefore primarily aims to compare the temporal dynamics of trace gas flux from two contrasting heathlands in the UK. . The second aim was to determine the relationship between flux response and key environmental variables (e.g. soil temperature, moisture, groundwater change). The third aim was to put these finding in a broader context relating to C and N cycling at each site. It is hypothesised that both sites will demonstrate efflux of N_2O, CH_4 and CO_2, and that these fluxes will be modified by driving variables of soil moisture and soil temperature. As both sites are characterised by having upland organic soils, the high moisture content associated with upland conditions was predicted to cause a notable efflux of methane. Due to the similarity in ecosystem types, it was hypothesized that the flux rates would be highly comparable between the two sites.

5.2 Methods.

5.2.1 Site description

Climoor and Peaknaze field sites are located in two of the major upland areas of central Britain (Figure 5.2.1). The Climoor field site is an area of upland heathland dominated by *Calluna vulgaris* and *Vaccinium myrtilis* growing on a thin (< 20 cm) organic podzol soil overlying shale. This site is typical of many upland acid sites in the UK, where although the soil is reasonably well drained, SOM accumulation has led to a substantial WHC and a degree of periodic soil saturation. Peaknaze is a similar site, however the vegetation is dominated more by the sedge *Eriophorum vaginatum* and the soil is a deeper, but more mineral organic podzol. Summary characteristics for each site are shown in Tables 5.2.1, 5.2.2 and 5.2.3.

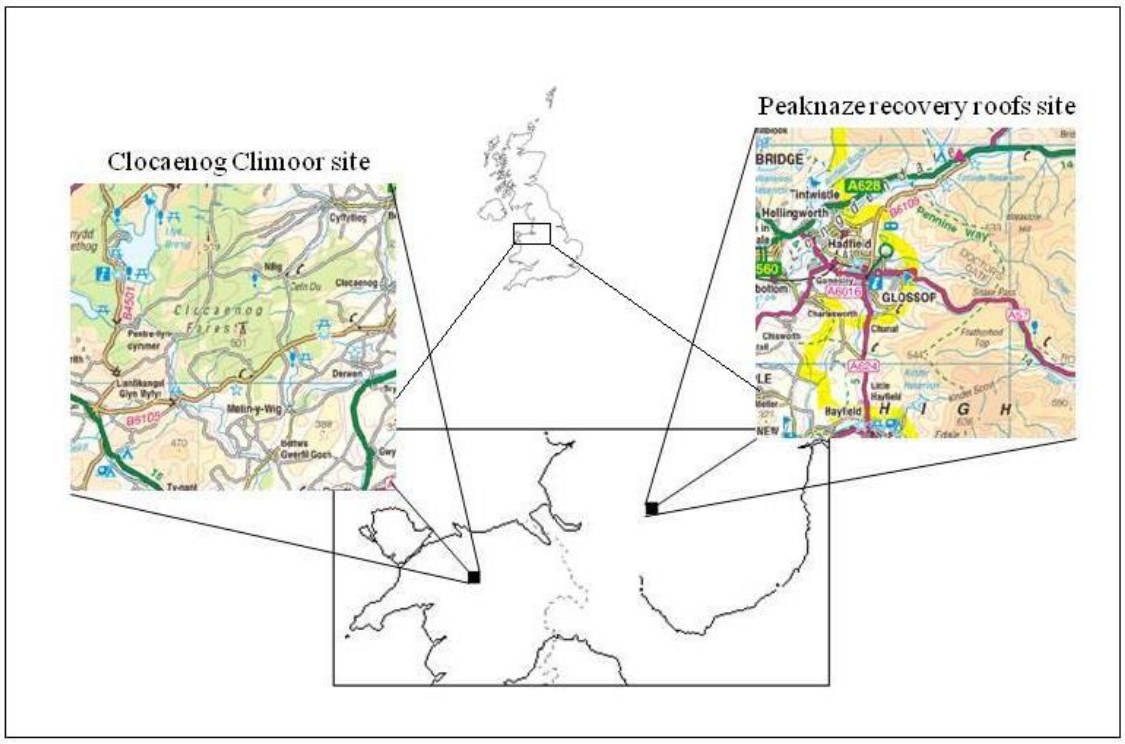


Figure 5.2.1 Relative location of the two field sites used in this study.

Table 5.2.1. Site characteristics for Climoor and Peaknaze. MAT and MAP indicate mean annual temperature and precipitation respectively. NVC indicates national vegetation class.

Site	MAT (°C)	MAP (mm)	Altitude (m ASL)	Parent material	NVC	Dominant vegetation
Climoor	6.7	1476	490	Shale	H12	*Calluna vulgaris*, *Vaccinium myrtilus*
Peaknaze	7.2	1685	433	Gritstone	M20b	*Eriophorum vaginatum*

Table 5.2.2. Selected soil characteristics of organic and mineral layers from the Climoor and Peaknaze experimental sites. LOI indicates loss-on-ignition.

Site	Horizon	Depth (cm)	LOI (% ADS)	pH	Bulk Density (g/cm^3)
Climoor	Organic	0-6	88.8	3.9	0.09
	Mineral	0-7	28.8	4.0	0.41
Peaknaze	Organic	0-7.6	34.4	4.1	0.19
	Mineral	7.6-21	1.6	4.2	1.44

Table 5.2.3. Wet deposition and soil water content of key reactive N and S species at the two experimental sites. Values are mean site values for wet deposition, and mean control plot values for soil water concentration.

Site	Year	*Wet deposition*			*Soil water concentration*		
		NO_3^-	NH_4^+	SO_4^-	NO_3^-	NH_4^+	SO_4^-
		kg/ha	*kg/ha*	*kg/ha*	*mg/l*	*mg/l*	*mg/l*
Climoor	2007	7.91	7.74	12.77	0.08	0.25	1.14
	2008	7.64	4.02	8.68	0.05	0.15	1.02
Peaknaze	2007	5.61	10.11	12.10	0.45	0.78	1.95
	2008	11.10	25.06	19.19	0.82	1.01	1.49

5.2.2 Experimental design

Both Climoor and Peaknaze employ the warming and drought roofs (Peaknaze also has other treatments not relevant for this study) which are outlined in Chapters 2 and 3. For the purposes of the inter-site comparison, only measurements made from the control plots were used. Three replicate plots from each site were used, and the plot means were obtained from three separate measurements made at fixed points within each plot. The plots are arranged in a randomised block design.

5.2.3 N_2O and CH_4 sampling

N_2O and CH_4 sampling was carried out fortnightly or monthly using the static chamber approach. Three chambers per plot were sealed using screw-fit lids and gas was allowed to accumulate for 30 minutes in the headspace. Gas samples were taken at time zero (ten seconds after lid closure), and then at two further time points of 15 minutes, and 30 minutes. Samples were taken using a 20 ml syringe and 23gauge hypodermic needle through a 17 mm silicone suba seal. An opposing needle was inserted at 90° to the sample needle to allow for pressure equilibration during sample withdrawal. Samples were immediately injected into re-evacuated glass sample vials before transport to CEH Bangor for analysis See appendix 1). Gas analysis was carried out using a Perkin Elmer Clarus 500 Gas Chromatograph (GC) equipped with a Porapaq QS (80-100 mesh) analytical column. Samples were analysed using a turbomatrix 40 headspace auto-analyser. N_2O was detected using ECD (at 400°C, sample oven at 40°C), CH_4 was detected using FID (at 375°C, sample oven at 40°C) equipped with a methaniser. Carrier gas pressure was 0.14 MPa, and injection pressure 0.16 MPa. All other analytical conditions were as specified in the Perkin Elmer standard setup. Calibration of the GC involved three calibration gas concentrations for each target gas (Cryoservice, UK) and calibration was accepted at $r^2 > 0.99$. Raw ppm output was then converted to mass/area flux expressions following standard formulae.

5.2.4 CO_2 sampling

Soil respiration was measured using portable Infrared Gas Analyers, namely the PP-Systems EGM-4 and the Li-COR 8100 systems. Both systems used a 60 second enclosure time and samples were carried out on soils with collars inserted into the ground. These two systems have been statistically shown to yield comparable results (Mills *et al.*, in press) when measuring fluxes in the field under similar methodology.

5.2.5 Temperature and moisture sampling

Soil temperature was measured at the time of gas sampling using a standard digital temperature probe inserted to 5cm below the surface. In the case of IRGA sampling, the temperature probe attached to the IRGA was used. Soil moisture was also measured at the time of gas sampling using a Theta probe (Model ML-2, Delta-T Services, UK). Both measurements were made in an area of soil outside the soil respiration and trace gas sampling areas.

5.2.6 Water table

At both sites, dip-wells constructed from 35 mm internal diameter PVC slotted pipe were placed in holes dug using a Dutch auger adjacent to each plot. The dip-wells were dug to be as close to the underlying parent material as possible. Water levels were measured using a steel tape and measuring to the observable water level in the centre of the well. In the absence of a visible water level, the depth was recorded as greater than the full length of the well.

5.2.7 Data analysis

Linear and non-linear regressions were applied to the data using Sigmaplot version 10 (Systat, 2009) after visual assessment of pair-wise plots. Multiple regression was carried out to assess for interaction of soil temperature and soil moisture. Between-site comparisons were carried out using T-tests. All statistical analysis was carried out using R statistics (R, 2010).

5. 3 Results

5.3.1 N_2O and CH_4 fluxes

Mean flux rates for N_2O and CH_4 for both sites are shown in Figure 5.3.1. N_2O flux means were comparable between sites, and when compared statistically (t-test) the difference proved not to be significant (p=0.53). CH_4 on the other hand was around three times greater at Climoor than Peaknaze, and despite the high variability throughout the year associated with the flux of CH_4 (Figure 5.3.4) the between-sites difference proved statistically significant (p=0.028).

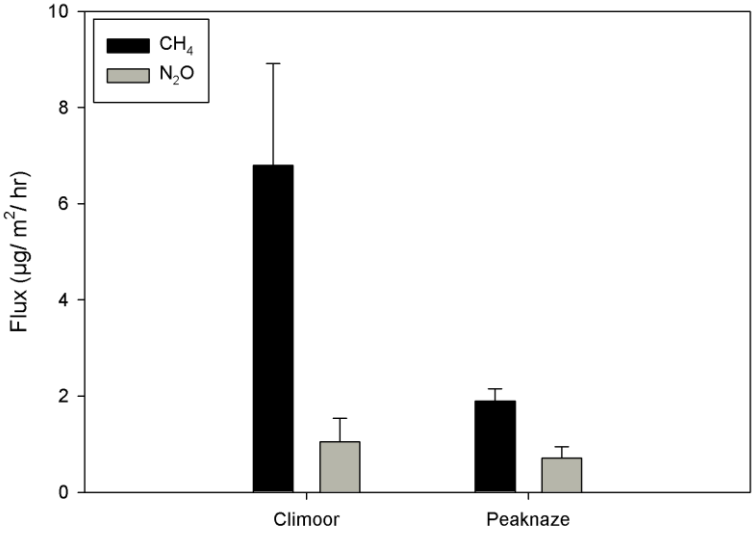


Figure 5.3.1 Mean gas fluxes for CH_4 and N_2O at the Climoor and Peaknaze experimental sites for the 12-month period Jul 2007 – August 2008. Fluxes are in µg N_2O-N/ m^2/ hr and µgCH_4/ m^2/ hr. Values represent means ± SEM.

Fluxes for both N_2O and CH_4 are shown for Climoor in Figure 5.3.2, and for Peaknaze in Figure 5.3.3. Overall, N_2O fluxes at Climoor appeared to follow no particular seasonal trend, however, the general pattern of low (both production and uptake) rates is punctuated by occasional notable bursts.

There also appeared to be a considerable degree of spatial variation on some sampling dates. Generally though, throughout the course of the year, Climoor is a net source of N_2O (1.05 µg N_2O-N/ m^2/ hr mean flux rate). CH_4 however appears to show some degree of seasonality to the flux dynamic, with flux increasing towards winter (peak flux during December). The flux rates during non-winter show a high degree of variability, with periods of large uptake being cyclical with periods of high efflux. Climoor is, despite notable periods of uptake, a net source of CH_4 (6.8 µgCH_4/ m^2/ hr mean flux rate).

Peaknaze net N_2O fluxes were of a similar order of magnitude to Climoor, but appeared to show a high variability around autumn and winter, with periods of high efflux and some consumption, but then much more circum-zero net flux rates during spring and early summer. Spatial variability appeared to be fairly constant throughout the course of the year apart from a couple of sample time points. As with Climoor, Peaknaze was also a small net producer of N_2O (0.7 µgN_2O-N/ m^2/ hr mean flux rate). The CH_4 dynamic was highly variable at Peaknaze, and didn't appear to show any discernable seasonal pattern. There were, however, some cyclical periods of high-low-high efflux during summer 2008 which are not repeated earlier in the data course. Fluxes were also much lower at Peaknaze, with peak flux rates around 20% of the peak flux at Climoor. However, Peaknaze remains a net source of CH_4 (1.9 µgCH_4/ m^2/ hr mean flux rate).

The seasonal dynamics of CH_4 (in terms of mean monthly flux rates) is shown in Figure 5.3.4, and demonstrates the difference not only in the magnitude of the flux, but also the difference in cyclical nature. Both sites, when averaged to a monthly flux, appear to show some degree of peak and trough behaviour, however, the steepness of the rise and fall is much greater at Climoor. The same cannot be said for N_2O though, and Figure 5.3.5 reinforces the message in Figures 5.3.2 and 5.3.3 that the flux dynamics of N_2O appear to be without a particular pattern or trend.

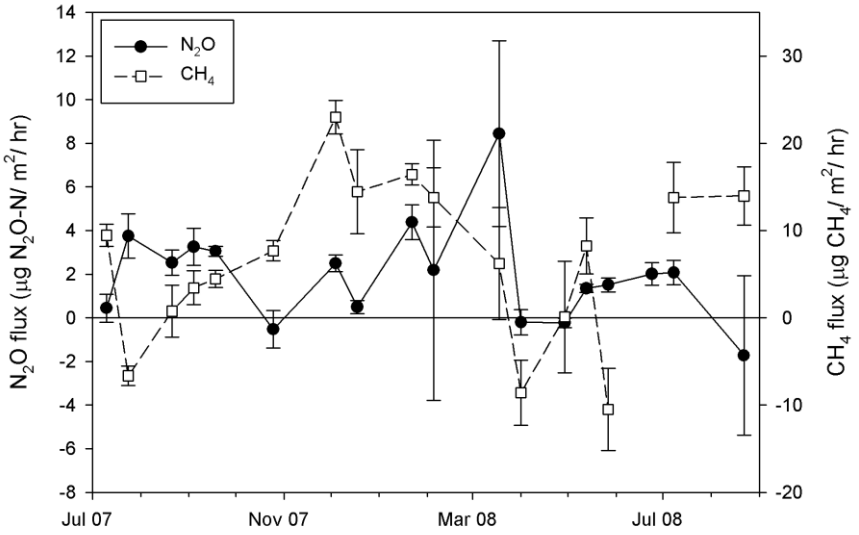


Figure 5.3.2 N_2O and CH_4 flux from Climoor control plots. Error bars are standard error of the mean.

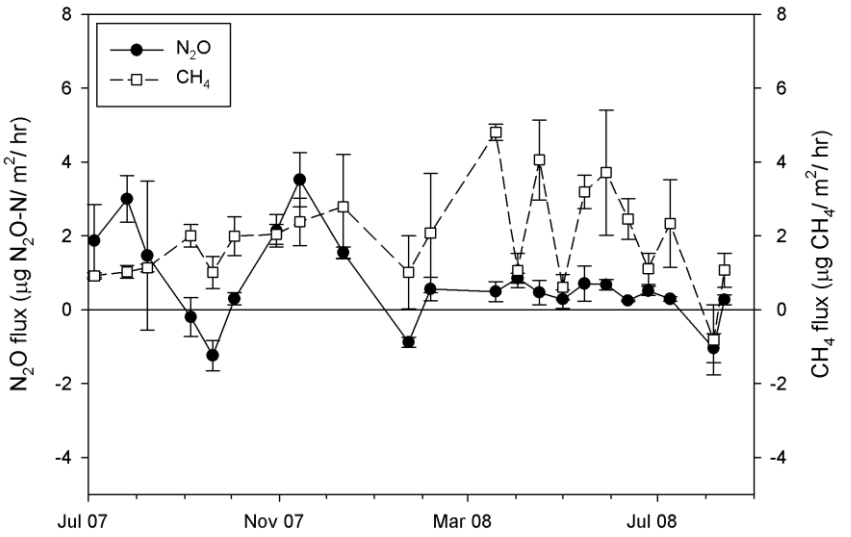


Figure 5.3.3 N_2O and CH_4 flux from the Peaknaze control plots. Error bars are ±SEM.

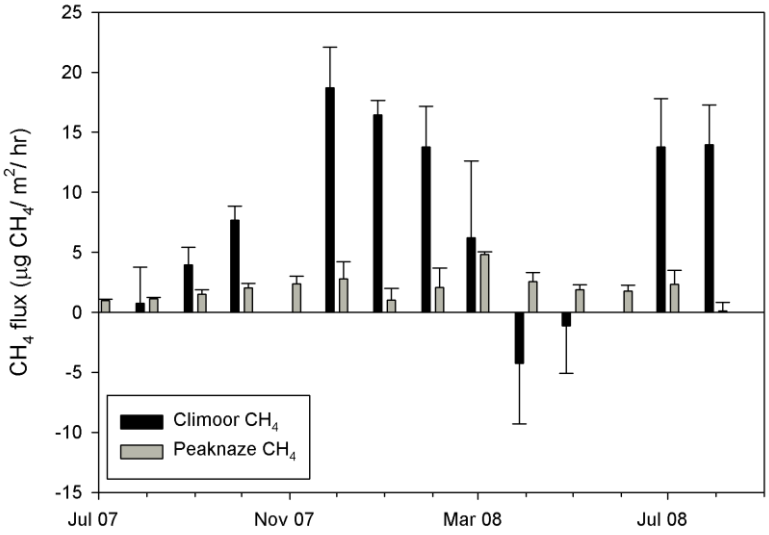


Figure 5.3.4 Mean monthly flux rates for CH_4 at both the Peaknaze and Climoor experimental sites. Values represent means ± SEM.

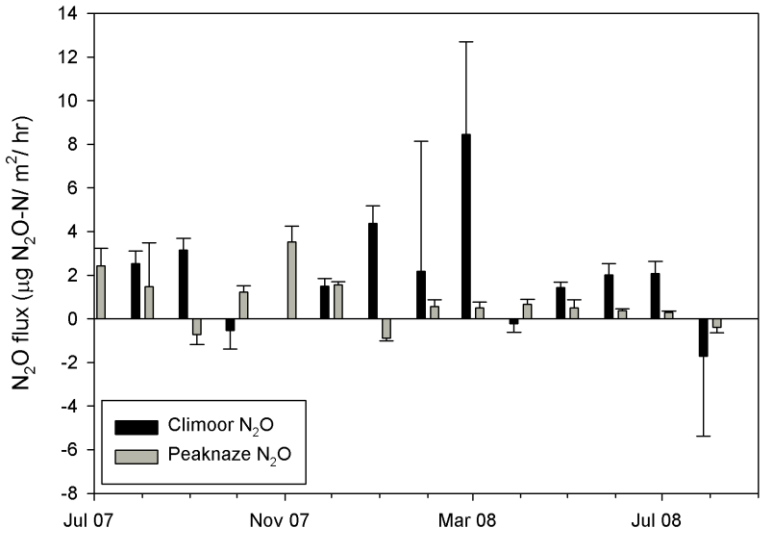
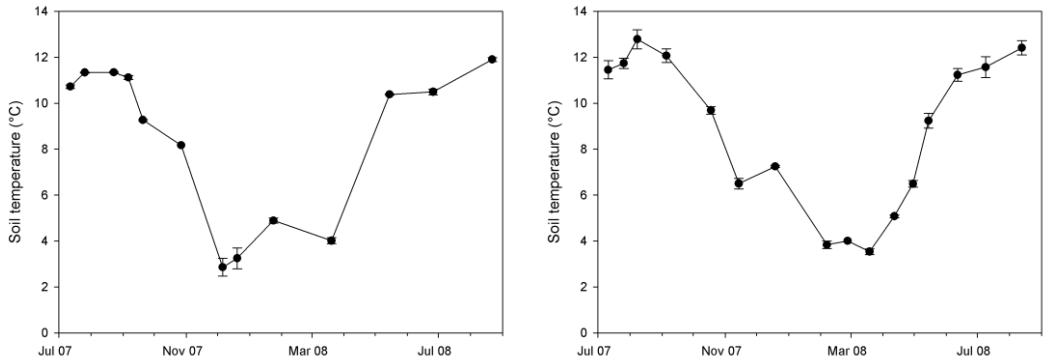


Figure 5.3.5 Mean monthly flux rates for N_2O at both the Peaknaze and Climoor experimental sites. Values represent means ± SEM.

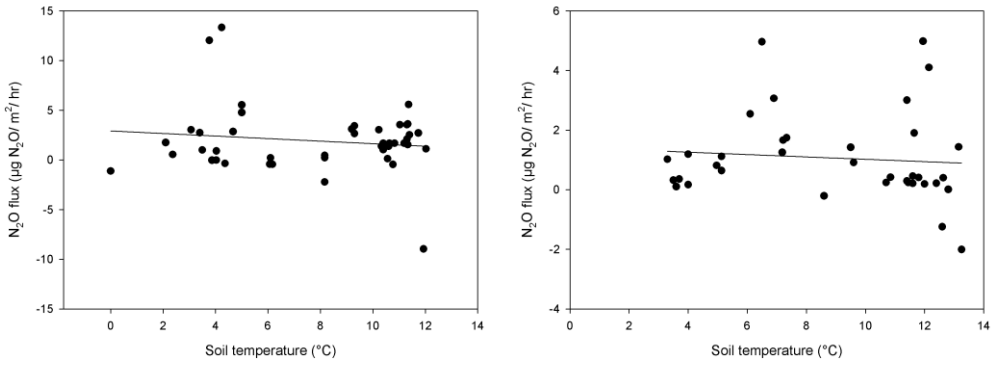
5.3.2 Sensitivity of N_2O and CH_4 fluxes to soil moisture and temperature

The seasonal profile of soil temperature was similar between both sites (Figure 5.3.6(a)). The yearly maximum temperature occurred during late summer (August) at both sites, however the lowest soil temperatures appeared somewhat later at Peaknaze than at Climoor, but the values are comparable. N_2O showed some marginal sensitivity to temperature, slightly more noticeable at Climoor, but the linear regressions suggested the relationship was weak (Table 5.3.1). CH_4 shows a strong sensitivity to temperature, with a reasonable linear relationship giving a much-reduced flux (actually observing CH_4 uptake in the case of Climoor) at higher temperatures. CH_4 therefore appears to be more temperature sensitive than N_2O at both sites.

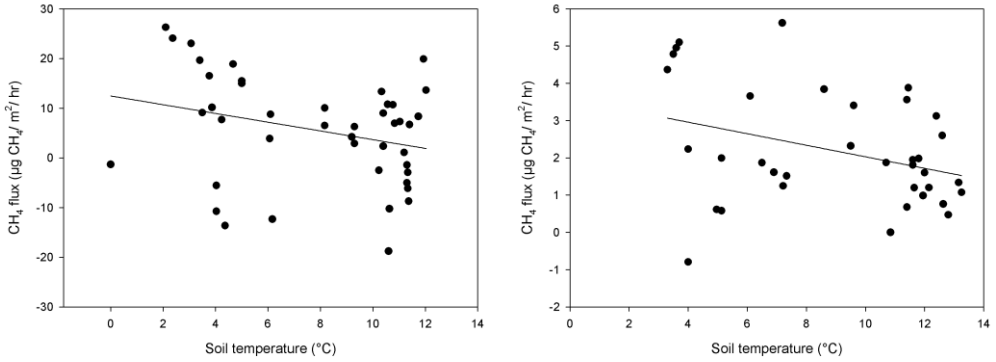
The temporal dynamics of soil moisture were quite different between sites. Although experiencing the greatest range (~0.5-~0.35 m^3/m^3) in soil moisture, Climoor showed only slight seasonal variation in soil moisture, apart from a modest decline during July 2008 to a summer low point. Other than the early summer low, soil moisture remained relatively stable for the remainder of the year. Peaknaze had much less variation throughout the year, with ~0.1 m^3/m^3 range in the data. There are, however, notable peaks and troughs in moisture content, but these are completely detached from the expected seasonality and do not show the expected summer-low, winter-high. In terms of sensitivity of N_2O and CH_4 to variation in moisture content, there appeared to be no significant relationships emerging for either gas from either site. This is shown in Figure 5.3.7 while the regression outputs are shown in Table 5.3.1.



(a)

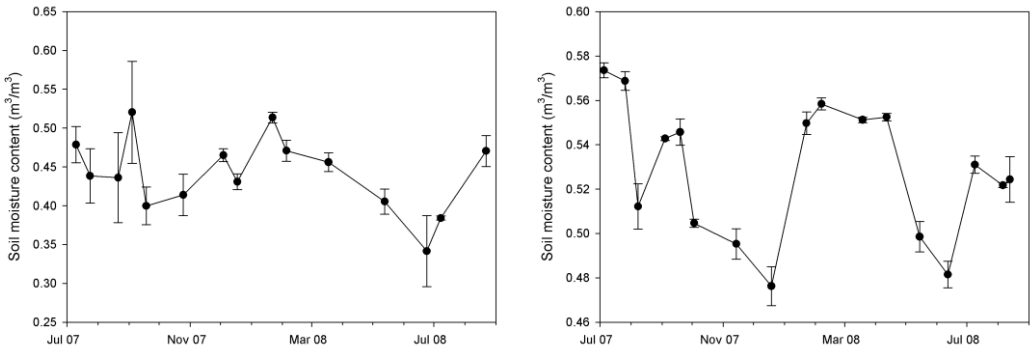


(b)

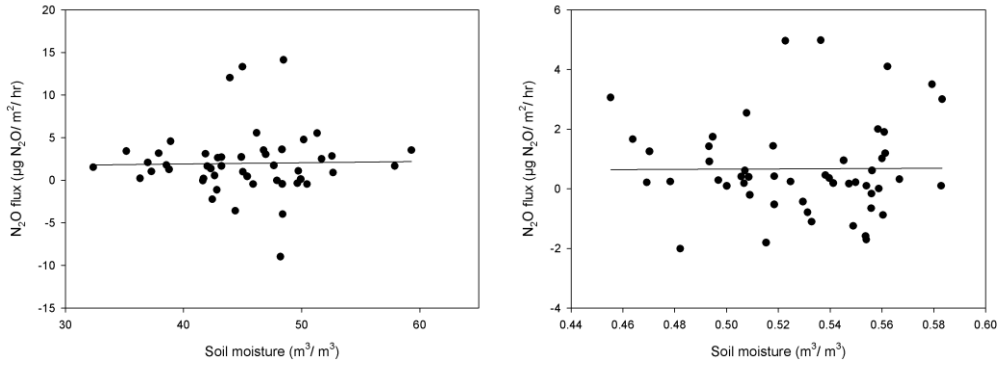


(c)

Figure 5.3.6. Soil temperature (a) at Climoor (left) and Peaknaze (right). Relationship between soil temperature and N_2O (b) and CH_4 (c) at Climoor (left) and Peaknaze (right). Linear regression output for panels (b) and (c) is shown in Table 5.3.1.



(a)



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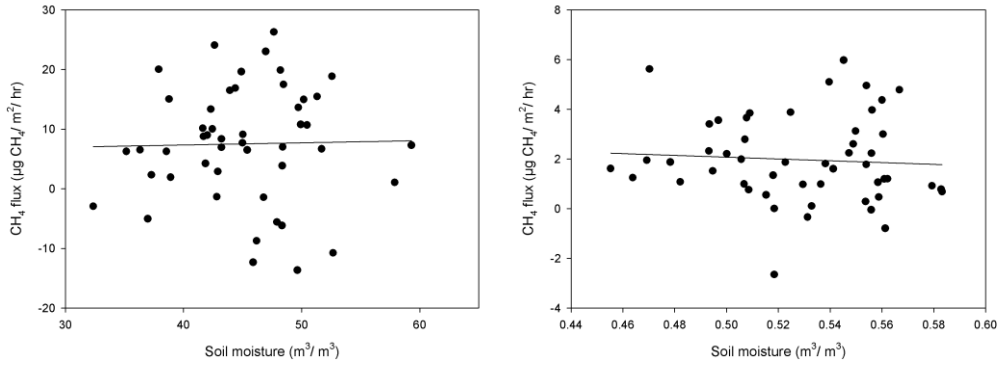


(c)

Figure 5.3.7 Soil moisture (a) at Climoor (left) and Peaknaze (right). Relationship between soil moisture and N_2O (b) and CH_4 (c) at Climoor (left) and Peaknaze (right). Linear regression output for (b) and (c) is shown in Table 5.3.1

Table 5.3.1 Linear regression output for temperature and moisture as variables in CH_4 and N_2O flux rates.

Site	Driver	Gas	p	r^2
Climoor	Temperature	N_2O	0.38	0.018
Climoor	Temperature	CH_4	0.058	0.08
Peaknaze	Temperature	N_2O	0.59	0.008
Peaknaze	Temperature	CH_4	0.04	0.12
Climoor	Moisture	N_2O	0.88	<0.001
Climoor	Moisture	CH_4	0.86	<0.001
Peaknaze	Moisture	N_2O	0.95	<0.001
Peaknaze	Moisture	CH_4	0.63	0.004

5.3.3 N_2O and CH_4 flux in response to water table depth

Changes in water table depth at Peaknaze are shown in Figure 5.3.8. Climoor water table was not active throughout the period of observation, and so was not included in this analysis. Water table depth appeared to be highly variable throughout the year, with the level entering the near-surface layers of soil on a number of occasions. There was a large amount of spatial variation between the individual control plots, and this variability remained reasonably consistent through the year. There is some evidence of seasonality in the data, with the near-surface episodes tending to occur around winter, with episodes of high variability occurring during summer months.

N_2O and CH_4 fluxes showed no significant relationship to water table height (Figure 5.3.9). Indeed, the full range of CH_4 fluxes observed in the data set could be found when water table was greater than 30 cm below the surface.

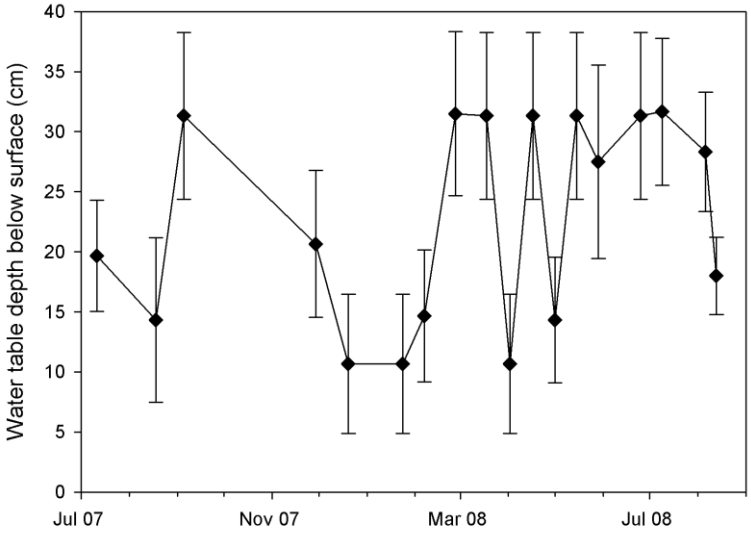


Figure 5.3.8 Mean water table depth below surface (cm) at the Peaknaze experimental site. Error bars ± SEM.

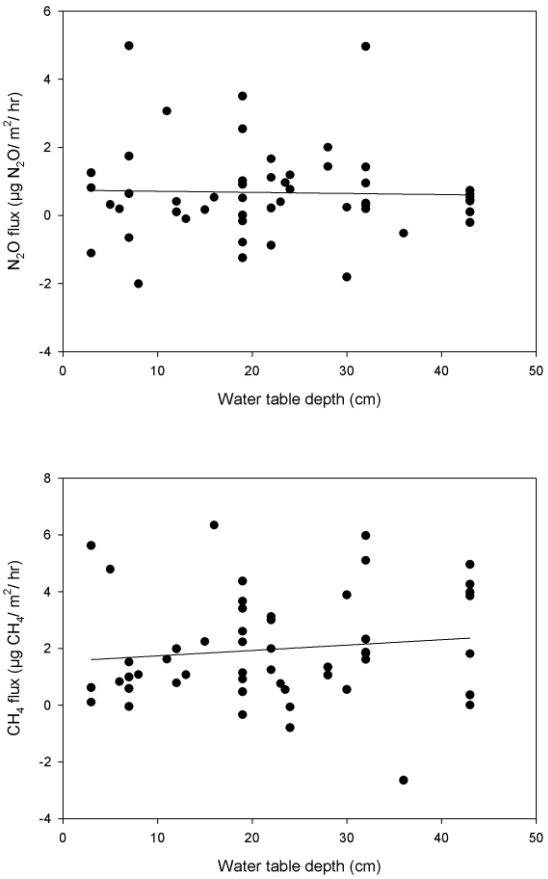
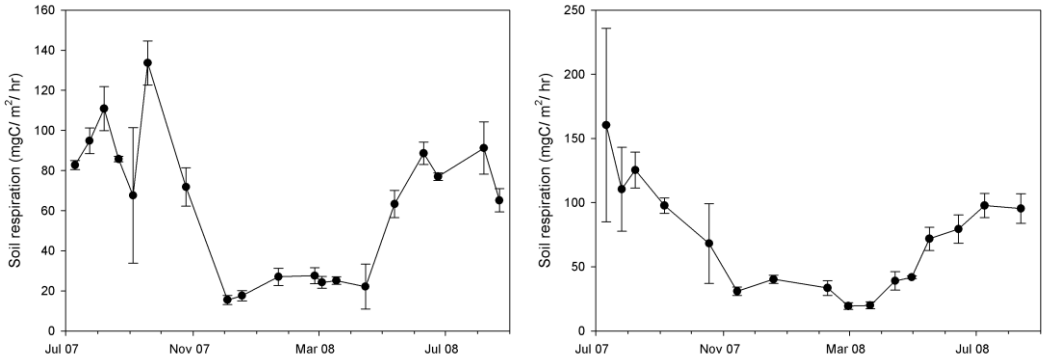


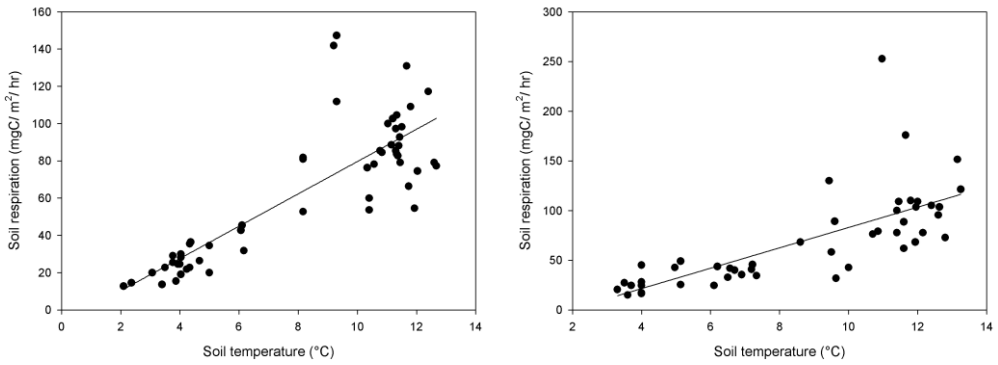
Figure 5.3.9 Relationship between flux of N_2O (top) and CH_4 (bottom) and water table depth below surface at the Peaknaze experimental site.

5.3.4 Soil respiration (CO_2 flux)

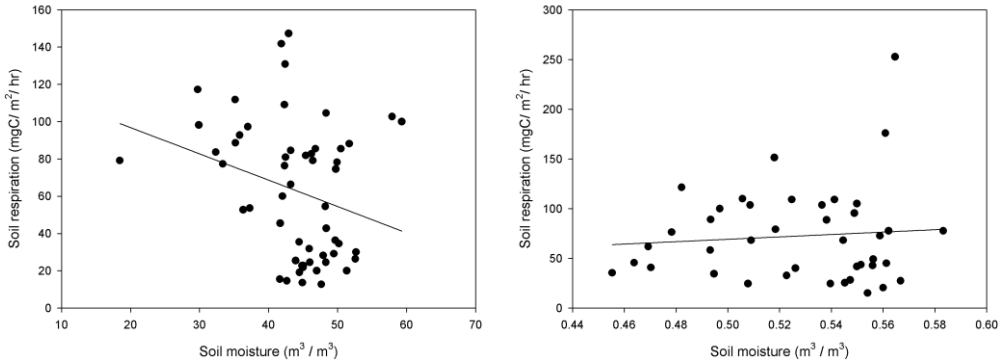
Soil respiration at Climoor followed a strong seasonal trend with peak flux rates (up to 140 mg C/m^2/hr) occurring during the late summer into the autumn, and a dramatic fall apparent during early winter to a baseline rate ~20 mg C/m^2/hr during the winter months (Figure 5.3.10). A rapid rise in CO_2 efflux occurred during spring was also noted during April and May 2008. Peaknaze, although having a greater overall peak and slightly higher basal respiration rate, shows less seasonal variation (Figure 5.3.10). The rise and fall between the seasons is much more moderate than the sudden drop and increase observed at Climoor. At both sites, soil respiration rate exhibited a high degree of temperature dependence, but Q_{10} values (Table 5.3.3) suggest Peaknaze to be more influenced than Climoor. Sensitivity to moisture was evident at Climoor, with a notable decline in rates coinciding with increasing moisture levels. No such connection was demonstrated at Peaknaze



(a)



(b)



(c)

Figure 5.3.10 Soil respiration flux (a) at Climoor (left) and Peaknaze (right) and graphs of soil temperature (b) and soil moisture (c) response of soil respiration at Climoor (left) and Peaknaze (right). Values in the upper panels represent means ± SEM.

Table 5.3.2 Linear regression output for soil respiration responses to temperature and moisture at the two experimental sites.

Site	Driver	Gas	p	r^2
Climoor	Temperature	CO_2	<0.001	0.69
Climoor	Moisture	CO_2	0.04	0.07
Peaknaze	Temperature	CO_2	<0.001	0.52
Peaknaze	Moisture	CO_2	0.58	0.007

Table 5.3.3 Linear regression parameters and calculated Q10 values for soil respiration sensitivity to temperature at the two experimental sites.

Site	y0	a	Q_{10}
Peaknaze	-23.4815	10.8562	4.52
Climoor	-6.9377	8.3974	3.39

5.3.5 CH_4 and CO_2 temperature comparison

The opposing temperature sensitivity of CH_4 and CO_2 flux is shown for Climoor (Figure 5.3.11) and for Peaknaze (Figure 5.3.12). Clearly the two processes respond strongly to temperature (linear regressions are shown in Table 5.3.4) and the dominance of one C-flux pathway over the other depends much on the temperature conditions of the time of sampling. The two sites appear comparable in terms of this relationship, however the flux rates are different at each site, and might go some way to explaining the dominant source of C efflux. Given the lack of significant soil moisture effect on either process, it is likely that temperature is the main factor in describing the C efflux pathway under the two soil types.

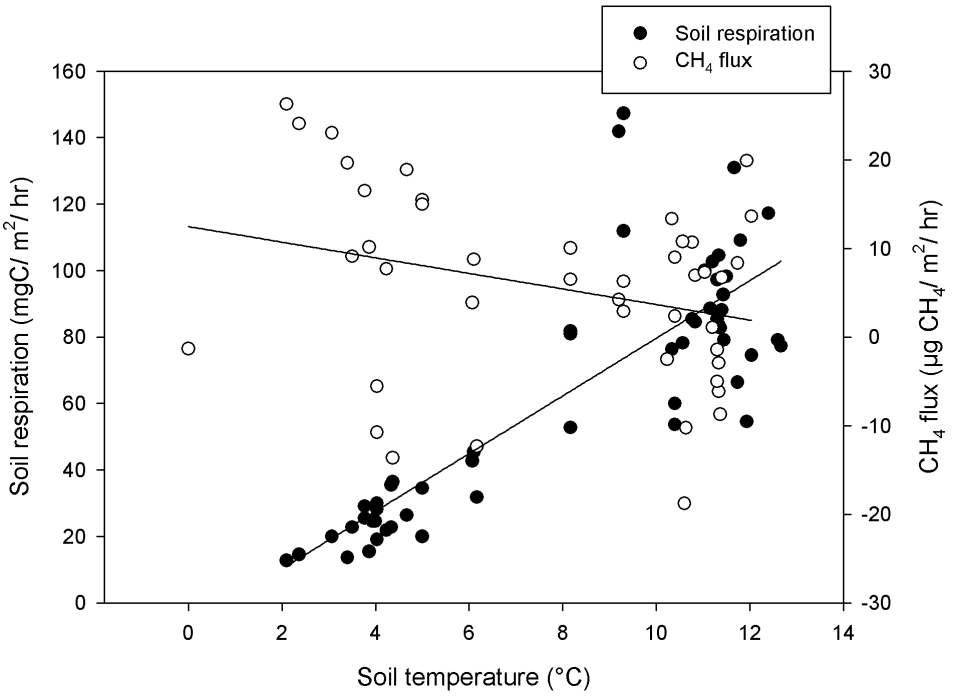


Figure 5.3.11 Relationship between soil respiration or methane flux and temperature at Climoor.

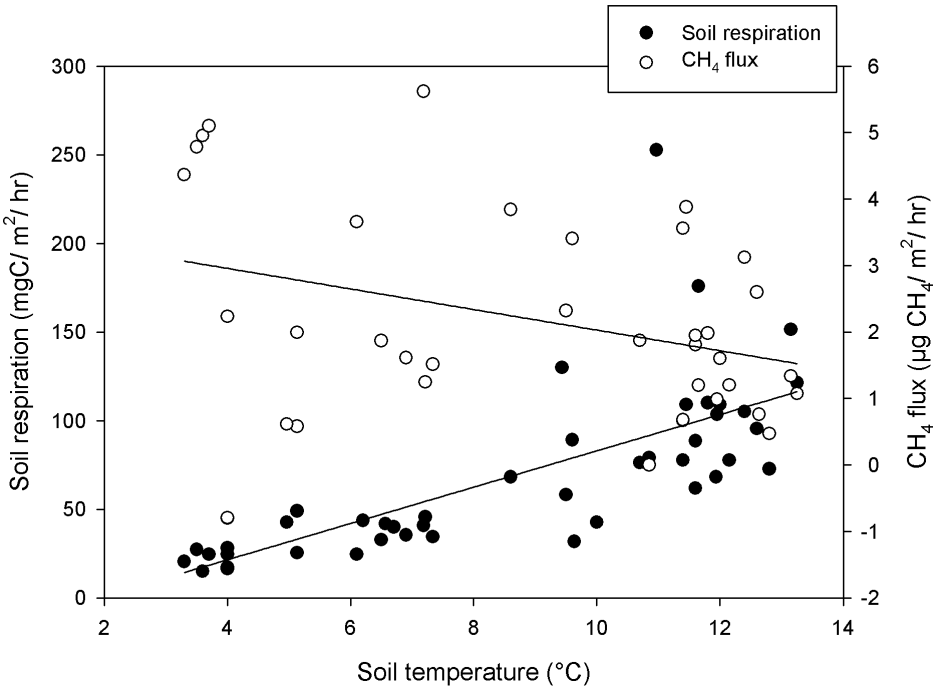


Figure 5.3.12 Relationship between soil respiration or methane flux and temperature at Peaknaze.

Table 5.3.4 Linear regression output for the relationships presented in Figures 5.3.11 and 5.3.12.

Site	**Gas**	**p**	**r^2**
Climoor	CO_2	<0.001	0.69
Climoor	CH_4	0.042	0.11
Peaknaze	CO_2	<0.001	0.52
Peaknaze	CH_4	0.058	0.08

5.4 Discussion

5.4.1 N_2O

Both sites exhibited N_2O production, albeit a very low rate. Rates observed in this study were comparable to other published studies investigating sites of similar vegetation and soils (e.g. 0.31-0.44 µg N_2O-N/ m^2/ hr (Dinsmore *et al.*, 2009), 2.6-3.2 µg N_2O-N/ m^2/ hr (Lohila *et al.*, 2010)). However, there are also larger estimated N_2O flux rates reported in the literature from similar soil types (e.g. ~20 µg N_2O-N/ m^2/ hr (Silvna et al, 2005), ~14.3 µg N_2O-N/ m^2/ hr (Koponen et al, 2006)). Overall, the flux rates were highly comparable between both experimental sites, and given the notably low net rates of production, it would appear that denitrification to N_2O may be inhibited in some way. Assuming denitrification would be the dominant source of N_2O, both sites would present favourable abiotic conditions; a reasonably consistent high soil moisture content (any by proxy, a low oxygen availability), high SOC content and a slightly acid soil pH. Loss of N via N_2 is, although the metabolic end-product in denitrification, likely to be somewhat retarded due to the low pH (Koskinen & Keeney, 1982), high C content and low temperature (Knowles, 1982). These factors were seen to increase the ratio of N_2O:N_2 produced during denitrification, so although there will invariably be some unknown amount of N_2 being lost from the process, it is sensible to assume N_2O flux is a sound measure of the rate of gaseous denitrification in general.

The low N_2O flux rate observed here would suggest then that substrate quality or availability might be limiting the denitrification rate. Although both soils have large amounts of accumulated SOM, most of the organic N contained therein will be only slowly mineralised (Pilkington *et al.*, 2005), mainly due to the highly stabilised nature of the accumulated SOM (e.g. through the formation of protein-polyphenol complexes). N-mineralised from fresher input of organic residue is likely to be rapidly taken up by plants or microbes due to the low available pool of mineral-N (Lohila *et al.*, 2010).

Both of these conditions will operate then to make the pool of potentially-denitrifiable N quite low. N_2O production in organic soils was shown by Curtis et al (Curtis *et al.*, 2006) to respond to addition of NH_4NO_3additions under controlled laboratory conditions whilst ambient fluxes remained comparably low to those observed in the current study. In addition to general N availability, the C:N ratio of the dominant substrates entering both soils (i.e. through shoot litter, root turnover, ericoid hyphal turnover) will be quite high favouring N limitation. N_2O production was shown by Nishina et al. (2009) to be negatively correlated with C:N ratio, supporting the need for more labile substrate to support denitrification of NO_3^- to N_2O. Given this situation, it is sensible to assume most inorganic N will be used during decomposition processes therefore leading to net immobilisation of N.

C-substrate availability may also be limiting the denitrification capacity of the microbial community, as the majority of more labile C is likely to be mineralised in the upper soil layers, leaving the more chemically and physically recalcitrant SOC to accumulate at depth (where we speculate that the N_2O production is potentially greatest due to the greater likelihood of water logging and anoxia). The amount of readily decomposable C was strongly correlated (r^2 = 0.99) with denitrification in a study on a range of soils by Burford and Bremner (1975) under laboratory conditions of nitrate excess. Also, In a substrate addition experiment, Murray et al. (2004) found N_2O production in a brown earth soil to be stimulated above control levels by glucose more so than starch, but inhibited relative to control by cellulose. In the field situation, if the lower quality substrate coincides with the vertical position of favourable denitrification, it is likely that low C-availability will influence the N_2O production rate. This was supported by an incubation study by Curtis et al (2006) where reduced fluxes at depth (despite the provision of favourable conditions) were deemed a consequence of a much lower availability of substrate-C.

There appears to be no seasonal variation in the flux dynamics of N_2O at either site. At first, this is surprising given the probable seasonal change in mineral-N demand (less demand during winter due to recued plant activity)

and the likely higher moisture excess during winter (although soil moisture itself doesn't vary markedly, especially on the expected seasonality). Given the points made previously about low substrate availability though, it seems unlikely that any major change to the prevailing conditions would in fact result in a modification to the denitrification potential, especially given that competition for dissolved organic N (DON) and inorganic-N within the microbial community will continue throughout the year. The leaching potential of inorganic-N is also high (Perakis & Hedin, 2002), and during the generally wetter periods around winter, it would be reasonable to assume the leaching of N would be an even greater cause of N-export than during the summer.

Temperature provided no strong explanatory power over N_2O flux at Peaknaze, and only slight control at Climoor (Figure 5.3.6 and Table 5.3.1) and whilst previous incubation studies have reported an increasing flux rate with temperature, this was not observed here in situ. Again, we speculate that this N_2O production is severely constrained by the low amount of available N. Temperature has often been shown to increase rates of N_2O production (Curtis *et al.*, 2006, Czóbel *et al.*, 2010, Dinsmore *et al.*, 2009). This relationship, however, has been observed to be variable between years (Lohila *et al.*, 2010) and it is probable that some of this variation could be explained by interaction with other driving variables such as water table behaviour.

Soil moisture also failed to help explain the temporal dynamics of N_2O fluxes. In terms of absolutes, denitrification will be heavily dependent upon saturation of soil causing reduced O_2 content (Bollmann & Conrad, 1998) and it is sensible to assume (as previously mentioned) that this will be the case for at least a portion of the soil. However, given the low variability in soil moisture content across the sampling period, it is unlikely that a denitrification optimum soil moisture (likely to be around field capacity) will be reached. Even so, it remains that despite any fluctuations in soil moisture and the impacts on O_2 content, the substrate limitation factors previously mentioned will continue to act as the dominant controller of flux rates. Moisture appears to have a variable control over N_2O emission in the

literature, with no explanatory power being suggested by Nishina et al (2009) (moisture content and water filled pore space correlation with N_2O flux -0.13 and 0.18 respectively). A strong positive relationship between moisture content and N_2O flux was found by Weslien et al. (2009) and Schaufler et al. (2010) but Bollman and Conrad (1998) suggest this moisture effect may only exist over a threshold moisture content (between 65-80% of WHC).

5.4.2 CH_4

The net flux of methane revealed some marked differences between the two sites, with Climoor having a much higher and more seasonal flux dynamic compared to the lower and fairly continuous flux rates observed at Peaknaze. A greater flux rate, especially in the winter, would imply there is soil moisture excess coupled with suitable substrate supply for methane production, and this is likely to be the case at Climoor. This is mainly due to the much larger amount of above-ground biomass depositing fresh litter, and the observation of a significant accumulation of partially decomposed, but recognisable, leaf and shoot litter at Climoor. Although soil moisture tends not to vary largely, the moisture measurement is made at 5 cm depth, and this may be insensitive to the seasonal fluctuations which occur at the soil surface where the majority of reasonably fresh litter input will be found. Given that carbohydrate decomposition under anaerobic conditions will often lead to acetate production (Le Mer & Roger, 2001), it is reasonable to assume that fresh litter input to wet surface soils at Climoor will undergo some degree of decomposition to acetate which may then lead to enhanced methanogenesis. Methane production in organic soils has been shown to be related to the particle size of the organic material, with the larger (> 2 mm) particles having the greatest overall flux (van den Pol-van Dasselaar & Oenema, 1999). Incidentally, in the same study, the larger particle size material also had the highest C:N ratio, and surface fluxes had some correlation to the C:N ratio of the various particle size fractions. In relation to the sites studied here, the larger amount of fresher organic material typically found at Climoor may link between CH_4 production and particle size. There

will still be an appreciable accumulation of litter and of peat material in the near surface layers at Peaknaze, and given this it would be expected that methane production would be high. However, it is possible that vegetation plays a role here. Despite the assertion of *Eriophorum* species being commonly associated with increased CH4 production due to the chimney effect (Greenup *et al.*, 2000), Eriophorum vaginatum is a major component of the vegetation at Peaknaze. An alternative may exist such that the abundance of *Eriophorum* sp. (with associated arenchyma tissue) may cause a notable degree of rhizosphere oxidation, potentially stimulating the methanotroph community to oxidise CH_4.Also, the more mineral soil at Peaknaze may facilitate a more oxic soil environment which obviously encourages the proliferation of aerobic methanotrophs.

The impact of historic acid deposition, and the relative levels of current deposition, could impact upon methane production. Sulphate deposition has been shown to suppress rates of methane production by around 30 % (Gauci *et al.*, 2005), and given the difference in historic sulphate loading between the two sites, it is reasonable to assume some of the methane suppression at Peaknaze could be due to excessive residual sulphate in soils. A similar situation and conclusion was reached by Watson and Nedwell (1998) when comparing the higher sulphate-loaded Great Dun Fell site with the lesser impacted Ellergower site, the former having a much reduced methane production rate.

Temperature sensitivity of methane flux rate is notable at both sites, with production tending to favour a lower soil temperature. This could be explained partly through competition for substrate, as during warmer months (tending to coincide with growing season) stimulation of aerobic decomposers will result in a greater substrate utilisation to mineralise SOC to CO_2. Also, methane produced at lower soil layers could be oxidised to CO_2 in the more oxic upper soil layers, and so the methanogenic activity rate during this time would be masked by the dominance of CO_2 production by methanotrophic processes. Temperature has been seen to drive methane production (Nakano *et al.*, 2004), but there is also evidence of a lack of

temperature sensitivity (Moore & Dalva, 1993), with some suggestions that the temperature sensitivity might only exist under certain water table conditions. Indeed, this was found by Dinsmore *et al*. (2009) with high water table showing a strong methane-temperature link, but this relationship disappeared when the water table was lowered. It is intriguing that the apparent temperature sensitivity of methane in-situ is opposite to previous observations (Le Mer and Roger, 2001), but given the comments above regarding the seasonal switch to aerobic decomposition pathways, it may not be methane production per se which is temperature dependent, more the efficiency of methanotrophy.

The lack of soil moisture driving methane production suggests that the soils studied here do not exhibit the range of soil moistures required to stimulate methane production. Indeed, the water logging classically associated with high methane production rates doesn't occur at either site. Although it is apparent that methane is produced, it is likely that this occurs at anoxic micro-sites within the soil only, and due to the lack of a significant water table (which is a common driver of methane production; (Moore & Dalva, 1993)), it is probable that much of the produced methane is in fact oxidised by methanotrophs and lost as CO_2.

Examining the figures relating CO_2 production (soil respiration) to methane flux, it becomes clear that there is indeed a temperature-mediated switch in the seasonal dominance of methanogenesis and methanotrophy. Whether this switch is a direct result of methane being oxidised during higher temperatures, or whether it is a reflection of a general reduction in methanogenesis (due to substrate competition, change in favourable conditions etc.) is unknown at this point.

5.4.3 Soil respiration

Flux rates for soil respiration were quite different between the two sites. Intriguingly, the peak summer rate was higher at Peaknaze, and the winter rate also slightly higher. The seasonality appeared more pronounced at Climoor with a much sharper transition between flux rates associated with particular seasons. This broad difference in the magnitude and dynamic of the respiration rates could suggest the rate to be more autotrophic-dependent at Climoor, and more reliant upon heterotrophic components at Peaknaze. In terms of soil characteristics, there are some highly relevant differences between the two sites in the likely distribution and quality of SOC which may influence soil respiration. LOI is over three times greater in the organic layer at Climoor than Peaknaze, although given the differing bulk densities, the C pool is only twice that at Climoor than Peaknaze (Climoor = ~8.9 kg C/ m^2, Peaknaze = ~3.7 kg C/ m^2). The majority of this surface SOC will be accumulated peat material and litter at various stages along the decay continuum, but considering the greater mineral content of the soils at Peaknaze, it is likely that the mineral component could lead to a greater variety of available niches (and therefore greater functional diversity) than the purely organic upper layers at Climoor. This could help explain both the overall higher rates of soil respiration, but also the slightly higher winter rates. The greater accumulation of C in the surface soil layers (in terms of C stock rather than pure LOI) also suggests (assuming NPP is comparable) the substrate to be potentially more recalcitrant at Climoor, so mineralisation of native SOC will be less of a contributor to total soil respiration than at Peaknaze.

The temperature sensitivity was high at both sites, and this is expected due to the generally temperature-limited nature of productivity in the two ecosystems. Calculated Q_{10} values for soil respiration were higher at Peaknaze (5.8 by exponential, 4.5 by linear) than Climoor (3.4 by linear). As both sites experience similar prevailing climatic conditions, and both sites are generally wet, the differing temperature sensitivity is most likely due to the relative recalcitrance of the mineralised C. Lower temperature sensitivity

tends to be associated with more labile substrate, (however this is subject to considerable debate (Hartley & Ineson, 2008, Wetterstedt *et al.*, 2010)) so it would follow that the bulk of mineralisable-C at Climoor (being less temperature sensitive) is more labile. If we assume previous comments about the soil respiration at Climoor being more dependent upon autotrophic input of substrate, it can be expected that this temperature sensitivity accurately reflects the dominance of rhizo-deposits and actual root respiration in the total soil respiration flux. Adhering with this theory, it would also follow that Peaknaze soil respiration rates are reliant on a more recalcitrant substrate source, more likely the native SOC.

5.5 Conclusion

The gaseous losses of N_2O, CH_4 and CO_2 express differential sensitivity to prevailing conditions included in this study. The low general fluxes of N_2O across both sites, despite the inherently high N content (and historically high deposition of reactive N), suggest upland soils are likely to be insignificant sources of N_2O. It is suspected that this is mainly due to low mineral N availability (N is stored mainly in recalcitrant organic forms), low labile substrate-C and a lack of complete saturation of surface soils. There appeared to be no detectable difference between the two sites in terms of N_2O production. Net CH_4 fluxes was much greater at Climoor, and there was evidence of a seasonal effect on the flux dynamics. The degree of soil saturation, substrate availability are proposed to be more favourable at Climoor for methane production due to the dominance or organic C at Climoor as opposed to the more organo-mineral dominance at Peaknaze. Historic sulphate deposition could also play a role in methane suppression at Peaknaze, however the contemporary concentrations of sulphate in soil are not excessively large at Peaknaze compared to Climoor. Soil respiration also differed, with Peaknaze having a higher, and more temperature sensitive flux. Coupled with the more distinct seasonality in respiration rates at Climoor, it is possible that respiration is more autotrophic-dependent at Climoor, and more heterotrophic (in terms of bulk SOC turnover) at Peaknaze. The temperature-dependency switch for CO_2 and CH_4 suggests that the thermal optima for methanogenesis, methanotrophy and soil respiration follow a continuum, and that although methanogenesis rates appear to be low at higher temperatures, this could be masked by the enhancement of oxidative processes at higher temperatures. The difference in vegetation could also help explain some of the observed differences, as the litter quality and quantity may ultimately determine the microbial response to substrate, and therefore characterise the nature of trace gas efflux. The relationship between CH_4 flux and Eriophorum species appears opposed to that typically found within the literature, this pointing to a possible site-specificity in the mode of effect played by such plants species on CH_4 fluxes.

It is clear that vegetation, physico-chemical characteristics and prevailing conditions may all help explain the observed differences in trace gas flux rates at the two contrasting heathland sites. The differences highlight how variable C and N dynamics can be between ecosystem types which, at some spatial resolutions, would appear homogenous. Understanding the connection between subtle differences in driving variables, and the resulting emission dynamics of trace gases will allow for a better understanding of the differing contribution of semi natural systems to terrestrial greenhouse gas flux.

Chapter 6. Soil respiration across three contrasting ecosystem types: comparison of two portable IRGA systems.

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Soil respiration across three contrasting ecosystem types: comparison of two portable IRGA systems.

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Specifically, the theme and direction originated from a joint discussion. R.Mills led on the introduction and the preparation of figures and tables and the abstract, H.Glanville led on the results section, methods and conclusion. The discussion was co-authored.

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Keywords: Carbon, CO_2. Flux chamber, Greenhouse gas emission, Methodology,

Abstract

An accurate assessment of soil respiration is critical for understanding and predicting ecosystem responses to anthropogenic perturbation such as climate change, pollution and agriculture. Infra-red gas analyzer (IRGA) based field measurement is the most widely used technique for assessing soil respiration flux rates. In this study, respiration rates obtained with two common IRGA systems (LI-COR 8100 and PP Systems EGM-4) were compared across three ecosystem types. Our results showed that both methods were highly comparable in their flux estimates, but the associated methodology used (notably the use or absence of a soil collar) resulted in greater uncertainty in flux rates and a greater degree of intra-site variation. Specifically, the use of collars significantly decreased the flux estimate for both IRGAs compared to the no-collar estimate. The disturbance caused by collar insertion was assumed to be a major factor in causing the differing flux estimates, with root and mycorrhizal severance likely being the main contributor. We conclude that the two IRGAs used in this study can be reliably compared for overall flux estimates but emphasis is needed to validate a common measurement methodology.

6.1 Introduction

Soil respiration is the major pathway of carbon (C) efflux from terrestrial systems and therefore represents an important integrated reporter of ecosystem functioning. Soil respiration includes root and microbial respiration, and bulk turnover of organic matter which all contribute to the release of CO_2 (Hill *et al.*, 2004, Nay *et al.*, 1994). Consequently, accurate quantification of gaseous fluxes from soil remains paramount to furthering our understanding of soil C flow and ecosystem resilience (Davidson *et al.*, 2002, Lützow *et al.*, 2006, Widen & Lindroth, 2003). The most common method for measuring soil CO_2 efflux employs infra-red gas analyzers (IRGA), which measure the increase in enclosed-chamber CO_2 concentration over a specified time (Luo & Zhou, 2006). There is currently no internationally recognized standard protocol for measuring soil respiration and rarely have the different measuring methods, which take subtly different approaches, been validated either in situ or in artificial media (Janssens *et al.*, 2000, Norman *et al.*, 1997, Pumpanen *et al.*, 2004). Therefore the results obtained from any individual method can be contentious due to a lack of a calibrated standard to which to compare the data, and any method for calculating soil respiration can only be compared relatively (Nay *et al.*, 1994, Widen & Lindroth, 2003). The two IRGA systems within the current study have not previously been directly compared in the field, and as they are two of the most widely used systems, the comparison is of significant relevance. Possible causes for differences between different IRGA-based measurements may include differences in IRGA design (e.g. cuvette area and volume, the use of collars, presence or absence of chamber vents), measurement parameters (e.g. enclosure time, chamber flow rate, purge parameters etc) and CO_2 flux algorithms (e.g. with and without moisture and temperature correction). It is likely that these effects may also be dependent upon soil type and vegetation in which the measurements are being undertaken.

This study was devised to directly compare two commonly used and commercially available IRGA based CO_2 analyzers; the LI-COR 8100 (LI-COR Biosciences, Lincoln, NE, USA) and the PP Systems EGM-4 equipped with a SRC-1 chamber (PP Systems, Hitchin, Herts, UK). The two main aims for this study were: (1) to assess if there was any inherent difference in measurements obtained from the two analyzers in the field, as supported by other comparative studies (Bekku *et al.*, 1995, Janssens *et al.*, 2000, Luo & Zhou, 2006, Pumpanen *et al.*, 2004) and (2) to assess whether the inclusion or absence of a collar influences the measured CO_2 flux (as postulated by Pumpanen et al., 2004).

6.2 Methodology

6.2.1 Site description

Three contrasting ecosystems were selected for this study. Site 1 (Eutric Cambisol; 53°14'N 4°1'W) constituted a freely draining, intensively sheep grazed (> 5 ewe ha^{-1}), fertilized (120 kg N ha^{-1} y^{-1}) agricultural grassland dominated by *Lolium perenne* L. and *Trifolium repens* L.. Site 2 (Haplic podzol; 53°12'N 4°0'W) constituted a freely draining, low intensity sheep grazed (< 1 ewe ha^{-1}), unfertilized agricultural grassland dominated by *Nardus stricta* L. and *Agrostis caillaris* L.. Site 3 (Orthic podzol; 53°03'N 3°28'W) constituted a poorly drained, ungrazed *Calluna vulgaris* L.and *Vaccinium myrtillus* L. heathland. The major characteristics of the soils are presented in Table 1.

6.2.2 Plot preparation

In October 2009, five PVC collars (10 cm diameter, 4.4 cm depth with a 0.2 cm bevelled edge at one end for easy insertion) were inserted into the ground to a depth of 2 cm at both grassland sites. Collars were distributed in a 'W' shape across the site, with 20 m between each collar. At each collar, vegetation was clipped to 1 cm above the soil surface both within the collar area, and in a similar sized area adjacent to the collar. This second clipped area would provide the 'no-collar' respiration measurement. Collars were then left for 14 days prior to measurements being made to allow the soil and excised roots to settle after disturbance. This approach gave a total of five collared and five no-collared respiration sampling points at each site. Soil respiration was determined at each site using both a LI-COR LI-8100 and an EGM-4 with an SRC-1 chamber. Both IRGAs used a 60 s enclosure time, a 15 s purge time and a 15 s equilibration/dead band time. Data was automatically fitted to either a linear or non-linear function by the LI-8100

software, and the linear option was chosen as the default fit for the EGM-4. The implications of this decision were investigated by comparing flux estimates with the linear and quadratic algorithm with both IRGAs. Both the linear and quadratic estimates were in very close agreement with each other (linear regression r^2 value >0.99; P = <0.001) from which it was concluded that the linear flux equation was sound.

6.2.3 Data analysis

Data were visually inspected for normality and were subsequently log transformed for analysis via a three-way ANOVA. Statistical procedures were carried out using the statistical package 'R' v 2.8.1 (R development Core Team, 2008), with P = 0.05 used as the upper limit for statistical significance. Data were back transformed for graphical representation using Sigma Plot 10 (Systat Software Inc., Chicago, IL).

Table 6.1. Site characteristics of the three ecosystem types. Where applicable, soil values are expressed on a dry weight basis. Values represent mean ± SEM (n = 3).

	Lowland grassland	Upland grassland	Upland heathland
Soil type	Eutric cambisol	Haplic podzol	Orthic podzol
Depth of organic layer (cm)	15	15	7
Organic matter (g kg^{-1})	64 ± 6	713 ± 39	527 ± 84
Bulk density (g cm^{-3})	1.14 ± 0.01	0.19 ± 0.01	0.26 ± 0.04
$pH_{(H2O)}$	5.9 ± 0.5	3.95 ± 0.04	3.7 ± 0.06
Electrical conductivity (µS cm^{-1})	123 ± 16	99 ± 36	99 ± 19
Total soil C (g kg^{-1})	38 ± 3	412 ± 13	370 ± 6
Total soil N (g kg^{-1})	3.8 ± 0.1	22.6 ± 1.6	12.3 ± 1.7
Microbial biomass C (µg g^{-1})	197.9 ± 32.8	221.4 ± 17.1	248.3 ± 3.7
Microbial biomass N (µg g^{-1})	23.1 ± 0.9	18.7 ± 1.9	13.1 ± 1.6
Exchangeable Na (meq kg^{-1})	1.4 ± 0.1	2.6 ± 0.2	2.8 ± 0.3
Exchangeable K (meq kg^{-1})	4.2 ± 1.6	3.0 ± 0.4	1.9 ± 0.4
Exchangeable Mg (meq kg^{-1})	3.5 ± 0.3	2.0 ± 0.3	8.1 ± 0.8
Exchangeable Ca (meq kg^{-1})	68.5 ± 1.3	3.4 ± 0.3	14.3 ± 0.7

6.3 Results

Significant differences in mean respiration rates were observed between the three sites (p< 0.001) and increased in the order Orthic Podzol (heathland) < Haplic Podzol (unimproved grassland) < Eutric Cambisol (improved grassland). Overall, there was no significant difference (p = 0.98) in the respiration from the three sites when measured with either the EGM-4 or LI-COR-8100 IRGA (Figure. 6.1). This result provides confidence when comparing studies that use two different IRGA approaches. The comparison of collar and no-collar treatment did, however raise some interesting findings. There was a significant (p< 0.001) difference between the collar and no-collar treatment estimate of soil respiration (Figure. 6.1). Across all sites, the soil CO_2 efflux in the presence of collars was 25 ± 11 % and 20 ± 6 % lower for the LI-COR-8100 and EGM-4 respectively in comparison to measurements made without collars (Figure. 6.2).

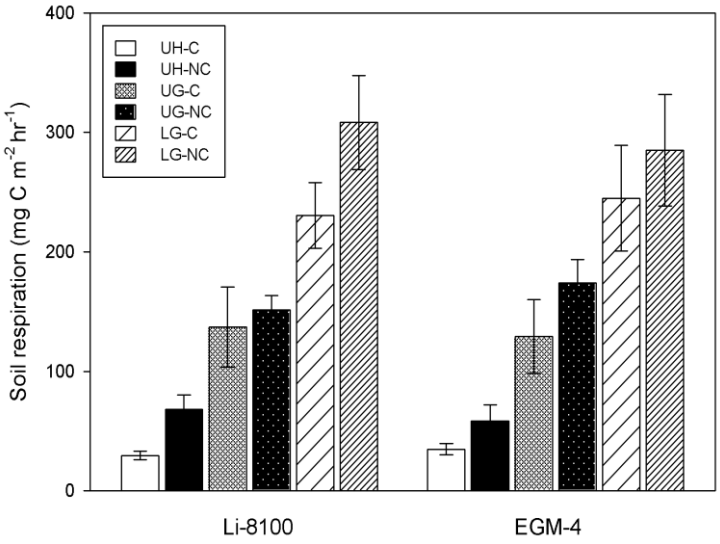


Figure 6.1. Mean (n = 5) soil respiration rates for each site (UH = Upland Heathland, UG = Upland Grassland, LG = Lowland Grassland) and collar/no-collar treatment (C = Collar, NC = No Collar) grouped by IRGA type. Vertical bars show one standard error of the mean.

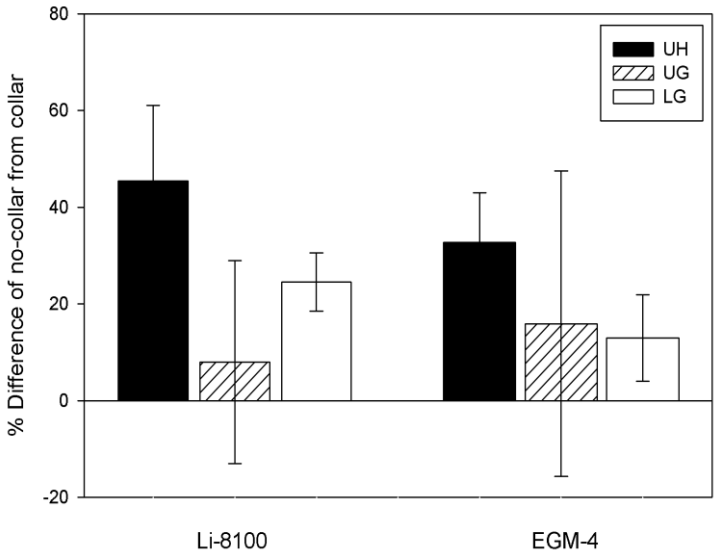


Figure 6.2. Respiration rates under the no-collar treatment, expressed as a percentage difference from collar treatment. Data is labelled by site (UH = Upland Heathland, UG = Upland Grassland, LG = Lowland Grassland) and grouped by IRGA type. Vertical bars show one standard error of the mean (*n* = 5).

6.4 Discussion

From the results presented here it is apparent that the presence of collars may result in a relatively small but systematic bias in both IRGA measurement systems. This is likely to be partly due to the effectiveness of the seal between the IRGA and the soil under the presence or absence of a collar. However, this must be balanced against the inherent variability in soil respiration over both space and time. Our results suggest that spatial variability in soil respiration was also highly site dependent with standard errors in measurements ranging from 8 to 24 % of the mean value. There are a number of biological considerations to be made when interpreting the effect collar insertion had upon measured flux rates. It would be expected that physical disturbances caused by collar insertion (Davidson *et al.*, 2002) would increase the rate of soil respiration by severing roots and mycorrhizal hyphae, thus contributing a greater pool of labile C to soil solution (Hanson *et al.*, 2000, Johnson *et al.*, 2002). However, this labile flush caused by excision is likely to be turned over rather rapidly and as such, it would be expected that this phenomenon would be short lived. Indeed, Edwards (1991) found excised roots to cause an initial increase in soil respiration compared to intact cores, but a stabilisation of rates to within 30% of intact core rates was found within 2 days of root excision. However, it has been shown in other studies that severing roots from above ground biomass causes a marked and rapid reduction in total soil respiration (Bingham & Rees, 2008). This would suggest that the rate of recovery after disturbance might be highly variable across ecosystem types, this helping to explain some of variation in collar versus no-collar differences found across the sites in the present study.

The maintenance of a physical barrier between excised material and live roots and hyphae could present a notable obstacle for the re-establishment of homogenous steady soil conditions. It is likely that the 14 day period between collar installation and measurement would be insufficient for this process to have occurred. The lack of live, intact roots within the collar soil

would have obvious implications for C transfer from plants to the microbial biomass, and therefore for total respired C. Soil moisture modifications created by removing the transpiration demand of live roots through collar placement could cause a reduction in decomposition, as excess moisture will retard mineralization. This might be more important for the lowland soils which typically have fairly low moisture content in comparison to the upland sites. Also, the contribution of root respiration to total respiration might simply make up this difference, if we assume severance causes a complete halt in the respiration of root material no found within the collar area. This would be a sensible conclusion given that root respiration has in other studies been found to account for around 50% of total soil respiration (Ohashi *et al.*, 2000, van Hees, 2005). Although this value is highly variable and ecosystem/plant/soil dependant, with reports ranging between 10 – 90% of total soil respiration (Hanson *et al.*, 2000).

The good similarity in respiration estimates between the two IRGA types is in agreement with a previous study on forest soils by Janssens et al. (2000), who found a 10% difference between two IRGAs. This confirms the reliability of comparing site estimates of soil respiration flux using the two different IRGAs studied here. The application of collars to aid in flux estimates continues to be a source of variability. It is suggested, however, that simple modifications to collar design taking into account soil and vegetation factors, such as moss and litter depth, keeping in mind the range of disturbances collar insertion could have on biological components should allow for a reliable, standardised approach.

6.5 Conclusion

In conclusion, the two IRGA systems used in this study have been shown to be reliably comparable when a common collar approach is used. However, disturbance caused by collar insertion is likely to affect both plant and microbial respiration, but the magnitude and duration of this effect is poorly understood and therefore requires further study.

Chapter 7. Investigating the drivers of basal soil respiration of soils sampled within National-scale survey of Great Britain.

7.1 Introduction

The drivers and dynamics of Soil Organic Carbon (SOC) decomposition are well studied in the literature, with sound and robust conclusions being repeatedly drawn about the effects of a small number of key controlling variables (Davidson *et al.*, 1998a). However, the majority of these studies are highly focussed and tend to concern drivers which operate on temporal scales, with comparatively fewer studies focussing on spatial scales. Of the spatial scale studies, many focus on the comparison of a small number of distinct vegetation types, such as forests (Saiz *et al.*, 2006), or croplands (Dupuis & Whalen, 2007), or on the transition between two contrasting ecosystems (Tang & Baldocchi, 2005). Some spatial studies have considered multiple vegetation types, and the output would suggest sensitivity to key variables such as soil water availability (Evrendilek *et al.*, 2005, Hibbard *et al.*, 2005). National-scale inventories of soils analysis have raised topical conclusions and primed a significant degree of discussion in the literature (Bellamy *et al.*, 2005, Smith *et al.*, 2007)Large-scale spatial studies concerning a wide range of vegetation and soil types are therefore key when attempting to understand some of the broader drivers of SOC decomposition dynamics. This greater level of understanding can inform soil C models, and thus improve our predictive capacity for estimating soil respiration response to change.

Decomposition of SOC can be split into three main processes

- mineralisation, whereby SOC is metabolised by the biomass and lost as gaseous CO_2
- assimilation, whereby organic material is incorporated into the biomass of soil flora/fauna
- alteration, whereby the original substrate is transformed into a material with a different chemical structure following some form of chemical action (often a form of metabolism)

These three processes collectively summarise the decomposition of SOC, and it is clear that the eventual loss of C from the soil through mineralisation (mineralisation and soil respiration are used interchangeably) may be an initial phase, or a process which occurs following a degree of alteration and assimilation of the substrate. As the latter two processes are difficult to measure directly, and the measurement of surface loss of CO_2 is relatively easy, respiration of CO_2 is universally used as a direct proxy for the rate of general SOC decomposition. Of course, mineralisation is a measure of the aerobic metabolism of C compounds, and so it follows that the measurement of CO_2 flux is a sensible indicator of the degree of metabolic activity.

Typically, soil respiration is controlled by the effect of soil moisture and soil temperature, with a strong interaction of these factors, and interaction with any other number of physico-chemical factors such as nutrient availability and substrate concentration/availability. These factors operate mostly at small spatial scales, or on any temporal scale, and it would be sensible to assume that at larger spatial scales (i.e. national scale, continental scale) broader factors such as climatic regime, latitude, and expressions of favourability of growing conditions would become more important.

A number of spatial studies looking at soil respiration in-situ have found soil physico-chemical conditions to be important in explaining flux variation. Within Sitka spruce forest stands, Saiz *et al.* (2006) found that the abundance of organic material found on the forest floor was the best variable for explaining spatial variation in respiration. Martin and Bolstad (2009) found soil chemical conditions to be the best explanatory variables in explaining small-scale (1-10 m) variation in respiration in afforested systems. In other forest studies, proximity to tree trunks was a significant variable for explaining spatial variation in respiration, with decreases in respiration with distance from the tree (Epron *et al.*, 2004, Tang & Baldocchi, 2005). On larger spatial scales, climatic gradients have been shown to have significant explanatory power in forest ecosystems, with climate explaining 48% of the variation in respiration (Campbell & Law, 2005) across a number of forests

in Oregon. In non-forested systems, the key soil physico-chemical conditions appear to dominate. Sommerkown (2008) found soil temperature and water table position to explain the majority of spatial variation between tundra microsites, whereas when studying at a larger spatial scale, Qi *et al.* (2010) found a precipitation gradient to best explain variation in respiration rates between three Steppe systems in China. The shifts between soil physico-chemical factors being dominant at smaller spatial scales, and climatic factors being predominant at larger scales supports the need to investigate a range of possible driving variables when considering any spatial investigation.

Laboratory approaches to measuring soil respiration using intact core measurements allow for assessment of soil respiration under standardised conditions in response to a particular set of prescribed experimental manipulations. Such laboratory approaches utilise intact cores or monoliths of collected soil which usually have had the aboveground biomass component removed, and therefore focus mainly on the heterotrophic response. Advantageous in the respect that conditions may be controlled, laboratory approaches also allow for large numbers of samples to be interrogated and measurements made relatively rapidly. However, disturbance associated with sample removal, transport and storage can have implications for the interpretation of measured fluxes. Severed roots (Rakonczay *et al.*, 1997) and mycorrhizal fungi may cause a flush of respiration, and then reduce in the relative contribution to observed flux rates variably over time (Lipp & Andersen, 2003), potentially affecting observed flux rates.

Intact core approaches have been used to study the effects of temperature manipulations (Koponen *et al.*, 2006, Reichstein *et al.*, 2005b, Schimel, 2005), soil moisture status (Haesebroeck *et al.*, 1997, Yuste *et al.*, 2007), nutrient content (Curtis *et al.*, 2006, Koops *et al.*, 1996, Liu *et al.*, 2007), altered substrate input (Hill *et al.*, 2008, Jones & Murphy, 2007, Roberts *et al.*, 2007)as well as a range of interactive approaches (Lagomarsino *et al.*, 2009, Rinnan *et al.*, 2007, Weier *et al.*, 1993). Larger spatial scale studies

are less common though, and there tends to be a focus on comparisons of either distinct vegetation types (Kammer *et al.*, 2009), treatment response (Yuste *et al.*, 2007) or climatic gradients (Kang *et al.*, 2003). There is therefore considerable scope for investigating the core drivers of respiration across large spatial scales without any treatment effects.

Countryside Survey (CS) is a large-scale survey of vegetation, soils and water across England, Wales and Scotland which aims to repeat-sample locations over a number of years (the first being 1978) to ascertain the nature of change in the countryside of Great Britain. As the survey is a large spatial assessment, and the collection procedure is standard across the entire project, the data set represents the most thorough and comprehensive approach available covering all major soil and vegetation types in Great Britain. Utilising the CS 2007 soils collection and analysis, a core-based mineralisation exercise was carried out on soils collected for N-mineralisation assays to attempt to assess the spatial variation in C-mineralisation on a national scale under controlled conditions. This strategy allowed for a comprehensive assessment of the nature of C-mineralisation under standard laboratory conditions and provided an estimate of the basal rate of soil respiration across a large range of vegetation types under the CS Aggregate Vegetation Classification (AVC) system. The basal nature of the respiration measurements is appropriate as a tool to assess the fundamental nature of C-mineralisation found in intact soils in the absence of plants.

The aims of this study were therefore:

- Assess the nature of basal C-mineralisation across a range of soils from different vegetation types across the UK.
- Identify the major drivers of variation observed within the C-mineralisation data and construct the best predictive model from the range of variables.

It is hypothesised that basal respiration rates will be best explained by a combination of soil physico-chemical characteristics, but that broad-scale variation will be best described by variables associated with vegetation type.

7.2 Methods.

7.2.1 Sample collection

As detailed in Emmett et al (2010), sampling strategy samples 1km x 1km squares selected randomly from the Ordnance Survey grid after prior stratification of the entirety of Great Britain into land classes. These land classes are based on a range of environmental gradients, and using this approach ensured a more representative sample of the range of land and habitat types found in GB. This sampling approach led to a total of 591 squares being sampled across GB. Each square contained five plots, each of which was sampled four times for soil. Of these samples, around 700 soils were incubated for N-mineralisation assays at CEH Bangor, during which time the basal soils analysis was carried out. Soil sampling followed the CS 2007 soils collection procedure (Emmett *et al.*, 2010). Soils were collected by inserting PVC cores (15 cm length, 3.8 cm internal diameter) into the ground after parting vegetation, and removing loose litter. Cores were cut into the soil and hammered until the surface of the core was flush with the soil surface. The core was then removed, bagged and posted to CEH Bangor for storage at 4°C until analysis.

7.2.2 Soil processing

Upon receipt at CEH Bangor, soils were extruded from sample tubes and placed onto specialised holders which contained the soil with one side exposed, and one side within a half-cylinder perforated with drainage holes. This design allowed soils to be wetted to field capacity by sequential spraying, thus bringing soils to an equilibrated standardised soil moisture. The approach to wet and drain horizontally avoided problems associated with ponding on the surface of poorly drained soil. Each sample was sprayed with an artificial rain solution containing (all in meq/L) 17.6 Ca^{2+}, 30.1 Mg^{2+}, 125 Na^{+}, 140 Cl^{-} and 57.2 SO_4^{2-}. Spraying continued until 150 ml

of leachate was obtained, after which suction was applied to each soil to drain larger pores before samples were bagged up and incubated at 10°C. Flux estimations were carried out on samples in respiration chamber after two weeks of incubation.

7.2.3 CO_2 flux estimation

Chamber design

Chambers were constructed from grey PVC pipe cut to 30 cm length. One end of the pipe was enclosed using a PVC end-cap and sealed in place using Dow-Corning acetyl-free sealant. The open end of the chamber was bevelled at the edge to accommodate a push-fit end-cap which was drilled with a sample hole and an equilibration hole, both fitted with 17 mm silicone suba-seals. The base of the chamber had two strips of PVC affixed to stop the cylindrical chamber from rotating during enclosures.

Enclosure and headspace sampling

Prior to enclosure for headspace sampling, soils were removed from plastic storage bags and returned to an incubator at 10°C to allow establishment of steady CO_2 flux. After 1 hour, soils were placed into chambers in a 10°C incubator, sealed and gas allowed to accumulate. Gas samples were taken at time zero and after one hour of enclosure by extracting a 20 ml sample with a hypodermic needle and syringe inserted into the suba-seal. An equilibration needle was inserted into the second suba-seal at 90° opposition to the sample needle position. The equilibration needle would reduce pressure fluctuations which are a known source of flux uncertainty. Gas samples were immediately injected into pre-evacuated 15 ml vials ready for subsequent analysis (see appendix 1.)

7.2.4 Gas analysis

Gas analysis was carried out using a Perkin Elmer Clarus 500 Gas Chromatograph (GC) equipped with a Porapaq QS (80-100 mesh) analytical column. Samples were auto-analysed using a turbomatrix 40 headspace auto-analyser. N_2O was detected using ECD (at 400°C, sample oven at 40°C), CH_4 was detected using FID (at 375°C, sample oven at 40°C) equipped with a methaniser. Carrier gas pressure was 0.14 MPa, and injection pressure 0.16 MPa. All other analytical conditions were as specified in the Perkin Elmer standard setup. Calibration of the GC involved three calibration gas concentrations for each target gas (Cryoservice, UK) and calibration was accepted at $r^2 > 0.99$. During gas analysis, standard samples were run after every 10 samples to check for drift of calibration.

7.2.5 Linearity checking

To determine the nature of gas accumulation in chamber headspace, and to ascertain the number of samples needed to flux calculation, linearity checks were carried out on a sub sample of soils from the first few batches covering mineral, organo-mineral and organic soil types. Five samples from batch one, and three from batch two were selected. The first set of soils were enclosed for two hours and samples taken at 0, 15, 30, 45, 60 and 120 minutes, the second set were enclosed only for one hour and samples taken at 0, 15, 30, 60 minutes. The gas concentration at each point was used to determine flux rates by linear regression equation. Both linearity check sessions revealed adequate linear accumulation of CO_2, but only over the one hour time period (Figure 7.2.1). The two-hour sample gave a much more variable result, and gave a very low power to linear flux calculation. It is expected that this was due to a reduced flux after such a long enclosure due to accumulation in headspace gas and negative feedback on microbial activity. Restricting the enclosure to one hour gave more reliable results, and given the vast number of samples expected (~700) a one hour enclosure was selected.

To ascertain the number of samples needed, a comparison of the flux estimate using multiple sampling (as previously detailed) or using only two samples (at time zero and at time one-hour) was carried out. The flux obtained from using only two samples was highly comparable to the flux obtained using linear regression over one hour when sampling four times. The mean difference between the two methods was 2.07 ppm/hr (+/- 1.01 ppm). Using the smaller number (two) samples over a one-hour enclosure was therefore chosen as a reliable level of agreement existed between the two methods, and the latter represented a more logistically sensible option given the number of samples.

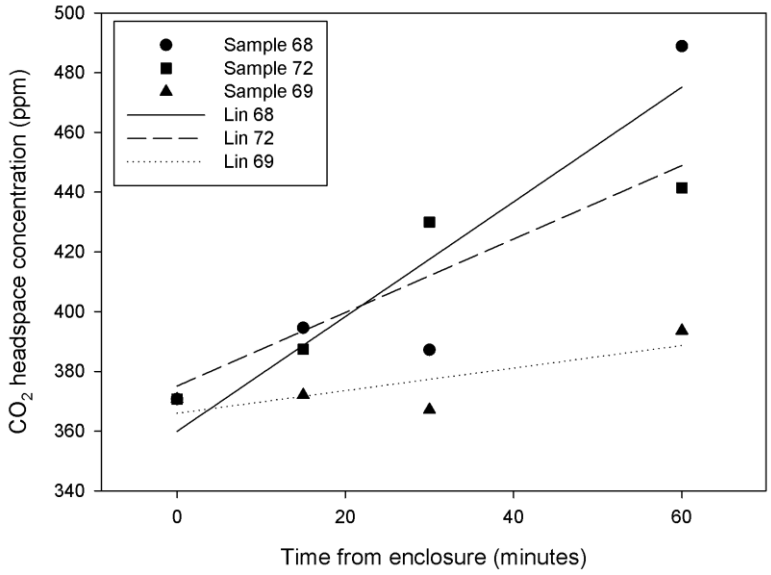


Figure. 7.2.1 CO_2 headspace accumulation after a multiple test, one hour enclosure. r^2 values for the fitted linear regression lines are 0.85, 0.87 and 0.65 for samples 68, 72 and 69 respectively.

7.2.6 Flux calculation

Accumulation of headspace CO_2 between time 0 and time 1 h were assumed to be linear (see above for linearity proofing), and were used to calculate a flux of CO_2 within the chamber according to a simple equation based on the ideal gas law. Pressure was assumed to be one atmosphere, and temperature was taken as 10°C.

Fluxes were expressed as weight of CO_2-C per gram of Air-Dried Soil (ADS) based on the calculated weight of soil in the measured core by inference from bulk density and soil moisture measurements. Flux was also expressed as a function of organic matter: as per gram of LOI, and as per gram of SOC, the SOC content being calculated as 55% of the LOI content(Emmett *et al.*, 2008). This expression reflects the mineralisation efficiency of the microbial biomass, in that it allows for an estimation of the quantity of respired C in respect to the substrate pool size. Expression of flux per unit area was based on up-scaling from the core surface area to flux per square metre. The up-scaling process relied on the key assumption that the flux measured from the extracted core would be equivalent to expected flux from the core surface when in situ.

7.2.7 Environmental data

Environmental data was acquired from the main CS 2007 SAS database and extracted using the filter form process. Each soil sample carried a unique ID which related directly to the square of origin. This meant that some data was available per sample, and some data per sample square. The primary soil data (such as chemistry data) was obtained by analysis of a paired sample from the same sample location as that used in the incubation study. Some of the more broad environmental data (such as rainfall) was available at the square level. Soils data were analysed and collected according to (Emmett *et al.*, 2008), and climatic data were obtained from the Meteorological Office 5km gridded square data for mean 1961 – 1990 values.

A hierarchy of influence was constructed to propose the likely usefulness of environmental variables in explaining flux variation. This allowed for grouping of variables into sets which could then be used to drive models and multivariate analysis.

Table 7.2.1. Environmental variables used for regression analysis.

Order of investigation	Group name	Variables included
Primary	Physico-chemical attributes	Bulk Density, Loss-On-Ignition, Olsen-P, pH (in water and $CaCl_2$), C-pool size, Mineralisable-N (in total soil, and in SOC only), %C, %N, C/N ratio, Soil Moisture at time of sample.
Secondary	Broad climatic features	Growing Season Length (GSL), Growing Degree Days (GDD), Mean Annual Temperature (MAT), Mean Annual Precipitation (MAP).

7.2.8 Data analysis and presentation

Environmental data was compiled and manipulated in Microsoft Excel 2007 after acquisition from SAS Enterprise Guide version 4 (SAS Institute Inc., (SAS, 2000-04)) Statistical analyses were performed using R statistics version 2.10.1 (R, 2010) Graphical figures were produced using Sigmaplot version 10 (Systat, 2009) and R statistics, and tables were prepared using Microsoft Excel 2007. All data, both flux and environmental, were visually inspected for normality prior to analysis using quantile-quantile plotting, with most data being log transformed prior to statistical tests. Linear models were constructed by selective deletion of non-significant terms after inclusion of all relevant environmental variables. Due to the large number of variables being

tested, the range of interaction terms possible for each data group was very large (55 two-way interactions for soil data). To deal with this, a list of possible interactions was made, from which sets of these were randomly selected, and then a number of models were constructed. This allowed for a more manageable assessment of interactions, and the model simplification progressed by taking only the significant interaction terms from this exercise and forming them into a larger model.

7.3 Results

7.3.1 Flux estimations for AVC classes

Flux rates for soil respiration are shown for the three flux expressions in Figures 7.3.1 – 7.3.3. Each Figure shows the significant differences found during pairwise comparisons using a common letter as an indicator of similarity. The expression as a function of Air Dry Soil (ADS) shows a general increase in flux rates moving from crops/weeds to heath/bog. It is interesting to note the similarity of the woodland classes and Moorland grass/mosaic.

The expression of flux as a function of SOC indicates the relative mineralisation efficiency under each AVC. Clearly the rate follows almost the opposite pattern to Figure 7.3.1, however the statistical differences are less marked. It is reasonable to state that Moorland grass/mosaic and Heath/bog are generally lower in mineralisation efficiency than the lowland grass and crop sites, with woodlands remaining comparable to both sets.

Flux as a function of soil area is less intuitive, other than to state that generally, lowland grasslands appear to have the highest overall flux rates per unit area.

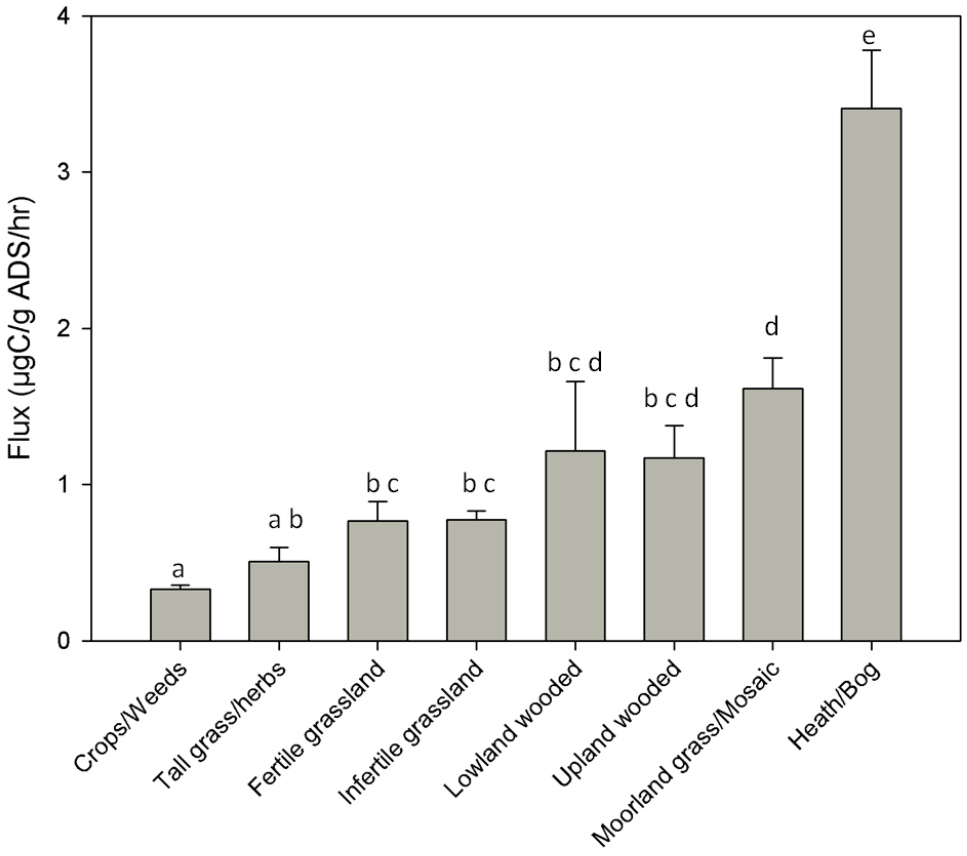


Figure 7.3.1 Mean flux rates for each AVC class expressed as µg C/ g air dry soil/ hr. Error bars show SEM. AVC classes with a common letter are not significantly different ($p>0.05$), actual p values can be found in Table 7.3.1.

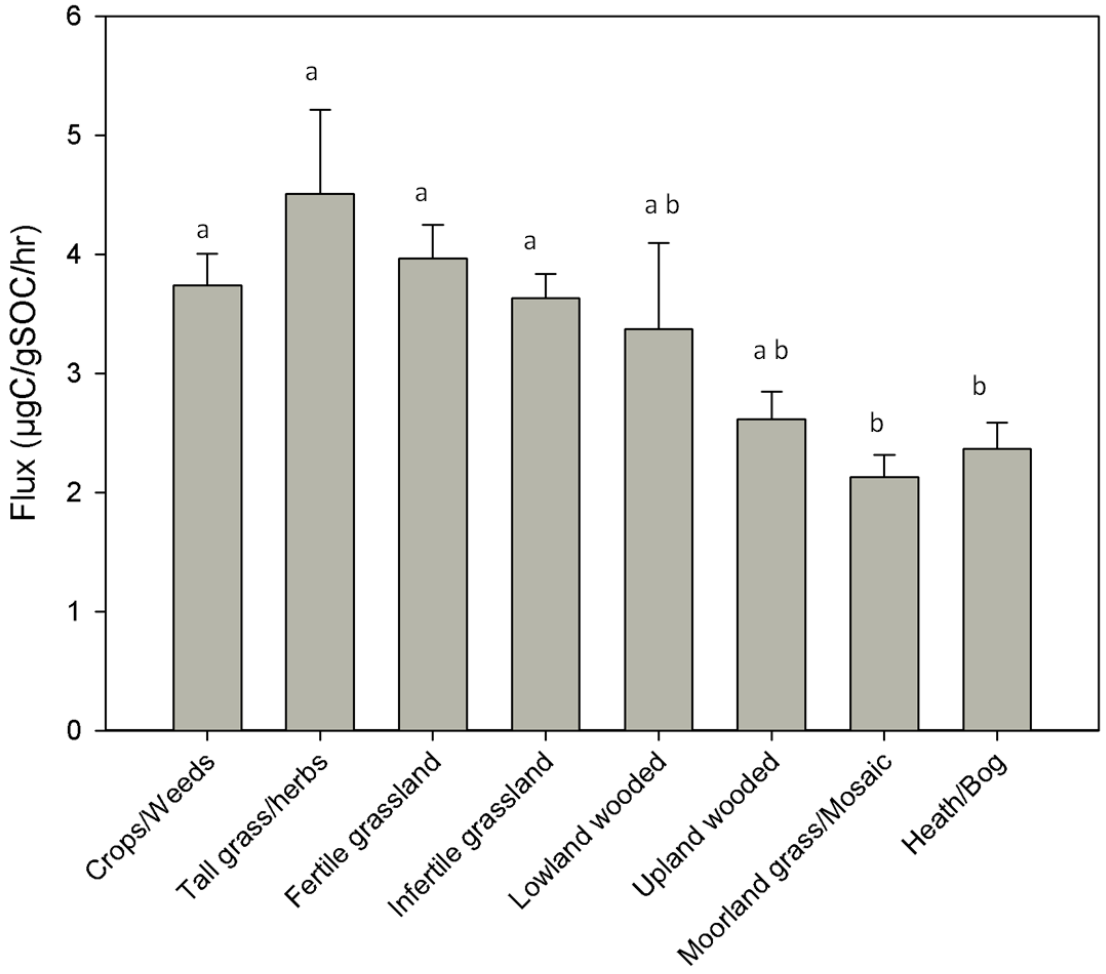


Figure 7.3.2 Mean flux rates for each AVC class expressed as µg C/ g Soil Organic Carbon/ hr. Error bars show SEM. AVC classes with a common letter are not significantly different ($p>0.05$), actual p values can be found in Table 7.3.1.

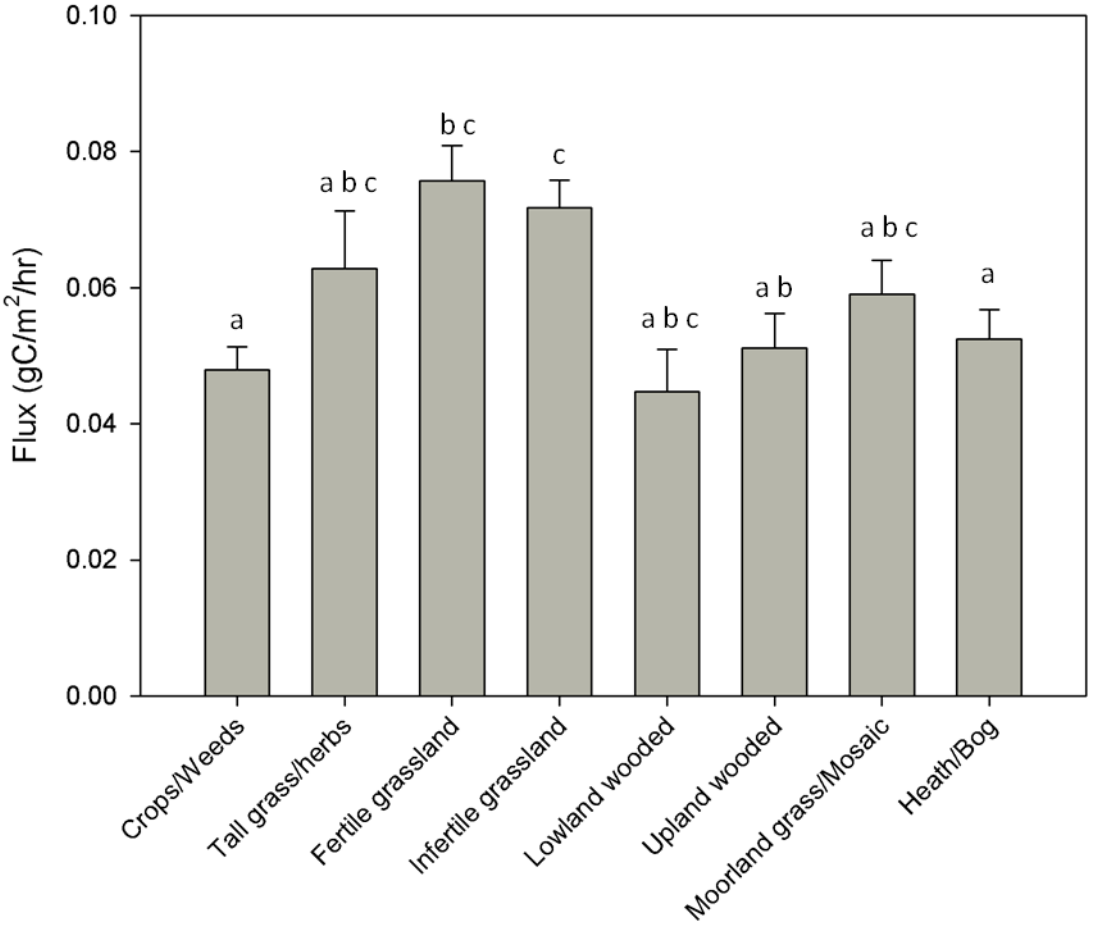


Figure 7.3.3 Mean flux rates for each AVC class expressed as µg C/ m^2/ hr. Error bars show SEM. AVC classes with a common letter are not significantly different ($p>0.05$), actual p values can be found in Table 7.3.1.

Table 7.3.1 P statistics from between-groups analysis of mean flux rates in Figures 7.3.1, 4.3.2 and 7.3.3.

AVC comparison		Flux /g ADS	Flux / g SOC	Flux / m^2
Tall grass/ herbs	Crops/ weeds	0.56	0.99	0.73
Fertile grassland	Crops/ weeds	< 0.001	1.00	< 0.001
Infertile grassland	Crops/ weeds	< 0.001	0.99	< 0.001
Lowland wooded	Crops/ weeds	0.01	1.00	1.00
Upland wooded	Crops/ weeds	< 0.001	0.62	0.98
Moorland grass/ mosaic	Crops/ weeds	< 0.001	< 0.001	0.56
Heath/ bog	Crops/ weeds	< 0.001	< 0.001	0.98
Fertile grassland	Tall grass/ herbs	0.94	1.00	0.98
Infertile grassland	Tall grass/ herbs	0.46	1.00	0.92
Lowland wooded	Tall grass/ herbs	0.76	0.98	0.99
Upland wooded	Tall grass/ herbs	< 0.001	0.43	0.99
Moorland grass/ mosaic	Tall grass/ herbs	< 0.001	0.02	1.00
Heath/ bog	Tall grass/ herbs	< 0.001	0.01	0.96
Infertile grassland	Fertile grassland	0.83	1.00	1.00
Lowland wooded	Fertile grassland	0.98	1.00	0.55
Upland wooded	Fertile grassland	0.77	0.24	0.17
Moorland grass/ mosaic	Fertile grassland	< 0.001	< 0.001	0.54
Heath/ bog	Fertile grassland	< 0.001	< 0.001	0.01
Lowland wooded	Infertile grassland	1.00	0.99	0.41
Upland wooded	Infertile grassland	1.00	0.16	0.07
Moorland grass/ mosaic	Infertile grassland	< 0.001	< 0.001	0.29
Heath/ bog	Infertile grassland	< 0.001	< 0.001	< 0.001
Upland wooded	Lowland wooded	1.00	0.99	1.00
Moorland grass/ mosaic	Lowland wooded	0.47	0.56	1.00
Heath/ bog	Lowland wooded	< 0.001	0.45	1.00
Moorland grass/ mosaic	Upland wooded	0.07	0.74	1.00
Heath/ bog	Upland wooded	< 0.001	0.55	1.00
Heath/ bog	Moorland grass/ mosaic	< 0.001	1.00	0.96

7.3.2 Multivariate analysis

Soils data set

Multiple regression approaches were used to assess the explanatory power of the variables contained within the soils dataset. Model simplification resulted in the most simple significant model for each functional measure. Respiration flux expressed as a function of Air Dry Soil (µg C/ g air dry soil/ hr) was best explained by a model containing soil moisture and LOI, with two interaction terms consisting of BD and pH, and LOI and N %. This model was significant ($p < 0.001$), and had an $r^2 = 0.43$. Flux expressed as a function of SOC (µg C/ g Soil Organic Carbon/ hr) was poorly explained by soils data, with the simplest model, although significant ($p < 0.001$) had an $r^2 = 0.095$. This model contained BD, LOI, C-stock, mineralisable-N (SOM), mineralisable-N (Soil) as well as two interaction terms containing pH and BD, and mineralisable-N (SOM) and mineralisable-N (Soil). Flux per unit area (µg C/ m^2/ hr) was also poorly explained ($p<0.001$, $r^2 = 0.069$), with the simplest model containing BD, C-stock and mineralisable-N (Soil), as well as two interactions terms containing BD and moisture, and mineralisable-N (SOM) and mineralisable-N (Soil).

Climate data set

As with soils data, climatic variables were used to drive multiple regressions for each functional measure. Flux expressed as ADS (µg C/ g air dry soil/ hr) was best explained ($p =< 0.001$, $r^2 = 0.26$) by a model containing altitude, MAP, GDD and relief, with two interactions between altitude and MAT, and altitude and MAP. Although not a significant independent driver, MAT remained in the model due to its inclusion in the interaction term with altitude. Flux per g SOC (µg C/ g Soil Organic Carbon/ hr), was poorly explained by climate data, with a model containing GDD, MAT and relief giving $p < 0.001$, $r^2 = 0.052$. Flux per unit area (µg C/ m^2/ hr) gave a significant ($p = 0.003$)

model containing MAP and MAT, with two interaction terms from GDD and GSL, and MAP and MAT. This model gave an $r^2 = 0.02$.

Overall model

As two flux measures (µg C/ g Soil Organic Carbon/ hr, and µg C/ m^2/ hr) were poorly explained by initial regression approaches, the remaining measure only was used to determine a combined model of both climate and soils data. This model was significant ($p < 0.001$), and explained less than half of the total variation ($r^2 = 0.44$) containing relief, LOI, N % with a single interaction term of LOI and N %.

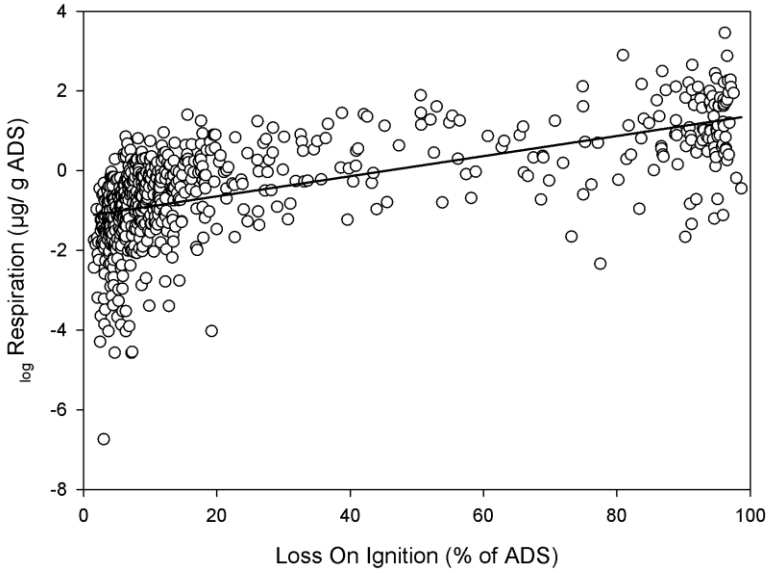


Figure 7.3.4 Loss On Ignition and the log of respiration flux expressed as a function of Air Dry Soil with linear regression ($p < 0.001$, $r^2 = 0.46$).

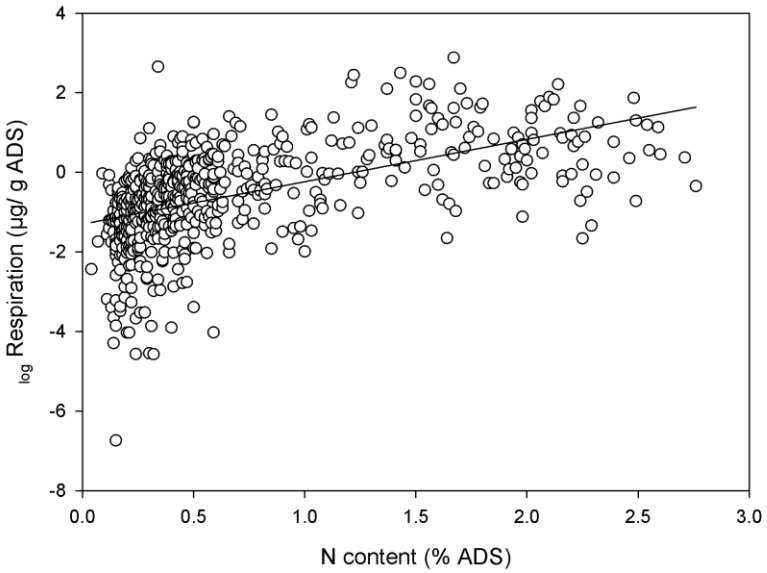


Figure 7.3.5 N % content and the log of respiration flux expressed as a function of Air Dry Soil with linear regression ($p < 0.001$, $r^2 = 0.29$).

7.3.3 Multivariate analysis of soils data within AVC.

To investigate the explanatory power of soils data within AVC classes, multiple regression approaches were applied to each AVC using the same soils variables is with the complete dataset. The output from these models are shown in Table 7.3.2

Table 7.3.2. Components of, and output from soils-data multiple regression models for flux expressed as a function of ADS (µg C/ g air dry soil/ hr). No significant model was determined for Tall grass/ herbs.

AVC	Variables	p	r^2
Crops/ weeds	LOI	0.001	0.09
Tall grass/ herbs	-	-	-
Fertile grassland	BD, moisture	< 0.001	0.22
Infertile grassland	LOI	< 0.001	0.29
Lowland wooded	N %	0.011	0.31
Upland wooded	LOI	< 0.001	0.61
Moorland grass/ mosaic	pH, LOI	< 0.001	0.35
Heath/ bog	LOI	< 0.001	0.26

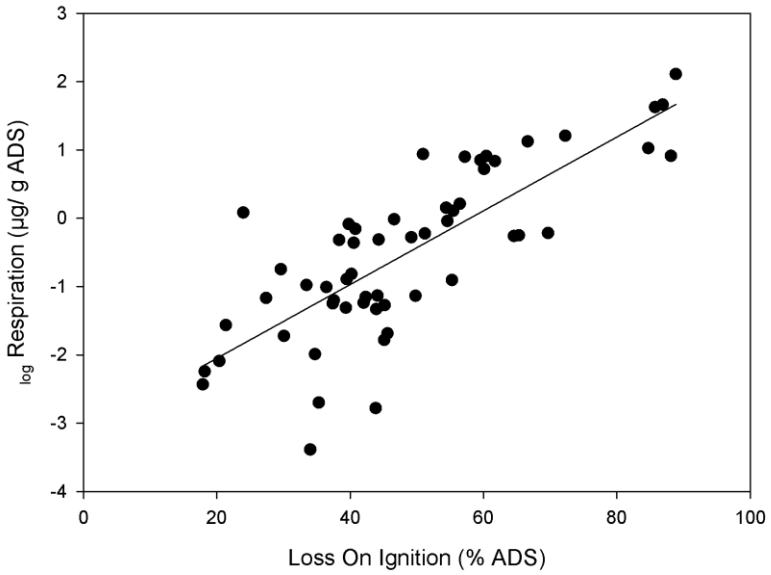


Figure 7.3.6 Loss On Ignition and the log of respiration expressed as a function of ADS for the Upland Woodland class. Linear regression gives $p<0.001$, $r^2 = 0.061$.

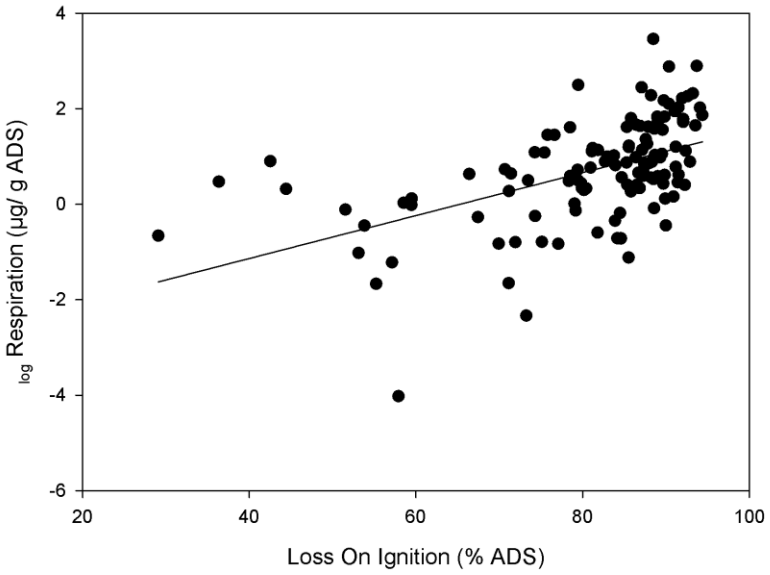


Figure 7.3.7 Loss On Ignition and the log of respiration expressed as a function of ADS for the Heath/bog class. Linear regression gives $p<0.001$, $r^2 = 0.026$.

7.3.4 Soil C/N

C/N ratio of SOM did not appear as a significant variable in linear regression, however, C/N ratio has some influence on C-flux rates when considering groupings of C/N ratio relevant to components of the decomposition community. Assuming the thresholds of C/N for bacterial and for fungal communities (Killham, 1994), it is obvious (Figure 7.3.10) that most samples fall within, or below the favourable threshold for bacterial decomposition pathways. If C-flux can be used as a proxy for decomposition, it could be expected that this grouping might relate some way to flux expressions.

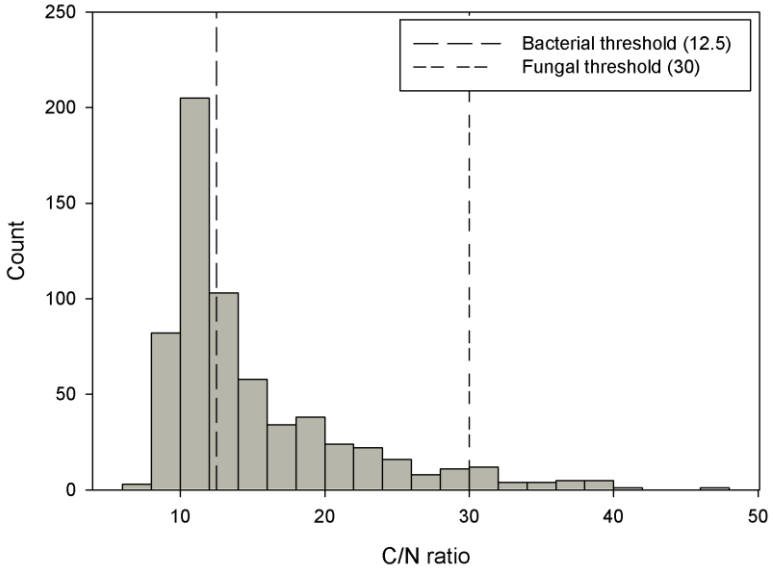


Figure. 7.3.8 Histogram of C/N ratio values across all dataset. Threshold lines are based on the C/N requirements of bacterial and fungal communities (Killham,1994)

When split into the groups specified in figure 4.3.10, mean C-flux rates (/g ADS) are significantly ($p < 0.001$) different between groups (Figure 7.3.12), with a notable rise in flux rates coinciding with C/N ratio grouping. The reverse is the case when flux is expressed as mineralization efficiency, with more efficient turnover (higher flux/ SOC) at the lower C/N ratio. The groupings for the latter expression show significant differences between the <12.5 and 12.5-30 groups ($p < 0.001$) and the < 12.5 and >30 groups ($p= 0.003$), but not between the 12.5-30 and the > 30 group.

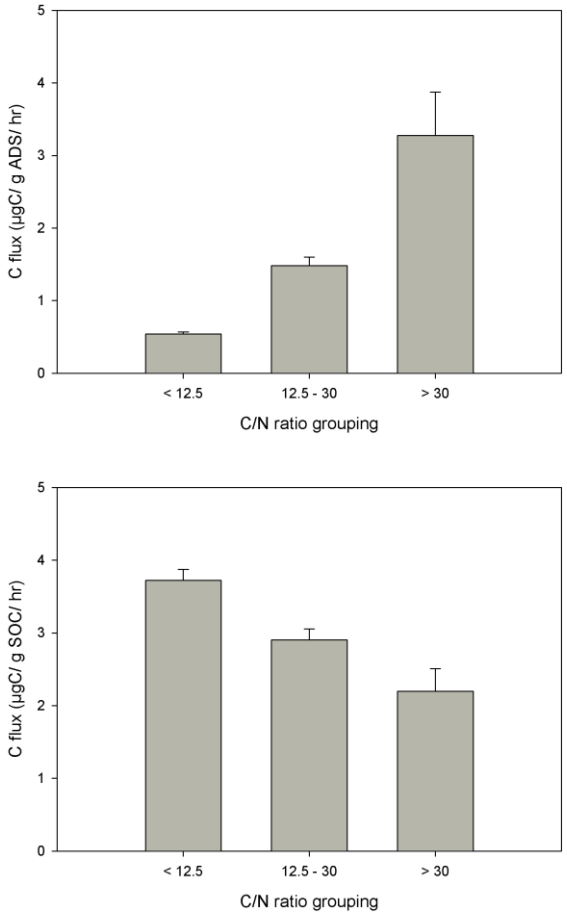


Figure. 7.3.9 Mean C-flux rate according to C/N ratio groupings expressed as /g ADS (left) and /g SOC (right). Error bars are standard error of the mean.

7.4 Discussion

7.4.1 Bulk density and loss-on-ignition

It is clear from regression analysis that there are a number of key variables which explain variation in the CO_2-flux data. BD and LOI were indicated as being the main driving variables for expressions describing CO_2-flux as a function of air dry soil (/gADS) and as a function of SOC (/gSOC). Higher fluxes were associated with high LOI, low BD soils, and lower fluxes are generally associated with lower LOI, higher BD soils. This suggests a significant organic-mineral gradient within the data. BD effects on soil respiration have been reported in a number of studies, such as Vincent *et al.*(2006), who found BD to be a controlling factor for the optimal soil water content for respiration. A negative relationship between BD and soil respiration was found in a transect study in a temperate steppe in Mongolia by Chen *et al.*(2010b). Pengthamkeerati *et al.*(2005) also reported a lower respiration rate associated with higher bulk density soils within a compaction study, the authors pointing to lower porosity leading to diffusivity constraints of gas transport. Although the latter represents an almost artificial example, it serves to highlight one of the physical processes which may underpin lower observed fluxes in higher BD soils.

Expecting higher CO_2 flux in soils which are generally more enriched with organic matter is not radical, and is often a major contributor to explanatory models (Saiz *et al.*, 2006). Making the connection between higher flux rates and soils which have a larger pool of C is a sensible comment, and as the ability for flux rate to be maintained over time after removal of a sample from the field is likely to be dependent upon the substrate pool-size, it is not surprising that the higher SOC soils show a greater CO_2-flux rate. However, as CO_2-flux rate is generally dependent upon the availability of labile-C (Belay-Tedla *et al.*, 2009) as opposed to total C, it is important to consider the likely size and availability of substrate under standard incubation conditions. The state of the SOC in terms of lability will be much dependent

upon the level of protection offered by the soil environment. Organic soils tend to have an abundance of more complex OM which is often chemically protected and so favours a slower decomposition dynamic (Paterson *et al.*, 2008) typical of certain fungal species (Chigineva *et al.*, 2009). More mineral soils will however tend to have a greater amount of mineral protection, whereby SOC is physically protected within the soil matrix by association with silicate or clay particles. Although this contributes to a reduced availability of some SOC, the majority of labile C enters the microbial pool rapidly and mineral protection will tend to occur when initial substrate has been modified by the biomass. Under field conditions, this is unlikely to be a limiting factor, as low LOI mineral soils will tend to have a SOC decomposition dynamic that is reliant upon rhizodeposition, and the prevailing conditions (pH, moisture status, N availability etc) will be favourable for rapid decomposition. However, the removal of this regular source of labile C (plant removal) will shift the substrate source for mineralization to more recalcitrant SOC. The switch to bulk SOC as the main substrate source will reduce mineralisation rates in soils where the SOC is in mainly physically protected (Wang *et al.*, 2003), and this need to acquire substrate from bulk SOC may lead to a reduction in total mineralisation, as seen here.

The much higher LOI soils will generally accumulate recalcitrant SOC, and this situation tends to favour a fungal decomposition pathway (Paterson *et al.*, 2008). Bringing these soils to their basal rates by leaching and incubating will remove the majority of free labile SOC (often DOC and POM (Paterson *et al.*, 2008)) but will retain the more complex SOC, which is a more common substrate for the fungal microflora (Meidute *et al.*, 2008). In this respect, the basal respiration rate will reflect a combination of substrate availability and the functional capability of the soil biology to mineralise the now-available substrate.

7.4.2 Soil pH

Soil pH is often linked to soil respiration rate measurements, (Kemmitt *et al.*, 2006, Reth *et al.*, 2005, Tufekcioglu *et al.*, 2009) and yet pH seems to have little control over overall flux rates, only appearing as an interaction term in the description of flux expressed as a function of ADS. Previous studies have suggested increases in respiration levels with increasing pH (Curtin *et al.*, 1998, Kemmitt *et al.*, 2006), however, these studies focus on pH manipulation and consequent effects on pH mediated change in respiration rather than comparison of soils with intrinsically different pH.

7.4.3 Soil P and N

Available P content as measured by Olsen-P fails as a significant predictor of any flux expression rates. This situation could arise because of the nature of P in soils and how Olsen-P estimates P availability. Previous studies have commented on P content as a modifier of soil respiration, with Keith *et al.*(1997) finding P addition to slightly reduce soil respiration (fall of 8% compared to non-addition sites) under a Eucalyptus forest, suggesting the P addition caused a reduction in allocation of photosynthate to root biomass. Amador and Jones (1993), however, found that addition of P stimulated soil respiration in peat soils, but only in soils which were P deficient, adding NH_4 to higher P soils increased respiration, supporting the dependence on the observable P content effect upon the associated N availability. Notable was the fact that the latter study was carried out on soils incubated in the laboratory rather than on intact cores with roots present, as in the study by Keith *et al.* (1997). Numerous other studies have shown increases in CO_2 evolution with P addition (Fierer *et al.*, 2003a, Priess & Fölster, 2001), however, comparatively few studies have demonstrated a reduction in respiration after P addition (Hartley *et al.*, 2009). Of course, these studies focus on inorganic P addition, and comparison with a measure of natural abundance of inorganic P is difficult.

Also to consider is the fact that as Olsen-P is an expression of the bicarbonate extraction of inorganic P (at pH 8.5), the amount of P present in organic forms will be essentially ignored by this analysis. This is a notable exclusion given the large amounts of P that will invariably be associated with organic material, especially in the higher LOI soils (Achat *et al.*, 2010). The availability of organic P is of course much dependent upon the structure and mode of association with the OM, and due to the complex and rapid phosphate sorption chemistry operating at low pH, it is difficult to estimate how readily available any mineralised P would be under the high OM, low pH soils. As Olsen-P considers weakly bound inorganic P, the tight sorption of P with metals and with mineral surfaces will also not be reflected in the measurement, bearing these points in mind, outside of circum-neutral to alkali soils, it is difficult to make any connections between Olsen-P measurements and the functional measures of C-mineralisation.

Mineralisable-N appeared as a component in regression analysis for the C-mineralisation efficiency expression, suggesting a possible link between the two functions. However, visual analysis showed that the relationship was weak, and there was no clear comment that could be made regarding the relationship across the entire dataset. As the mineralisable-N will be much dependent on the amount and availability of organic-N, a similarity in the C and N mineralisation rates could be expected. However, the temperature, moisture and pH optima for both processes may vary considerably across soils types, and the proximity of the standardised conditions to these optima may well account for a degree of the un-relatedness of these functional measures.

Total N occurred in a significant interaction term with LOI in the expression of flux as a function of air dry soil. The relationship between N% and flux is shown in Figure 7.3.5, and there is a clear trend for higher flux rates at greater N accumulations. As the regression analysis includes N% as an interaction with LOI, and the direction of Figure 7.3.5 is highly similar to that of 7.3.4, it is most likely that the effect of N is through SOM. As organic materials tend to accumulate and stabilise organic N, the greater amounts of

SOM, which through substrate abundance, appear to drive most of the flux observations, are likely to co-occur with high N. This suggests that the beneficial effects of N abundance might appear to drive flux, but in fact are co-occurring with high LOI, and that most of this total N is, in fact unavailable.

7.4.4 C/N ratio

C/N ratio represents a useful indication of the general quality of SOM in terms of palatability to decomposing organisms. In the context of the basal C-mineralisation studied here, using the C/N ratio of SOM as an indicator of substrate quality assumes a homogenous substrate mass, which is, of course not actually the case. Nevertheless, C/N ratio does give a broad general picture of the nature of the SOC and therefore the potentially-mineralisable substrate. C/N ratio did not act as a significant driver in regression analysis of any flux expression. This is in agreement with Craine and Wedin (2002) who found C/N ratio accounted for only 6% of the variation in soil CO_2 emission from a temperate grassland. Increasing C/N has been shown to reduce C-mineralisation (Lamparter *et al.*, 2009), however, in the study by Lamparter *et al*. (2009), only three C/N ratio soils were compared, two with C/N ratio ~8-10, and one with C/N ~20. The situation found here is likely to be due to the general comment C/N ratio makes of the SOM, whereas the mineralisation rate will more likely be linked to the C/N of the actual substrate, which in most cases will be a distinct fraction of the SOC. This is well demonstrated by the presence of black carbon, or charcoal which would give a high C/N ratio but is essentially inert and does not reflect the quality of the metabolisable substrate (Hassink, 1994).

Killham (1994) gave threshold C/N ratio values for SOC which would be most common as a substrate for bacteria and for fungi, these values representing a continuum from soils with a generally low C/N ratio dominated by bacterial mineralisation, to soils with a higher C/N ratio where decomposition is dominated more by fungi. This is linked to previous comments made about

the role of LOI content on flux expressions, only here, the quality of the substrate has more functional meaning. Killham (1994) splits the SOC into three groups, two corresponding to the major biological groups mentioned above, and one to a C/N ratio <12.5, most likely corresponding to a substrate class which has been substantially decomposed. Very low C/N ratios have been attributed to generally more mineral-associated C (Baisden *et al.*, 2002a) which might be viewed as a poor substrate due to being physically protected. Linking the C/N ratio to these distinct components of the microbial flora did yield some interesting relationships. When expressing the flux as a function of ADS, it can be seen from Figure 7.3.12 that the higher C/N ratio soils have a much greater flux, suggesting mineralisation was retarded in the bacterial dominated soils and much greater in those soils dominated by fungi. The lower flux associated with lower C/N ratio soils may be due to the exhaustion of the preferred substrate during incubation, as lower molecular weight substrate is used up rapidly during initial stages of incubation, and the residual flux represents the turnover of microbial biomass-C for the most part. As discussed in Baisden *et al.* (2002), the low C/N ratio may also reflect the mineral association of partially decomposed material, giving a situation whereby not only is the majority of preferred substrate long been mineralised, but remaining substrate may be energetically expensive to mineralise due to physical and chemical protection mechanisms.

N availability may also be an issue in the lower C/N ratio soils, as, because these tend to be more mineral soils, N species may well have been removed to a large part by the leachate exercise prior to incubation. Higher CO_2 fluxes observed in the more fungi dominated soils may be partly due to the more substantial pool of substrate associated with the higher levels of total SOC found here. And as the higher C/N soils will also tend to have a larger amount of organic N (in total rather than in relation to substrate-C), the ability to obtain a source of N may be prolonged in the organic soils relative to the more mineral soils. Overall, the higher C/N ratio soils would appear to have an elevated C-mineralisation rate, but as with the LOI data, it is likely that this is due to the shear relative abundance of preferred substrate found in the higher C/N soils.

Mineralisation efficiency proved to give results which differed from the expression /g ADS, however, with the lower C/N ratio soils showing a greater CO_2 flux/ gSOC. This is not wholly surprising, as the mineralisation of a lower C/N ratio substrate (and therefore less complex substrate) will invariably be a more efficient process than the decomposition of a highly complex organic material such as that which makes up the bulk of the SOM in the higher C/N ratio soils. However, this is potentially misleading, as if the low C/N in fact reflects a state of considerable decomposition and mineral protection, then the higher mineralisation efficiency in the lower C/N ratio soils is more likely a comment on the higher degree of biomass turnover in the absence of a suitable external substrate.

Overall, soil C/N ratio represents a poor predictor of flux rates, and due to the complex nature of substrates within soil, using an expression for the total soil quality will invariably be at a scale which is too far removed from the quality indices required to evaluate links between substrate quality and mineralisation. However, when considering C/N ratio in the context of functional decomposition processes, it is clear that the bacteria dominated soils, although having a greater flux efficiency, are likely to be respiring on a small supply of substrate, possibly mostly acquired from the biomass itself, which highlights the dependence of bacterial communities on the 'drip feed' of substrate from plant exudates and from biomass turnover. C/N ratio is therefore useful in identifying likely differences between major decomposition pathways (i.e. bacterial or fungal mediated), but a more targeted measure of actual substrate quality is likely to act as a more accurate driving variable.

Considering the mineralisation efficiency expression where flux is given as a function of SOC content, the major finding suggests that there are two main groups with a transition group also. The higher efficiency grouping contains the lowland and generally grass or agriculture dominated systems, the lower grouping containing the two upland systems, with the two woodland habitats making up the transition. The efficiency expression could be interpreted as a link to likely SOC quality, suggesting that a greater efficiency represents an

inherently higher quality of available SOC. Within this finding, GB soils appear to be not wholly dissimilar, suggesting that quality indices of SOC could be broadly split into two or three categories in terms of expected functional response. However, without direct assessment of the actual quality of SOC, this relationship remains un-asserted yet tantalising, and limited to the stoichiometric categorisation using C/N ratio.

7.4.5 Climatic drivers

Of the climatic drivers included in regression analysis, MAP, relief and growing degree days (GDD) give the best explanatory power over flux data. Under field observations of soil respiration, it is common that rainfall will act as a major driver of soil respiration (Fierer *et al.*, 2005, Wichern & Joergensen, 2009), with timing and frequency of rainfall being highly significant for within-year observations of CO_2 flux (Harper *et al.*, 2005). As rainfall will be a major contributor to the variation in soil moisture, it is likely that an optimum rainfall will exist as a function of other prevailing conditions and limiting factors (Ruehr *et al.*, 2010). Rainfall amount has also been modelled as a significant driver of variation in soil respiration (Ouyang & Zheng, 2000). As some of the factors determining respiration rate in the field will be less relevant for a core study, it is unsurprising that the rainfall-mineralisation relationship is less strong. One possibility for the most excessive rainfall levels limiting flux rates may be due to the quality of the derived SOM that may accumulate under such conditions. As higher rainfall areas tend to cause a plant life strategy which leads to the production of less palatable biomass, this will translate to the SOM leading to a poorer substrate quality. The same could also be true of excessively low rainfall areas, where NPP is again reduced, but this time by drought stress. Relief takes the difference between minimum and maximum altitude in the sample square, and so gives an idea of the steepness of terrain, but also the complexity of the landscape. Finding relief as part of the model best predicting flux suggests that it is in the higher relief areas (more complex uplands) where a higher flux may be estimated. The Relationship to MAP

through orographic enhancement is likely to explain the inclusion of relief in this model.

GDD data shows a general reduction in CO_2 flux associated with an increase in GDD, giving a reasonable link between the in-situ growing conditions and the basal respiration rate. Observing lower fluxes associated with sites which typically experience a higher GDD value would suggest that higher NPP (assumed higher NPP under increased GDD) sites have a reduced storage of substrate-C for subsequent mineralisation. As with comments previously made regarding total C and C/N ratio of SOC, it is sensible to surmise that the decomposition dynamics of higher NPP soils are more closely linked to the turnover of LMW-C and that the majority of residual SOC is mineral associated. It is expected that the observation of a lower basal rate with GDD would be reversed in-situ, as the contribution of root respiration and rhizosphere respiration of root exudates would contribute a much greater percentage to the overall flux in higher NPP sites, whereas slow turnover of SOC would perhaps contribute more in lower NPP sites. Indeed, spatial studies have revealed a positive relationship between CO_2 efflux and NPP (Hibbard *et al.*, 2005)

7.4.6 AVC Categorisation

The AVC class structure provided some ability to differentiate between broad categories of flux estimates, and across the three flux expressions, the situation was quite different. Expression as a function of ADS gave a much greater flux in the upland classes (moorland grass/ mosaic, heath/bog) and woodlands than the lowland grass-dominated classes. This is a fair reflection on the outcome of some of the regression output, whereby the generally more productive (NPP wise) sites would translate to having a lower basal flux rate. This is a likely to be a further expression of the combined variables (LOI, C/N, %N, BD) which would explain the flux in a multiple component model. In terms of the independence of each AVC class, it would appear that AVC class structure is not structured in an appropriate way to

fully reflect the likely variation in mineralisation rates. This is exemplified by the comparison of the fertile and infertile grassland, which would be expected to differ markedly in flux rates, but in fact are almost identical. The fertility score gradient along which these two groups are differentiated is likely to be less relevant under the conditions of the basal rate estimate, as the rate becomes more related to the functional substrate quality as previously discussed. The expressions as a function of area shows well the differences in flux when up-scaled, and it is immediately obvious that the lowland grassland sites exhibited a greater flux than the upland classes. The difference between grass and crops is interesting, suggesting that perhaps the cropland sites retain little SOC (explainable by crop removal) and therefore have a reduced basal mineralisation capacity. Mineralisation efficiency gives a significant difference between the lowland groups and the upland groups, suggesting that AVC, although illustrating a general trend, might be too high in resolution when attempting to categorise a functional expression such as mineralisation.

Testing the within-groups effects of the soils and climatic variables on measured flux suggested some marked differences. As with the complete dataset, LOI dominated most of the AVC classes (Table 7.3.2), but was absent for three of the eight classes. Upland woodland provided the strongest driving by LOI (Figure 7.3.6), accounting for 61% of the variation. A similar picture was also found in the heath/bog class, although explanatory power was somewhat lower. This suggests that the abundance of SOM and its effects on flux is variable between vegetation types. This reinforces the general comment that vegetation type might characterise the observed flux by forming a SOM which, under standardised conditions, is variably decomposable. Moisture appeared alongside BD as a significant component of the model explaining Fertile grassland fluxes. This suggests textural quality might play a role in fluxes such that lower BD soils with a greater porosity (and therefore high water holding capacity/ soil moisture) will favour a greater respiratory flux. Given this is confined to the fertile grassland, the intensive management of these systems could be inferred to a degree from this observation, and further investigation of this situation could link the soil

textural qualities and management to C turnover dynamics on a large spatial scale. Lowland woodland was best explained by total N content. As previously discussed, this could be a proxy for LOI, however, LOI did not appear in the regression analysis of lowland woodland. This could therefore link higher N content with a greater flux such that nutrient supply acts a stimulatory component of woodland respiration. This would follow that SOM quality was a greater limiting factor than quantity as in other AVC classes. The very low explanatory power found in Crops and weeds, and the lack of a significant model in tall grass herbs suggests that constrains on respiration are not covered by this study, and that the variables classically thought to control respiration are not so under more intensive land classes.

In terms of overall usefulness, the AVC classification obviously provides a reasonable framework for the categorisation of soils in respect to mineralisation rates. However, because of the major criteria upon which the AVC classes were formed (soil nutrient content and the level of disturbance/shade), groups exist to separate vegetation types, which in respect to SOC decomposition dynamics, are very similar. Thus it would possibly be more sensible to adapt the AVC structure to combine some groups to reflect the broader scale controls that exist on general C turnover. It may also be of interest to link classifications based on the vegetation types, with some functional expression of soil type. This might include a comment regarding soil texture (which is likely to be more relevant for functional response than the conventional soil-type classifications) to create a vegetation-soil class system. This might better reflect the conditions which are more relevant to the functional responses of mineralisation, as the quality of the derived substrate and the physical environment within which it is decomposed are ultimately likely to be more important than differences between above-ground species assemblages.

7.4.7 Overall model.

Taking into account both sets of descriptive variables, an overall model was formulated which best described the flux as a function of air dry soil. This model contained LOI, N % and relief, with a single interaction term of LOI and N %. Given the previous observations regarding the repeated role of LOI and N % in the regression analysis, this reinforces the role of SOM accumulations in leading to a higher flux under standard conditions. This also suggests that if greater fluxes are possible for these more organic soils when conditions are right, it is more the prevailing conditions than the inherent chemical recalcitrance which controls their in-situ decomposition. This model explains more than the soils or climatic data alone, and at 44%, is reassuring given the size and complexity of the dataset. However, crucially, the remaining 66% is explained by measurements not currently made, and suggests more attention is needed on the possible variables which might control respiration. A quantitative interpretation of the impact of vegetation type will possibly add to this model, as the individual AVC classes were seen to differ both in flux and in the relationship of variables to flux.

7.5 Conclusion

Across the range of soils studied here, the broad scale drivers of basal mineralisation appear to be dominated by SOM content. Climatic drivers of rainfall, and the value obtained for growing degree days, also appear to have some controlling effect on measure basal soil respiration. The latter relationships are the opposite to what might be expected in natural systems, with the lower productivity systems giving a greater basal flux rate. It is proposed that this relationship is a further expression of the greater flux being observed in higher LOI soils, demonstrating an accumulation of organic matter under less productive conditions leads to a greater potential mineralisation. Higher productivity systems will conversely produce a soil which has lower stocks of potentially decomposable-C, and residual C-mineralisation is likely to be derived from microbial biomass turnover rather than SOC turnover. There is a possibility that the linking assessment of SOC quality indices with the observed groupings derived from the mineralisation efficiency expression, could provide a useful means of categorising GB soils based on a small number of SOC quality groupings. Unlike the flux as a function of dry mass, and inferences regarding C-stock and expected quality, mineralisation efficiency may prove a more useful link between actual quality and functional response.

Nutritional status of the soils appeared to be less important in predicting basal C-mineralisation apart from when C/N ratio was used as a categorisation tool for demonstrating substrate use efficiency of distinct microbial functional groups. AVC grouping allowed for differentiation between some groups, but it is suggested that a broader functional grouping strategy would better fit the data and provide a more intuitive approach to estimating expected basal CO_2 flux from the observed vegetation grouping.

The reasonably poor climatic sensitivity of fluxes is expected to be a result of the combination of resolution issues (e.g. rainfall is a poor substitute for soil moisture, which is a much better flux predictor) being unable to adequately pick up on the variability in flux caused by interacting factors, coupled with

the inherent low variability in climatic conditions observable across the British isles.

Overall models and interpretation of the driving effect of variables within AVC classes suggest that there is a large amount of residual variation not explained by the suite of variables used here. Understanding the broad-scale drivers on respiration will undoubtedly be improved by increasing the focus on collecting information on soils related not only to the physicochemical conditions at a sample, but also of the interaction of vegetation type with soil textural quality.

Chapter 8. Radiocarbon estimates of SOM turnover in British top soils using samples collected during a national-scale survey of Great Britain.

8.1 Introduction.

Radiocarbon (^{14}C) exists naturally in terrestrial systems due to uptake of $^{14}CO_2$ by plants and subsequent incorporation into biomass and soil. Natural abundance of ^{14}C is small (~.0000000001% of total C) and due to its radioactive decay (half life of ~5730 years) can be used as a dating tool on a millennial timescale. The production of 'bomb carbon' due to atmospheric weapons testing during the late 1950s and early 1960s caused a pulse in atmospheric $^{14}CO_2$ content which peaked at roughly twice the pre-bomb levels. This produced a near-conservative tracer within terrestrial systems. Due to the availability of high-resolution atmospheric data, bomb-^{14}C can be used to estimate the incorporation and loss of C from soil, and therefore turnover of Soil Organic Carbon (SOC) can be estimated on a decadal timescale. This approach allows for estimation of slower-cycling SOC which is typically not possible during experimental studies of surface fluxes, which tend to focus on fast pools. This makes radiocarbon a uniquely useful tool in understanding SOC turnover.

The application of bomb-^{14}C as a modelling tool has been used in a number of previous studies (Bol *et al.*, 1999, Gerasimov, 1974, Harkness *et al.*, 1986, Harrison, 1996, O'Brien, 1984, O'Brien & Stout, 1978, Tipping *et al.*, 2010, Trumbore, 2000, Trumbore, 1993). Generally these approaches identify pools with fixed turnover times that aim to represent functionally different components of SOC with likely differences in terms of stabilisation and recalcitrance. Pools usually reflect a passive component with a very long turnover time (millennial scale) and one or more faster cycling components which have turnover times of hundreds or tens of years. The pool approach used in the current study is similar to those proposed by a number of previous studies (as per references above), however the terminology assigned to the pools provides a small source of inconsistency. In this study, we use the terms 'slow' and 'passive' to identify pools with either a 20, or 1000 year turnover respectively. However, previous studies have used terms 'active' and 'passive' to describe similar turnover pools (Harrison, 1996).

Baisden and Parfitt (2007) use ‘active’ to describe a pool with a ~1 year turnover, and ‘stabilised’ to refer to a decadal turnover pool (equivalent to the slow pool used in the current study). This situation arises due to the theoretical nature of distinct SOC pools, and the extension of the theory to ascribe turnover rates to said pools. Whilst using minimal pools, the variation in terminology is likely to be only a minor issue, as the assigned turnover times represent large functional differences between the pools. The need to identify SOC pools with distinct turnover times and stabilisation properties is common within established SOC models (e.g. CENTURY (Parton *et al.*, 1987), Roth-C (Jenkinson & Coleman, 2008)). Linking theoretical pools to actual components of SOC is the logical step towards verification of the pool approach, and some studies have achieved reasonable agreement between recalcitrance indices and model pools (Zimmermann *et al.*, 2007). The ^{14}C-derived turnover time of SOC has also been linked to recalcitrance indices with some success (Gaudinski *et al.*, 2000, Trumbore & Zheng, 1996), supporting the increased age of SOC with increased recalcitrance in some, but not all circumstances. This latter point highlights the need to better understand the means by which C becomes stabilised in soil, and how the intrinsic recalcitrance of a substance might interact with protection mechanisms within the soil structure.

To investigate the general rate of SOC turnover on a national scale, we carried out radiocarbon modelling of surface SOC from soils originally collected during Countryside Survey 2007. Steady-state models were applied to the data to derive the Mean Residence Time (MRT) of bulk SOC and the allocation of SOC to pools with pre-defined turnover times. These pools are comparable with those observed by Amundson (2001), and are broadly similar to pools used by Foley (1995) or those used in the CENTURY model (Parton *et al.*, 1987). The data was investigated using a range of climate and soils characteristics as possible explanatory variables. The vegetation classification system used in CS 2007 formed the basis of the categorisation process to investigate differences between vegetation types.

It was hypothesised that C cycling would be strongly influenced by the climatic variability across Britain, specifically that conditions more favourable for growth (warmer, only moderately wet) would show a faster turnover. It was also hypothesised that there would a strong effect of litter quality of turnover of SOC such that more complex litter would reside longer in the soil, and therefore lead to a dominance of slower-turnover components.

8.2 Methodology

8.2.1 Sample choice

The experimental aims of this study required that sampling would obtain a number of samples from a range of Countryside Survey (CS) Aggregate Vegetation Classes (AVC). The requirement for systems to be semi-natural and in some degree of stable vegetation cover restricted the AVC classifications that could be selected from. This process is shown in Table 8.2.1 and shows the exclusion of the more intensively managed systems which are likely to have had a regular change in vegetation cover and experience a high degree of biomass removal.

The remaining constraint on sample choice was a purely logistical one of financial and time implications of analysis. Radiocarbon dating of organic material using conventional Accelerator Mass Spectrometry (AMS) is both a costly and lengthy exercise. Given these issues, a total of 60 samples were chosen for analysis. A key assumption of the modelling process (detailed in section 8.2.6) is that systems are to be in steady state in terms of C input and loss. This of course is highly unlikely to exist under natural conditions, with systems usually either aggrading or losing C. However, assuring a continual cover of vegetation type would ensure errors associated with disturbance and land-use change were minimal, whilst satisfying the requirement for a sample to be reasonably representative of the specific vegetation type. The CS surveys have been carried out three times in recent decades, and due to the common vegetation assessment process, the vegetation can be assured back to the survey of the 1970s. This provided the first filter of sample collection, and by selecting only those sites which had a consistent AVC class over the three CS surveys, sample selection could begin. Within each AVC class, the samples were sorted using the Rand() command in Excel, and from this list, samples were then put through a second filter for assessment of vegetation persistence.

Table 8.2.1 CS AVC classes and inclusion in ^{14}C analysis.

AVC Class	AVC Class description	Used in ^{14}C analysis?
1	Crops/Weeds	No
2	Tall grass/herbs	No
3	Fertile grassland	Yes
4	Infertile grassland	Yes
5	Lowland wooded	Yes
6	Upland wooded	Yes
7	Moorland grass/Mosaic	Yes
8	Heath/Bog	Yes

The UK Land Use Map created by Dudley Stamp during the 1930's (Stamp, 1932) gave a vegetation classification which can be compared with current AVC classes to find common definitions. Comparison required some further assumptions to be made about land use categorisation and rules of acceptance or rejection were defined. The comparison of land use classes are found in table 8.2.2. Stamp's classifications were much broader than the current AVC classes, and lacked the definition between some of the more subtly different vegetation types. This could become problematic when making assumptions about continual fertility of grasslands, for instance. Most notable is the possible crossover from infertile to fertile grassland which would be obvious during the CS definitions, but not so under Stamp definitions. However, there was no other method to further support the exact vegetation type over as long a period of time as the Stamp maps, so these small assumptions were made in order to be surer of consistent vegetation.

8.2.2 Method for comparison with Stamp maps.

Using National Grid Reference (NGR) locations for each sample, comparison with the Stamp maps was made by identifying common features and then confirming the sample position visually on an ordinary Ordinance Survey

map. Rules for comparison were defined such that common features were likely to not have changed between 1930's and present day. These are listed below.

1. Coast line features such as headlands, stacks, bays.
2. Historical features such as tumuli, burial chambers, castellations.
3. Major watercourses.
4. Roads (careful comparison was needed here).
5. Topographical features such as valleys, ridges, hills, summits.
6. Mainline railways

Care was needed to not place emphasis on a small number of discrete features, especially drainage features such as ditches, field boundaries, vegetation boundaries and urban boundaries. Rules of acceptance or rejection were based on ascertaining the degree of commonality between mapped points. These are such that:

1. Commonality is assumed when:
    a. The modern AVC is clearly within a well-defined patch of allocated land that agrees with table 8.2.2.
    b. At least three common features can be confirmed that adequately assure correct sample location.
    c. There are no obvious changes of (non vegetation class) features in proximity of the defined point.
2. Rejection is assumed when:
    a. The above are not all satisfied.
    b. The sample point lies on or close to a vegetation class boundary.
    c. Ambiguity arises due to issues with regard to map resolution.

The process of sample selection and continuous vegetation resulted in having 12 samples for AVC classes 3, 4, 7 and 8, and six samples for AVC classes 5 and 6. The small number obtained for the two woodland classes

was due to the generally low number of woodlands which were sampled, and the few which got through the filtering processes.

able 8.2.2 Assigned Stamp classes to AVC classes

AVC Class	AVC Description	Stamp's Class	Stamp's Description
3	Fertile grassland	Light Green	Meadow and permanent pasture
4	Infertile grassland	Light green	Meadow and permanent pasture
5	Lowland wooded	Dark green	Forest/Wooded
6	Upland wooded	Dark Green	Forest/Wooded
7	Moorland grass/ Mosaic	Yellow	Heath moor & rough pasture
8	Heath/Bog	Yellow	Heath moor & rough pasture

8.2.3 Collection

Soils were collected during countryside survey 2007 using protocols adopted by CS 2007 (Emmett *et al.*, 2008). Briefly, soils were sampled in PVC tubes having a length of 15cm and an internal diameter of 3.8cm with one end of the tube bevelled to a finer edge for easier ground penetration. Surface vegetation (if present) was parted, and the tube placed on the soil surface after removal of surface litter. The tube was cut into the soil with a sharp knife by cutting around the outside of the tube. The tube was pushed into the soil and then hammered until the full 15 cm was filled with sample. The tube was removed from the soil using pliers, bagged and labelled before being sent by the field team to CEH Lancaster.

8.2.4 Processing for radiocarbon

After selection, soils were collected from storage at CEH Lancaster and a subsample was ball-milled. Due to the requirement by the NERC Radiocarbon Lab (RCL) for a minimum of 1g C per sample, Loss On Ignition (LOI) data for each sample was used to calculate the necessary mass of soil to be submitted for analysis assuming a C content of 55% of LOI. To ensure sufficient sample mass was available to cover any possible issues with analysis, twice the required amount was sent for analysis. Representative samples were taken from selected soils and delivered to the RCL for analysis.

8.2.5 Radiocarbon analysis

Samples were analysed for ^{14}C content at the Scottish Universities Environmental Research Centre (SUERC) using the Single Stage AMS (SSAMS) as described by Freeman et al (2008). Samples are prepared by first soaking in 0.5 M HCL at room temperature (to remove carbonates) before being washed with deionised water and dried. Carbon is then obtained from the sample by combustion in a high-pressure bomb in the presence of high purity oxygen after which carbon is converted to an iron-graphite mix for analysis. The ^{14}C content is expressed as a percentage relative to an oxalic acid standard, where 100% enrichment would be equivalent to the activity in 1950, prior to any anthropogenic effect on the ^{14}C activity. Further details on the analytical process and accuracy can be found in Tipping et al (2010).

8.2.6 Modelling and data processing.

Two models were used to provide residence time and pool allocation data for each analysed sample. Both models used measured ^{14}C values to predict allocation of C to SOC pools based on the following process:

Total SOC pool is calculated using C content and bulk density data. This data is then used to calculate annual input of C to the respective pool (i.e. 20 year pool), and therefore the amount of ^{14}C. Soils are assumed to be in steady state, such that the annual input of C is balanced by losses from CO_2 and DOC leaching. The residual ^{14}C in SOC is then calculated based on the annual input (relative to atmospheric concentration data) minus the natural radioactive decay of ^{14}C. There was a lag of two years built in to the model in terms of the delay between transfer of atmospheric ^{14}C to SOC, this to take into account the residence time of ^{14}C in the vegetation. The models were optimised by minimising the sum of the squared differences between observed and modelled values of soil ^{14}C using the solver add-in in Microsoft Excel (Tipping *et al.*, 2010). Model output is summarised in section 8.3, but raw model output can be found in appendix two.

Single-pool (MRT) model

This model contains a single, homogeneous SOC pool that receives litter input, as described above. There is a fast turnover pool fitted to the model in which the litter turns over rapidly such that, in comparison to the main SOC pool, this fast pool is essentially zero.

Two-pool model

The two-pool model expands on the single-pool model such that the litter input (after the assumptions about the fast pool exclusion) is allocated to one of two pools, termed slow and passive, which are not connected to each other, and have fixed residence times of 20 and 1000 years respectively. Adjustment of the slow-pool size (using Solver) is made to fit the modelled ^{14}C value to the observed ^{14}C. This is similar to the approach used in the single-pool model, where only one parameter in the model is adjusted.

8.2.7 Data analysis

All statistical analysis was carried out using R statistics (R, 2010). Modelled output was assessed for normality using quantile-quantile plotting prior to any analysis, and log-transformation was carried out if necessary. T-tests and ANOVA were used for investigating between-groups differences, and in the case of non-normality, Wilcoxon rank-sum tests were used. Regression analysis was carried out to identify relationships between modelled output and environmental variables. Visual assessment was carried out using pair-wise plotting of variables and modelled output, and models were constructed using terms expected to relate to modelled output. Manual deletion of non-significant terms resulted in the minimal most statistically significant model.

8.2.8 Driving variables

Variables associated with soil physic-chemical characteristics, climate data and other data were obtained from either the CS 2007 SAS database or from The Meteorological Office (for climatic data 1961-90 averages). Specific Leaf Area (SLA) index data was obtained from personal communication with Simon Smart at CEH Lancaster, and is calculated by expressing the leaf area as a function of the leaf dry biomass. Analysis for explanatory variables was carried out prior to analysis by the CS 2007 team according to Emmett et al (2008). Climatic data for the 1961-1990 averages were referenced to the 5 km square of sample origin, and the data for Mean Annual Precipitation (MAP), Mean Annual Temperature (MAT) and Growing Degree Days (GDD) was extracted and included in the dataset. GDD is calculated by the Meteorological Office and is defined as the mean number of degrees the temperature has gone above or below a defined temperature threshold. This is then summed from daily values to give an annual value describing the suitability of a location fro growth above an assumed threshold of 5.5°C. GSL is derived by summing the number of days within a period extending from the first day in the year in which the mean temperature is > 5°C for five

consecutive days, to the last day in which the mean temperature is > 5°C for five consecutive days.

For regression analysis, data was split into a hierarchical system to permit investigation into variables which would likely have more control over modelled output, in an order. This was done so as to reduce the complexity of regression models and to allow for interaction terms to be estimated in a sensible manner. Soil physico-chemical characteristics were placed as the primary data set as it was proposed that these variables might offer greatest control over general SOC turnover. Climatic variables were then grouped into a second tier of investigation as it was proposed that they would act more broadly in any controlling capacity. The variables included in analysis are listed in Table 8.2.3.

8.2.9 Classification effects

One of the key questions of this study was to assess the usefulness of the AVC classification system in terms of modelled radiocarbon SOC turnover. After assessment of the between-groups differences and exploration of classification systems, soil type and soil texture was also investigated as a possible means to classify modelled output.

Table 8.2.3. Variables structuring for hierarchical data analysis.

Broad Grouping	Data type	Name
Soil Physico-chemical	Continuous	Bulk Density, pH, Loss On Ignition, C %, N %, C/N ratio, Olsen-P,
Climatic	Continuous	Mean Annual Precipitation, Mean Annual Temperature, Growing Degree Days
Vegetation Groupings	Categorical	Aggregate Vegetation Classification
Soil Classifications	Categorical	Soil type, Soil texture class

8.3 Results

8.3.1 AVC Class physico-chemical summary

The basic characteristics of soils making up the six AVC classes used during this study are outlined below. In order to identify the potential usefulness of the AVC class system in terms of explaining radiocarbon data, it was important to investigate key soil properties and underlying patterns between and within each class. All trends observed in soil physico-chemical properties were consistent with those reported for the whole CS dataset (Emmett *et al.*, 2010).

8.3.2 Soil pH

The distribution of pH across all AVC classes is shown in Figure 8.3.1 and the histogram followed an expected pattern, with the majority of soils being found in ph 4-6 range. When classified by AVC, pH is shown to fall with increasing AVC class (Figure 8.3.2). There was significant effect of AVC class on soil pH ($p < 0.001$), and pairwise comparisons between AVC classes are shown in Table 8.3.1.

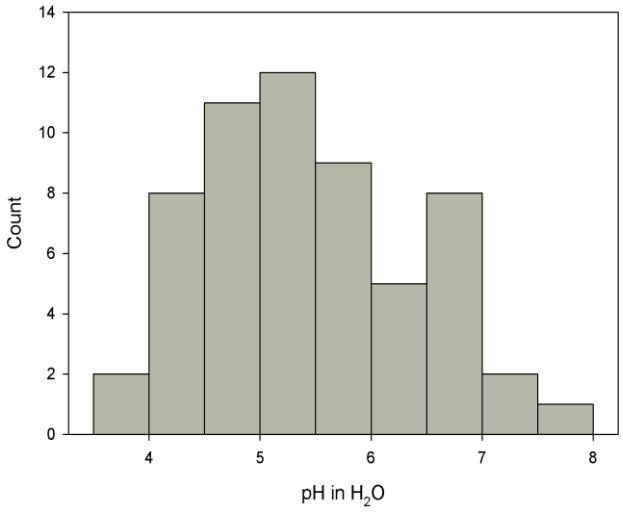
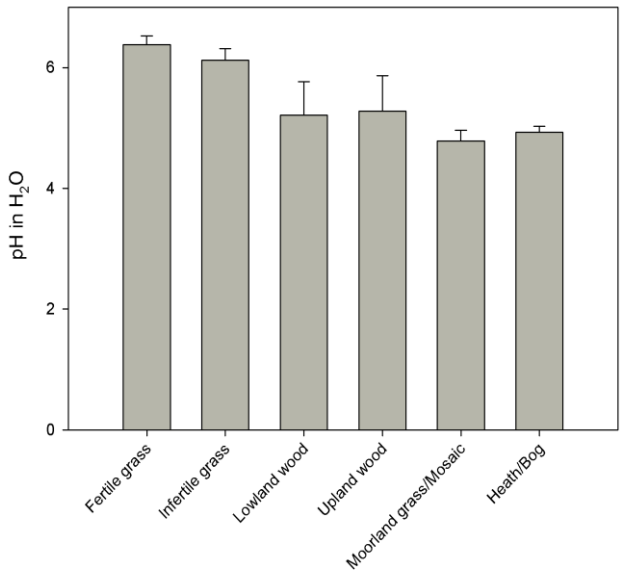


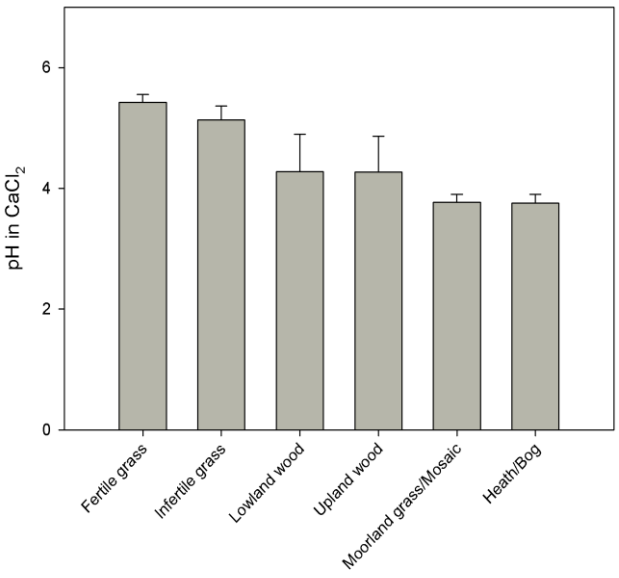
Figure 8.3.1 Histogram of pH in deionised H_2O across all AVC classes.

Table 8.3.1 Significant pairwise comparisons of AVC class for soil pH.

Class Pairing	*p* value
Lowland wood- Fertile grass	0.031
Moorland grass/mosaic- Fertile grass	< 0.001
Heath/Bog-Fertile grass	< 0.001
Moorland grass/mosaic- Infertile grass	< 0.001
Heath/Bog-Infertile grass	0.003



(a)



(b)

Figure 8.3.2 pH in deionised H_2O (a) and $CaCl_2$ (b)

8.3.3 Bulk density

Bulk density variation across AVC (Figure 8.3.3) showed a general fall in bulk density from fertile grass to heath/bog. The transition in bulk density values is reinforced by the ANOVA significance (p= <0.001) of this relationship. As with pH, the pairwise comparisons revealed a lowland-upland split (Table 8.3.2), but the split between lowland woodland and upland woodland, although appearing notable based on figure 8.3.3, fails to be significant at this level. The upland group is less homogenous though than the lowland group, with significant difference (p= 0.05) between moorland grass/mosaic and heath/bog.

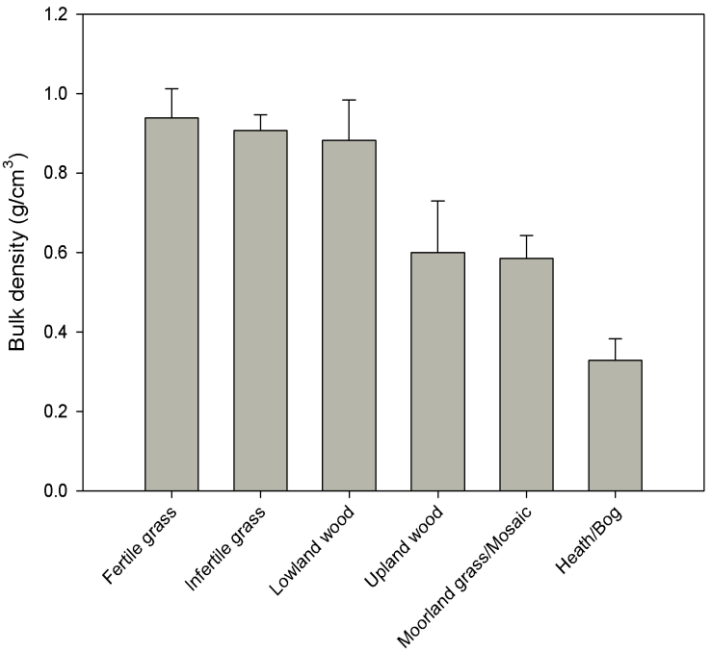


Figure 8.3.3 Bulk density (g/cm^3) across AVC class.

Table 8.3.2 Significant pairwise comparisons of AVC class for bulk density

Class Pairing	*p* value
Upland woodland – Fertile grassland	0.045
Moorland grass/mosaic – Fertile grassland	0.002
Heath/bog – Fertile grassland	< 0.001
Moorland grass/mosaic – Infertile grassland	0.006
Heath/bog – Infertile grassland	< 0.001
Heath/bog – Lowland woodland	< 0.001
Heath/bog – Moorland grass mosaic	0.05

8.3.4 Soil C, N and P

Soil C and N percentage content varied significantly across AVC class (p= <0.001). As seen in Figure 8.3.4, the upland classes tend to be associated with higher total C and N. Pairwise comparisons for these values can be found in Table 8.3.3, based on which is the general situation that the heath/bog class was significantly different from the remaining classes in respect to both % C and % N. C:N ratio, although variable across the AVC classes, was not significant at the 5% level (p= 0.06). The weak significance does suggest some relationship, and in pairwise comparisons, Heath/bog and Infertile grass (p= 0.053) appeared to be the main driver behind this.

The general pattern noted in C % in figure 8.3.4 continued in the calculated total C pool values (Figure 8.3.5), although it is clear that pool size was not vastly dissimilar across the classes, with pair-wise comparisons only giving lowland woodland and heath/bog a significant difference (p= 0.018). The relationship between bulk density and carbon content is shown in Figure 8.3.6, the exponential decay regression giving a highly significant fit (r^2= 0.88, *p*= <0.001).

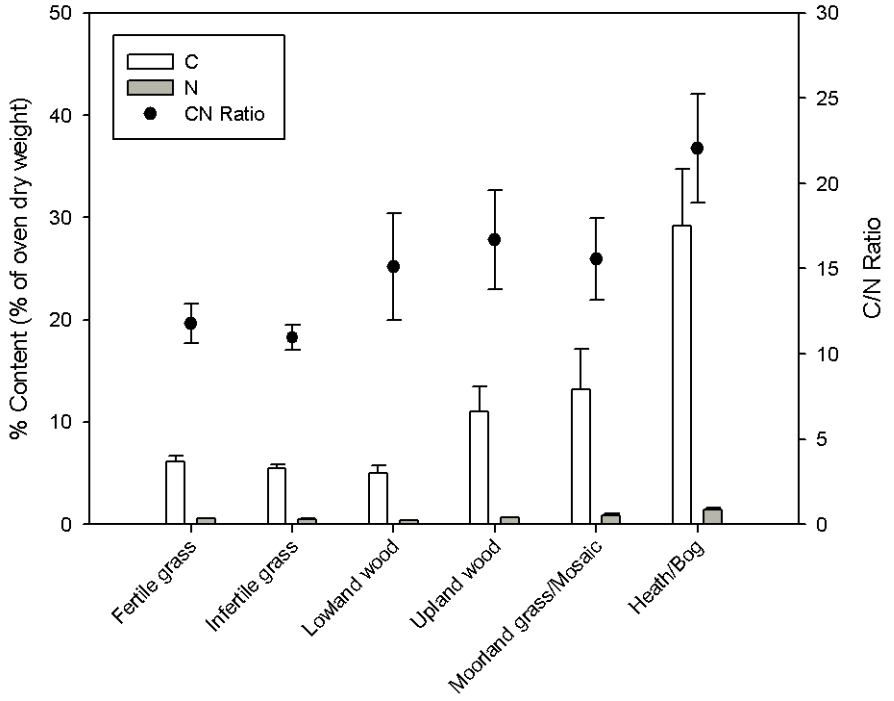


Figure 8.3.4 Percent C and N content and the associated C:N ratio of air dry soil.

Table 8.3.3 Pairwise comparisons across AVC classes for C% and N% content. *NS*=non-significant

Class Pairing	p value (for %C)	p value (for %N)
Heath/bog – Fertile grassland	< 0.001	< 0.001
Heath/bog – Infertile grassland	< 0.001	< 0.001
Heath/bog – Lowland woodland	< 0.001	< 0.001
Heath/bog – Upland woodland	0.038	*NS*
Heath/bog – Moorland grass/mosaic	0.002	*NS*
Heath/bog - Lowland	*NS*	0.020

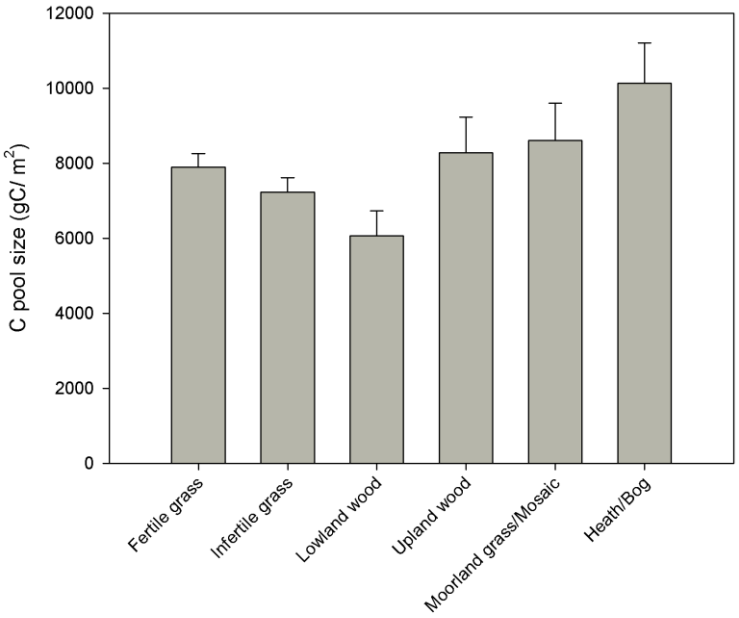


Figure 8.3.5 Calculated C pool size by AVC class

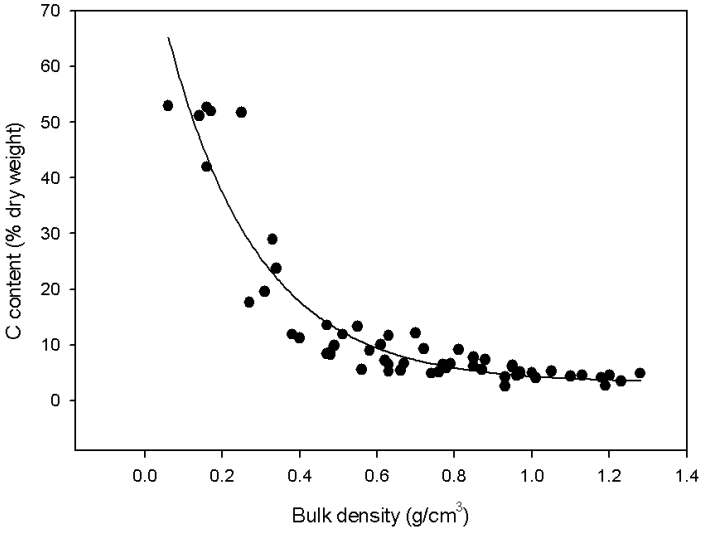


Figure 8.3.6 Bulk density and carbon content. Regression uses a single, 3 parameter exponential decay model and gives r^2= 0.88, p<0.001.

8.3.5 Olsen-P

Phosphorus content (Olsen-P) varied across AVC class (p= <0.001), and as seen in Figure 8.3.7, the trend was for a decrease from fertile grass through to moorland grass/mosaic. Deviating from this pattern, the heath/bog class had an Olsen-P content comparable with that of the fertile grass class (p= 0.16), which was markedly higher than the four remaining classes. Post hoc tests show significant differences between fertile grass and the infertile grass, lowland wood, upland wood and moorland grass/mosaic classes (p values 0.003, 0.002, 0.011, <0.001 respectively). Heath/bog-moorland grass/mosaic comparison narrowly failed significance at the 0.05 level (p= 0.052) and was not significantly different from the remaining classes.

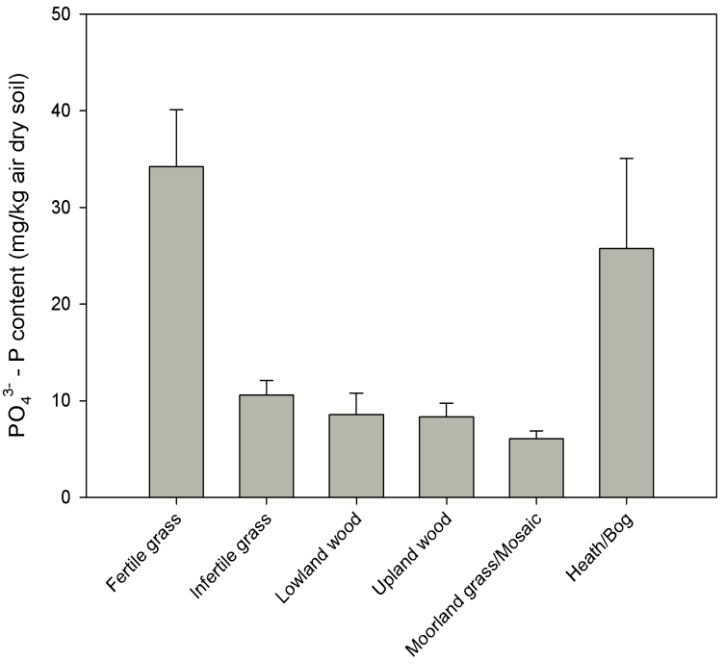


Figure 8.3.7 P content of soil (Olsen P) by AVC class

8.3.6 AVC class climatic summary.

Rainfall and temperature.

Rainfall and temperature summary values from the 1961-1990 average is shown in Figure 8.3.8. Between-groups differences in both measures were observed, and these are summarised in Table 8.3.4. Figure 8.3.8 appeared to show a lowland-upland shift in both temperature and rainfall data across the AVC classes, this is supported statistically, with temperature and rainfall differing between groups when assigned to either lowland (fertile grassland, infertile grassland and lowland woodland) or upland (upland wood, moorland grass/mosaic, heath/bog) (p=< 0.001).

Table 8.3.4 Significant pair-wise comparisons for 1961-90 MAP by AVC class.

Class pairing	*p* value
Fertile grassland - Infertile grassland	0.019
Moorland grass/mosaic - Infertile grassland	<0.001
Heath/bog - Infertile grassland	<0.001
Lowland woodland - Infertile grassland	<0.001
Lowland woodland - Upland woodland	0.028
Lowland woodland - Moorland grass/mosaic	<0.001
Lowland woodland - Heath/bog	<0.001

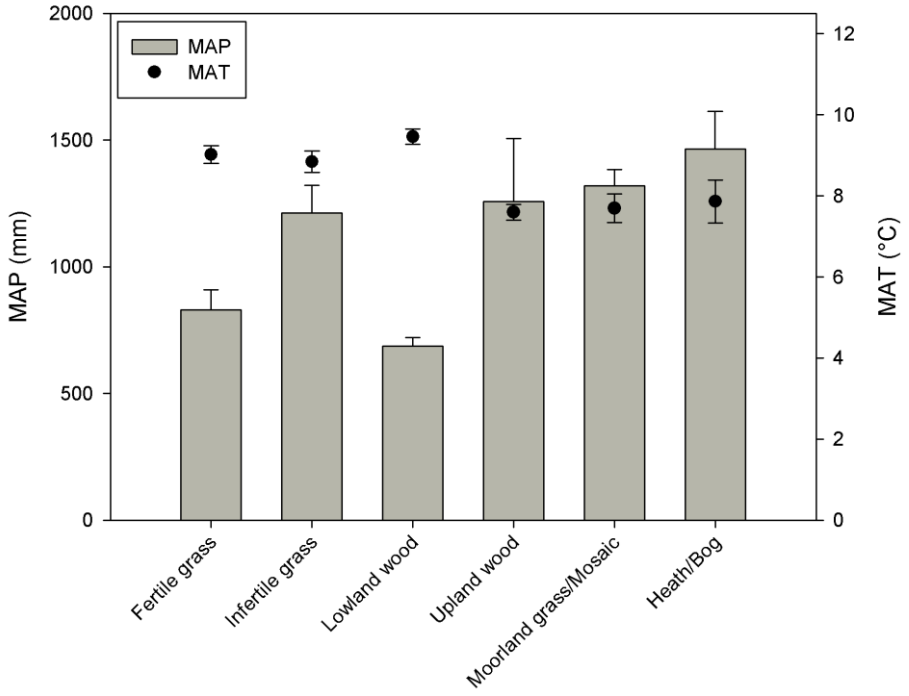


Figure 8.3.8 Mean annual air temperature and rainfall for the period 1961-1990 across AVC classes.

Growing Season Length (GSL) and Growing Degree Days (GDD)

Figure 8.3.9 showed fairly uniform GSL values across all AVC classes, with no significant difference (p= 0.75). GDD did vary across AVC however, with the upland-lowland split being statistically supported (p= <0.001).

The relationship between GSL and GDD (Figure 8.3.10) showed the two quotients are related, but not interchangeable terms. As a linear relationship would predict GSL values beyond 365 (which is impossible), this relationship cannot be usefully extrapolated beyond the current data set. An exponential rise to max (max being 365 GSL days) provided a more useable relationship. However, as there was data for 365 days GSL that does not fall on either regression line, it sufficient to conclude the two quotients to be independent of each other.

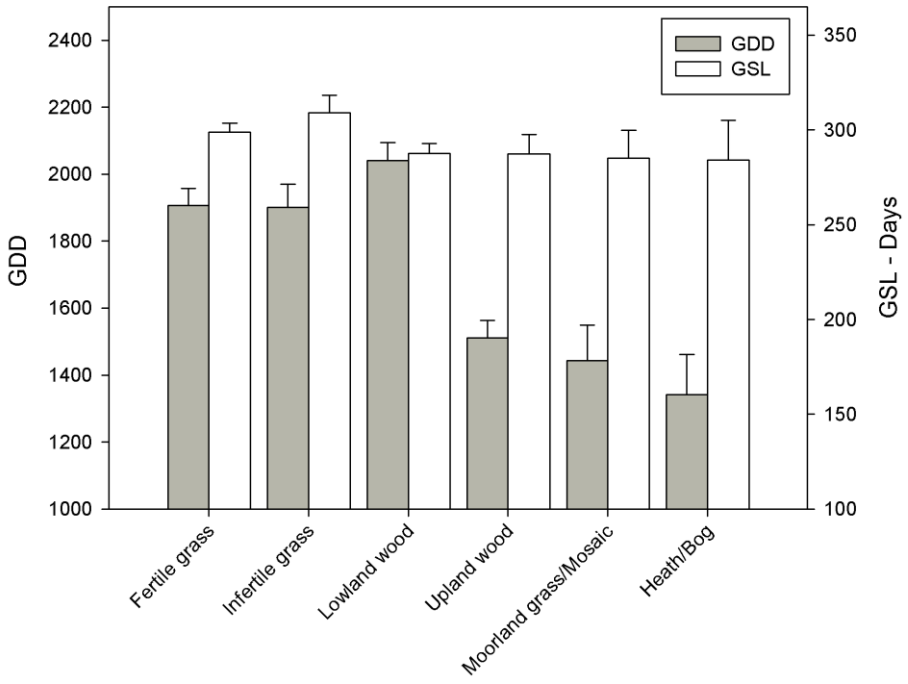


Figure 8.3.9 GDD and GSL values for AVC classes.

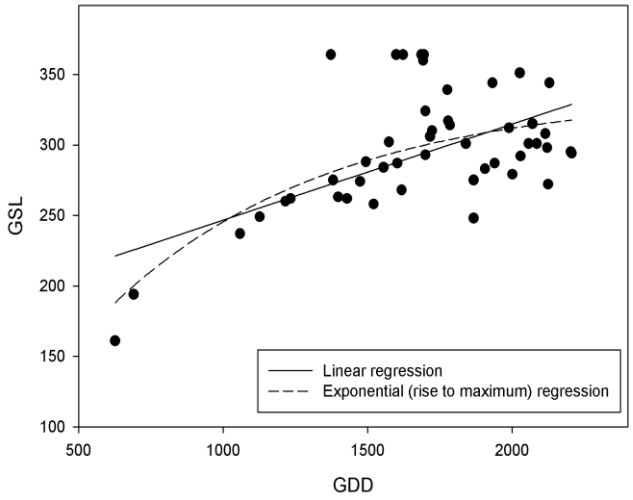


Figure 8.3.10 GSL and GDD values across all data. Linear and exponential regressions are significant (p=<0.001, adj r^2 = 0.36, p=<0.001, adj r^2 = 0.48 respectively)

8.3.6 Specific Leaf Area index

As shown in Figure 8.3.11, Specific Leaf Area (SLA) index varied considerably across AVC class, but most striking was the relative tightness of the distributions, with the grass-dominated classes having a much smaller range than remaining classes, especially upland wood. Statistical analysis was carried out to identify differences across the AVC classes, the output of which is summarised in Table 8.3.5, the overall variation being significant ($p = <0.001$).

To determine how related SLA values are to soil characteristics, multiple linear regression was carried out between SLA and the selected soil characteristics after visual assessment of pair wise plots. Sequential removal of non-significant terms in the linear model resulted in three significant factors. Bulk density acted as a significant driver of SLA ($p = 0.007$) and an interaction between C/N ratio and N% interacted in a significant model ($p = 0.037$)

The same approach was also carried out using climatic data and expressions of growing season length and growing degree days. The linear model output suggested a positive relationship with mean annual air temperature ($p = 0.013$), as well as a significant interaction ($p = 0.040$) between rainfall and growing degree days.

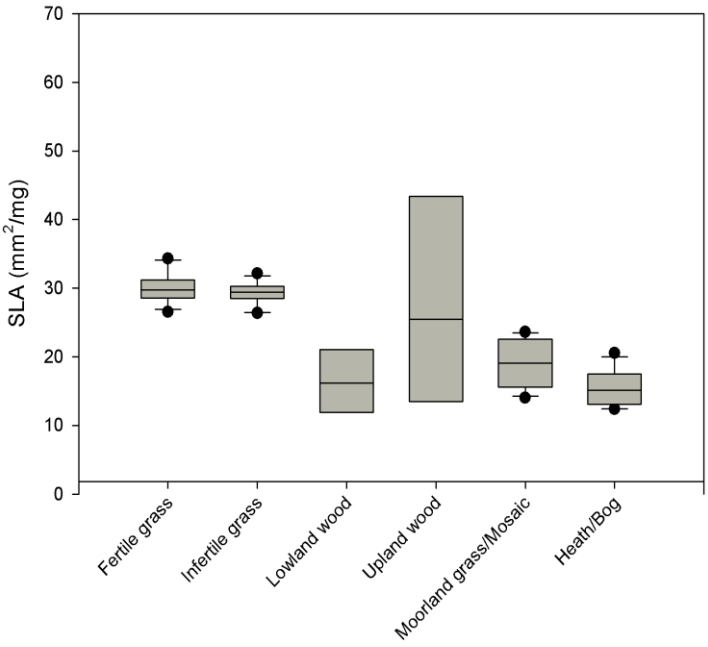


Figure 8.3.11 box plot of SLA values across the six AVC classes

Table 8.3.5 Significant (p=<0.05) comparisons from ANOVA analysis of SLA across AVC types. Comparisons were made using Tukey's HSD test.

AVC comparison	p value
Lowland wood-Fertile grassland	0.003
Moorland grass/mosaic-Fertile grassland	0.004
Heath/bog-Fertile grassland	0.000
Lowland wood-infertile grassland	0.005
Moorland grass/mosaic-Infertile grassland	0.009
Heath/bog-Infertile woodland	0.000
Heath/bog-Upland woodland	0.007

8.3.7 Raw ^{14}C (% absolute modern) data.

Investigating the general spread of radiocarbon content for samples across all AVC classes revealed that 63% of samples were highly enriched with modern (bomb) carbon. The histogram (Figure 8.3.12) shows a degree of skewness (-1.4) and two notable outliers with ^{14}C (% abs. modern) values of 60.6 and 69.9, were found in the moorland grass/mosaic and fertile grassland classes respectively. These samples were removed from further analysis due to concerns about the possible contamination of these samples from atmospheric input of ^{14}C-dead particulates from fossil fuel combustion. Mapping of these points revealed they were in proximity to urban or industrial areas, and so the removal was justified. After the removal of two outlying data points, ANOVA was carried out to determine any AVC class effect. Although the overall ANOVA suggested a significant effect of class type on ^{14}C value (p=0.036), post-hoc tests failed to reveal any significant between-groups differences.

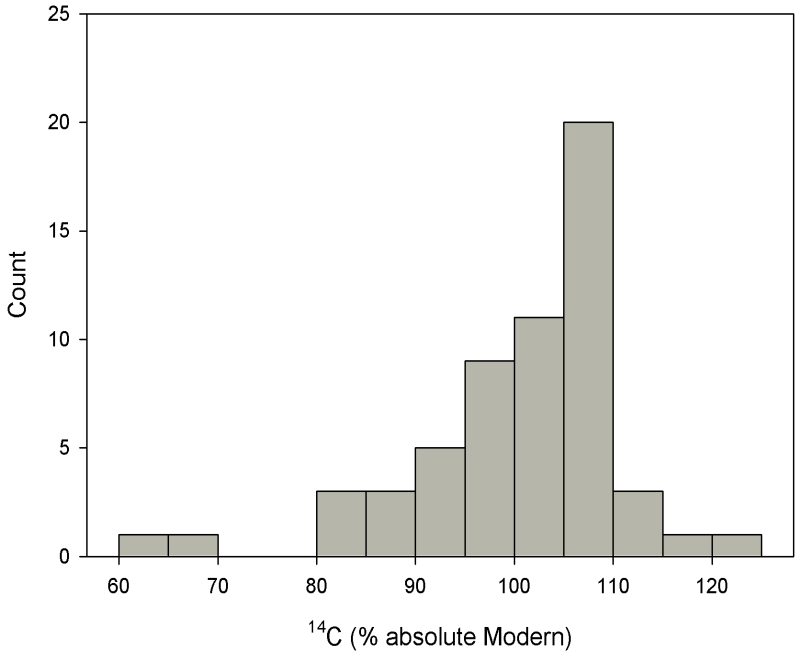


Figure 8.3.12 Histogram of raw ^{14}C data across all AVC classes.

8.3.8 Mean Residence Time (MRT) data

Histogram of MRT across the entire dataset is shown in Figure 8.3.15, with the majority of samples having a MRT < 400 years. In terms of AVC class differences, Figure 8.3.16 shows a range of mean MRT values for each class, with some significant differences being picked up; Fertile grassland and Lowland woodland (p= 0.016), Lowland woodland and Moorland grass/ mosaic (p= 0.008).

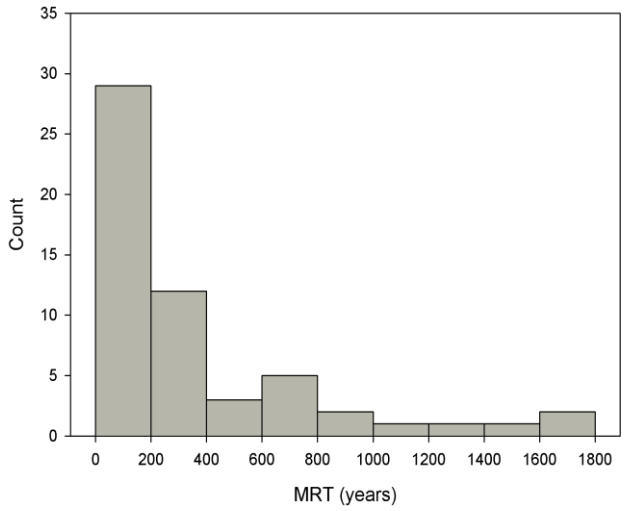


Figure 8.3.15 Histogram of MRT data across all samples.

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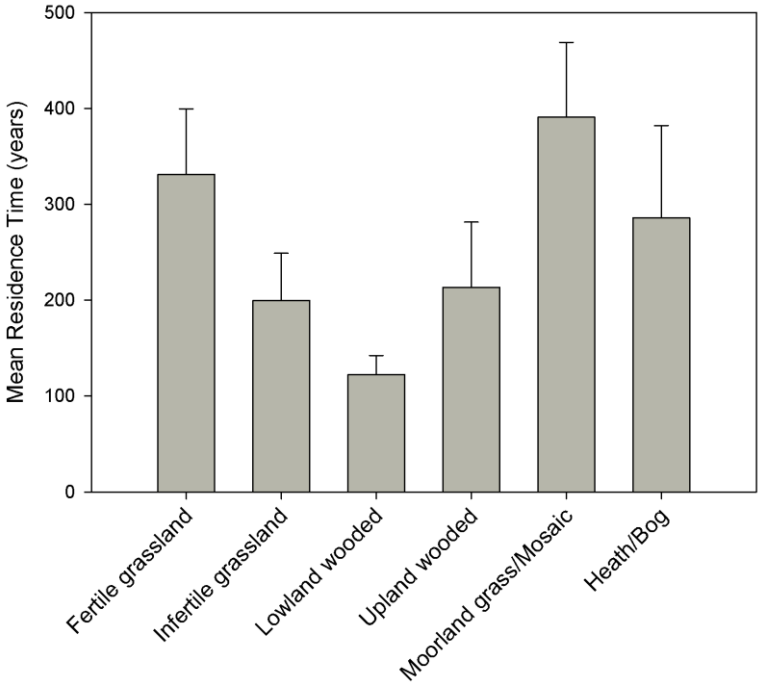

Figure 8.3.16 mean MRT value by AVC class.

To assess the driving variables (irrespective of AVC) behind variation in MRT data, multiple linear regression was carried out using hierarchical data drivers (as outlined in section 8.2). Soil drivers revealed no single driver of MRT data, but there was a significant interaction term between bulk density and C% content ($p< 0.001$). The conditioning plot shown in figure 8.3.17 attempts to visually display the interaction of bulk density and carbon content in acting as an explanatory model for MRT. The figure suggests that low C content, MRT is little affected by changes in bulk density, whereas at higher C content, the more mineral soils (higher BD) tend to give a greater MRT value. This is especially so for the fifth panel. When bulk density and C% are expressed as C stock, the linear regression, although significant (p= 0.004), explains little variation in MRT data (r^2 = 0.16). The second regression, using climate and deposition data also revealed no single driver of MRT, however, rainfall and altitude did give a significant interaction term (p= 0.039). The most complex climate model, involving all four terms gave a similar interaction (p= 0.031).

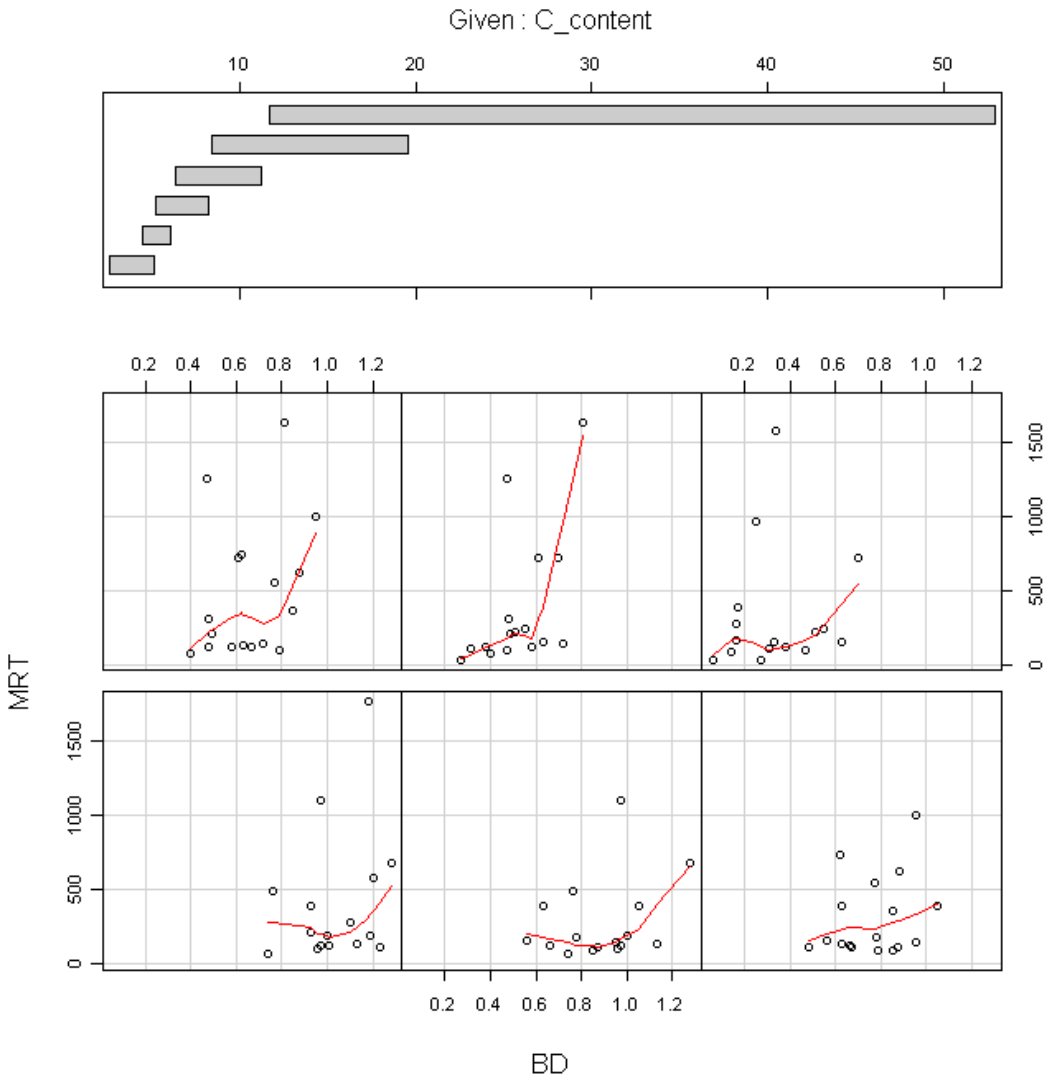

Figure 8.3.17 Conditioning plot showing the MRT (years) against bulk density (BD) under different percent-carbon content groupings (C_content). Lower left panel corresponds with lowest % C goup, and panels move left to right to finish with upper right panel corresponding with the highest % C group. Smooth lines indicate the trend.

8.3.9 Reciprocal of MRT

The reciprocal of MRT is shown for each AVC class in Figure 8.3.18. The higher decomposition rate constant associated with lowland woodland was significantly different from both moorland grass/mosaic and fertile grassland (*p*= 0.013, 0.03 respectively).

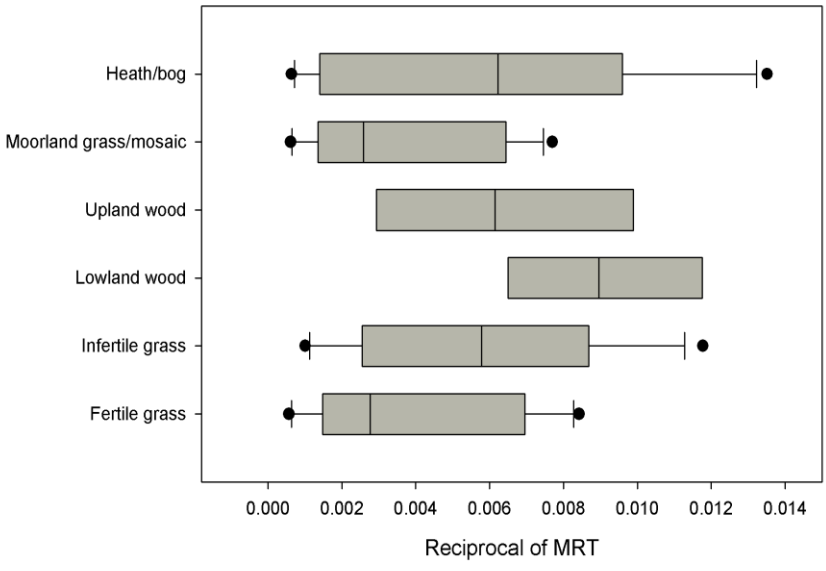

Figure 8.3.18 Box plots of reciprocal of MRT by AVC class (a), and with outlying data points removed (b).

8.3.10 Two-pool model

The two-pool model allocates SOC to a 20 year MRT pool (hereafter ‘slow pool’) and a 1000 year MRT pool (hereafter ‘passive pool’). The main output from this model is concerned with the relative pool sizes, and therefore the fraction of total SOC contained in each pool. Figure 8.3.19 shows average AVC-class values for pool sizes and pool input.

Although the actual pool sizes are informative, the ratio of the pools (or the relative percentage allocation) gives a standardised approach to viewing the modelled compartment fraction of total SOC. Figure 8.3.20 shows the portion of the total pool which is found in each class, expressed as a percentage. Most striking is the ratio variation across AVC classes, with fertile grassland and moorland grass/mosaic favouring the passive pool by ~ 60%, infertile grassland, upland woodland and heath/bog allocating in roughly equal quantities, and the lowland woodland allocating the majority (~60%) to the slow pool.

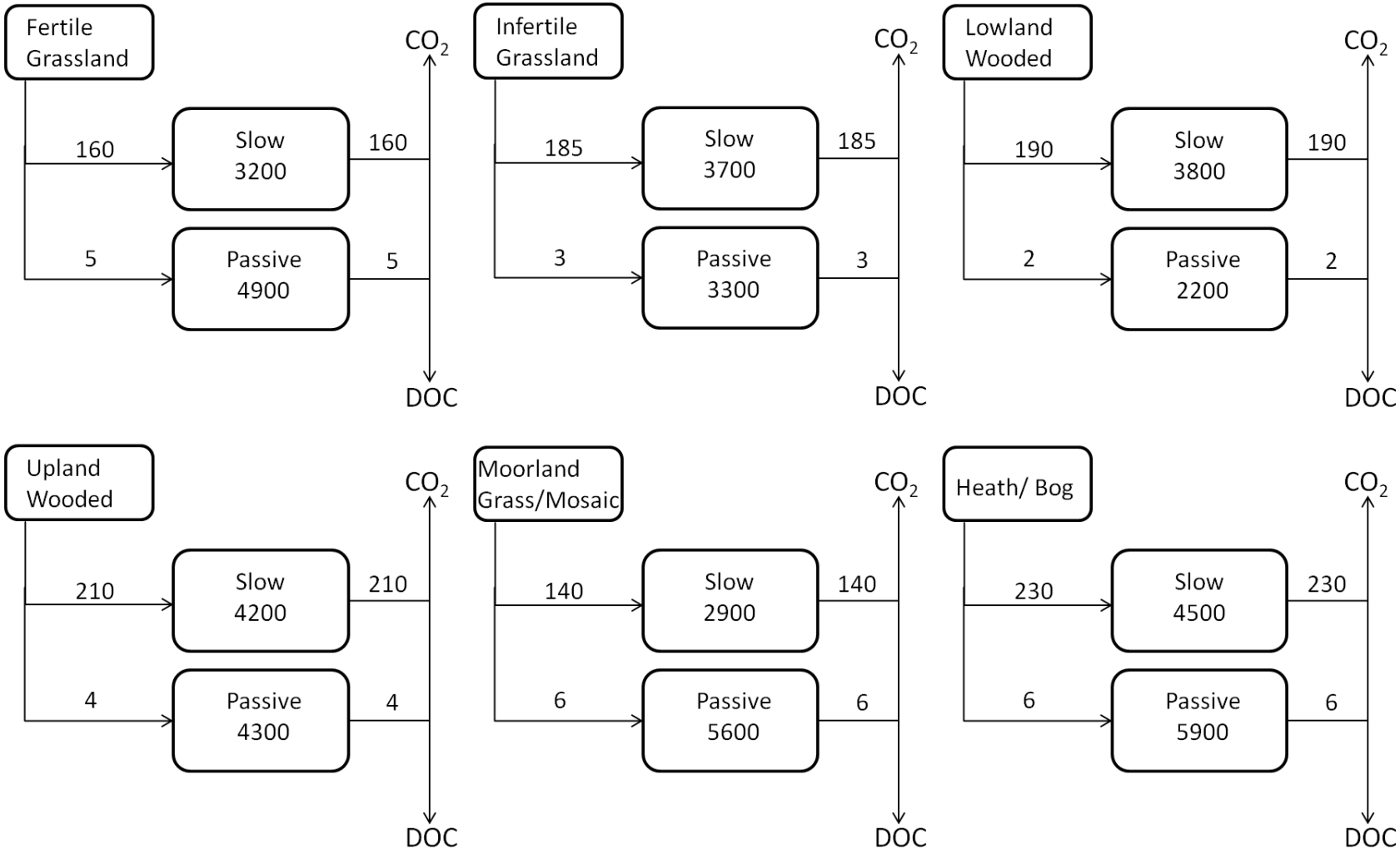

Figure 8.3.19. Model illustration showing mean pool size and input to the slow and passive pools for each AVC class. Values are correct to two significant figures for clarity.

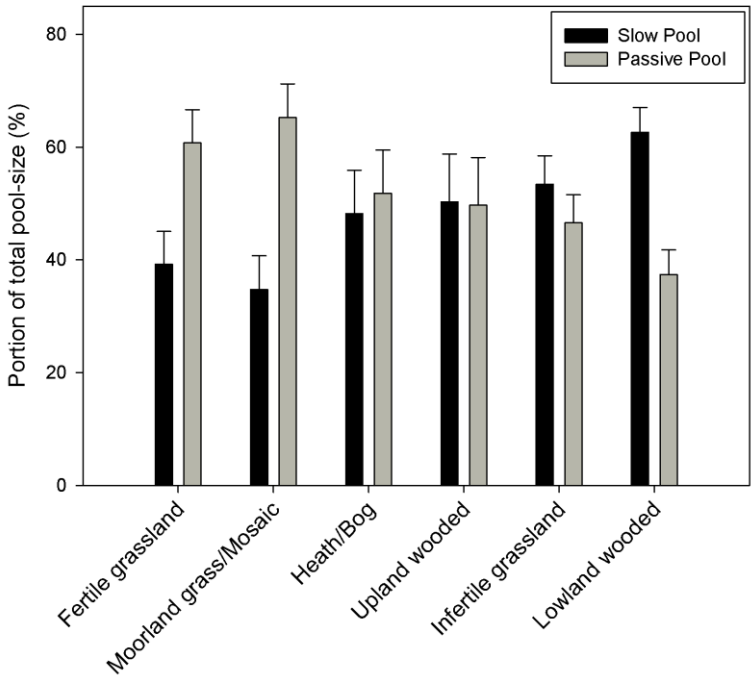

Figure 8.3.20 Percentage pool allocation between modelled slow and passive pools.

Linear regression techniques were applied (as previously) to the pool fraction data. Soil data suggested that bulk density may account for some variation in pool fraction ($p= 0.064$), although this statistic is non-significant, it was the best predictor from the soil grouping. Climatic data provided no single predictor variable, but again, the complex model of all four climatic data variables provided a significant predictor ($p= 0.034$), with rainfall and altitude also interacting significantly ($p= 0.046$).

SLA data had no explanatory power in terms of pool allocation ($p= 0.252$) when considering the entire data set, and to confirm there were no within-class effects, linear regression was carried out within each class. This process returned the conclusion that SLA had no detectable effect on pool fraction data.

The relationship between passive pool size and total carbon stock is shown in figure 8.3.21 giving a strong (r^2 = 0.73) driving of total C-stock by passive-pool size. The same regression was made with the slow pool, and the relationship is much weaker (r^2= 0.05), although in the same direction as the passive pool relationship.

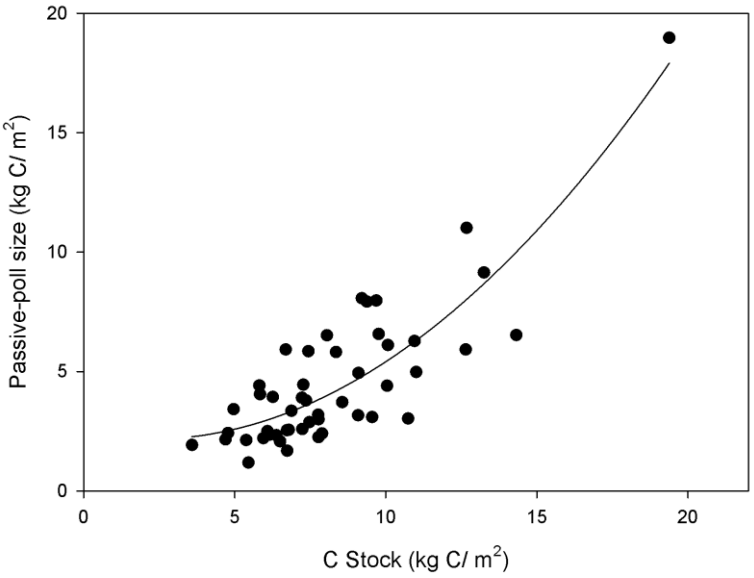

Figure 8.3.21 Total C stock and modelled Passive-pool size. Quadratic regression gives r^2 = 0.73, p< 0.001.

8.3.11 Investigating Soil type and texture

Soil type and soil texture were used as a potential grouping strategy, however none of the modelled data varied significantly across either soil type, or soil textural classes. Figure 8.3.22 shows the variation in MRT across soil textural types, and although there was some suggestion from the boxplot that texture may influence MRT values, there were no significant differences found between the groups. Figure 8.3.23 appears to suggest some difference between major soil types, but the differences remained non-significant.

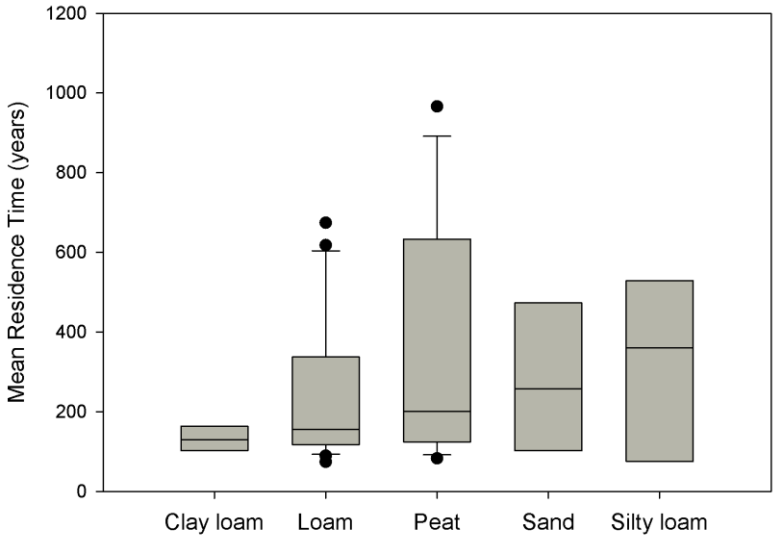

Figure 8.3.22 MRT data for samples allocated to soil textural types.

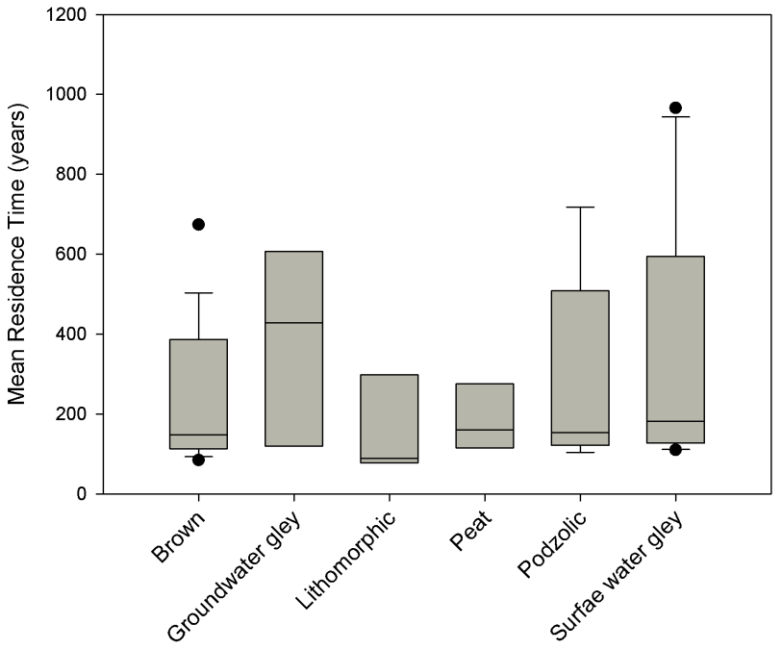

Figure 8.3.23 MRT for samples allocated to soil type classification.

8.4 Discussion.

Analysing surface soils using radiocarbon takes particular advantage of the ability to make estimations of turnover on a decadal timescale using the incorporation of bomb-^{14}C. Coupled with the natural abundance radiocarbon dating that allows for estimations on the millennial timescale, soils with a range of turnover times can be modelled using a standard approach. Given the expectation that surface soils will have turnover times ranging from the almost instantaneous loss of C typical of rhizosphere respiration (van Hees, 2005), through to the hundreds or thousands of years associated with highly stabilised or recalcitrant material radiocarbon plays a crucial role in our interpretation of general C cycling.

The assumption of steady state is a necessary component of this approach, and although it is not strictly realistic in natural systems, we can estimate a relative steady state by assuring constant vegetation type over time. Using the detailed vegetation surveys carried out as part of CS 2007 coupled with a referencing method to the land use maps of Stamp(Stamp, 1932), there was some assurance of consistent vegetation made. However, it is pertinent to note that the land use intensity and the semi-natural nature of GB ecosystems carries a caveat such that constant vegetation cover could still include management practices leading to disturbance of C cycling. Grazing and biomass removal from grasslands is the most likely management practice, but the extent to which this would alter the general turnover rate of slower-cycling C is unclear. Upland land management often includes biomass removal by mowing or burning, and as with grazing, this could disturb C turnover.

8.4.1 Summary of output

Two modelling approaches were used to interpret the measured ^{14}C value in the context of the calculated C-stock. The single-pool (MRT) approach

assumes a single, homogenous SOC pool, but despite this drawback, there were clearly variable MRT values across the AVC classes. Lowland woodland had the lowest mean MRT value, and this was significantly different from both fertile grassland, and the moorland grass/ mosaic class. Faster turnover under lowland woodland systems than two of the grasslands suggests that something intrinsic about the properties of litter quality might be controlling turnover. However, the lack of significance from heath/bog and infertile grassland reinforce both the complexity of factors controlling stabilisation of SOC, as well as the relatively crude nature of the single MRT as a metric. MRT data across the entire dataset appeared only to be related to C content and bulk density (Figure 8.3.17). This relationship was complex though, and an initial interpretation could be of C-stock (C content multiplied by bulk density) controlling MRT. However, the conditioning plot sugested the combination of bulk density and C content into C stock failed to adequately describe the relationship, with the main interaction of bulk density and C content only occurring at a narrow (~8- 20% C) range of C content. This interaction might represent the point at which MRT is most controlled by SOC-mineral stabilisation, whereas at higher C content, mineral components are less relevant, as chemical recalcitrance controls the majority of stabilisation. At lower C contents, bulk density does not vary considerably, and the shear fact that there is little SOM suggests that stabilisation (and therefore higher MRT) is not dominant.

Defining pools with fixed turnover times allowed for assessment of the rate of input to a pool with a decadal turnover (the 20 year, slow pool), or a pool with a millennial-scale turnover (the 1000 year, passive pool). These pools are similar to approaches used in previous studies, and represent distinct components of SOC which are likely to exhibit contrasting stabilisation mechanisms. The ratio of slow:passive pool size will therefore give an indication as to the portion of total SOC that is stabilised on a long, or an intermediate timescale. This approach suggested that total input to soil pools decreased in the order Heath bog > Upland wooded > Lowland wooded > Infertile grassland > Fertile grassland > Moorland grass/ mosaic. The total input being higher in the shrub and tree dominated systems than

the grass dominated systems suggests that (assuming a comparable NPP) a greater portion of litter is cycled through a fast turnover component under grasslands.

The split of total input to the slow and passive pools appears to have a large impact on both the size of the passive pool, and the portion of total SOC which is found within the passive pool. AVC classes which have a passive-pool input of 5 or 6 g C/ m^2/ yr show a passive pool dominance, whereas those with passive-pool input of <5 are either roughly equal in pool size, or have a slow-pool dominance. This appears to be irrespective of slow pool input variation, such that it would appear that subtle differences in the 'drip feed' of C to the passive pool are likely to be more important than changes in input to the more rapidly cycling pools when considering the total SOC storage characteristics of a given soil.

The relationship between passive pool size and total C-stock is highly significant, and has a dominant effect (Figure 8.3.21), whereas the slow pool size was poorly related to total C-stock, despite the apparent importance under trees. Given that the relationship of C-stock dependence is common across all of the AVC classes, it follows that the C-stock is ultimately controlled by the annual input equivalent to only a few percent of NPP. Changes in slow pool input of a similar magnitude to the total input to passive pool are therefore unlikely to exert a strong effect on overall C-stock.

The majority of SOC being turned over within the slow pool in lowland woodland suggests surface soils under some woodland dominated systems tend to have a fairly rapid turnover component which dominates the SOC. This is likely due to the large amount of reasonably labile material which enters the system as litter input, coupled with the generally favourable conditions for decomposition found in most lowland woodlands (generally very sheltered and therefore buffered from abiotic extremes). Crucially though, the issue of ecosystem stability is likely to be important in determining the observed pattern. As the persistence of woodland (when mature) in a state of very low disturbance can be assumed, the steady state

input and loss of C through soil is likely to be operating at a degree of optimum. Thus, the pool size ratio scenario observed in lowland woodland could be representative of the decomposition dynamics of a stable system, with the majority of SOC being cycled through a pool which operates on an intermediate timescale between the rapid yearly turnover of fresh detritus, and the longer turnover of more protected SOC. In terms of stability influencing decomposition dynamics, stand/woodland age has been shown to influence the microbial community, with older woodlands tending to have a more substantial fungal decomposer community (Bauhus *et al.*, 1998). This could contribute to the observed lower accumulation of more recalcitrant SOC, as the large and well evolved fungal communities (especially saprophytic) are central to the turnover of complex organic residues.

In opposite trend to the lowland woodland, fertile grassland and moorland grass/mosaic show a dominance of passive pool SOC. Although substantially different in terms of the actual species present, both of these systems will be dominated by grasses and under a degree of grazing pressure/management. Grazing has been shown to have an impact on the amount of SOC by altering species assemblages (Ingram *et al.*, 2008), but this is only under heavy grazing, and lower grazing of natural pasture lands showed no change in species assemblage (Tracy & Sanderson, 2000) or an increase in species richness (Collins *et al.*, 2002). The amount of OM entering the soil may also be influenced by grazing pressure (Zhao *et al.*, 2007), and previous studies have shown that continuously grazed plots tend to have a lower radiocarbon content than grazed plots (Steffens *et al.*, 2009), most likely due to the reduction in fresh biomass input. Grazing pressure in upland areas may be coupled with a degree of fertilisation or lime application. Both of these processes have been seen to alter decomposition of SOC (Emmerling & Eisenbeis, 1998, Jin *et al.*, 2008), and this could explain a degree of depletion of the slow-pool SOC due to increased decomposition. Fertile (generally lowland) grassland will also experience the grazing induced changes to litter quality input, but it is expected that physical disturbance may also be responsible for the dominance of passive SOC. Tilling has been shown to cause a loss in more labile and intermediate

fractions of SOC (Halpern *et al.*, 2010, Huggins *et al.*, 1998), and the time periods after establishment of permanent pasture to recovery of SOC levels will be long, but continuous (McLauchlan *et al.*, 2006). As most fertile grassland will have been included in some degree of rotational management, it is highly likely that at some point prior to the period of known steady cover, these systems may have been under crop or woodland management.

Of course, microbial functional diversity may come into play here. With grassland systems tending to receive a fairly constant supply of rhizo-deposited substrate during the growing season, the decomposition dynamics of grassland soils could be more geared-up to deal with more simple (and therefore potentially lower MRT) SOC. More complex SOC being left to accumulate without any significant fungal biomass able to compete sufficiently to then access this pool. Fertile grassland systems and those which are intensively managed tend to have a greater dominance of bacterial decomposition pathways than more mature fungal dominated systems (de Vries *et al.*, 2007), this linking in with the greater accumulation of passive SOC. The mineral protection of this passive SOC is also likely to be very high under grassland systems,

8.4.2 Possible driving factors

To assess the possible driving factors that might explain some of the observed patterns irrespective of AVC class, a number of climatic and soil characteristics were considered. Due to the diverse sources of the data, this suite of potential factors was limited to a number of basic attributes. There appeared to be only limited effects of GDD, MAP and MAT on the modelled output. This is not hugely surprising given the low range and general similarity in climate across much of GB. Although broad-scale climatic factors have been shown to have a notable effect on SOC storage and turnover (Schimel *et al.*, 1994), these differences were often over much greater ranges (Yang *et al.*, 2007) and included systems with much more extreme environments than typically found in Britain. The stabilisation

mechanisms that must operate to control the residence time of SOC are likely to be more related to intrinsic recalcitrance and physical protection mechanisms than the environmental constraints on turnover. Soil Bulk density (BD) and pH were also investigated as possible drivers, but both had only weak or no relationship with the modelled output. This suggests pH control over broad scale stabilisation is not important, contrasting with reports of pH acting as a factor controlling shorter timescale decomposition (Hobbie & Gough, 2004). Soil BD lacked any explanatory power over modelled output. Whilst BD is a good estimate of the mineral component of soil (which will contribute significantly to the stabilisation of SOC), BD doesn't allow differentiation between the textural components of the mineral phase. Distinct textural components are likely to influence the degree of stabilisation (Sollins *et al.*, 2007) and the observed residence time (Trumbore & Zheng, 1996), although this was not found in the current study under the textural classes described. Also, this finding highlights the possible role of chemical stabilisation mechanisms that are likely to take place under low-BD soils through the accumulation of recalcitrant material under unfavourable conditions (i.e. peat).

Specific Leaf Area (SLA) index has been included in the analysis procedure as the best estimate available of litter input quality. It therefore represents a possible link between the intrinsic physico-chemical quality of leaf litter and the turnover dynamics of the derived SOC pool. It has been noted in the literature that SLA may be a useful attribute to link above-ground structural components with the nutrient status of litter (McIntyre, 2008). SLA is useful also as an expression of the inherent 'toughness' of litter, with smaller specific areas tending to be associated with lower decomposition rates in woody species (Gallardo & Merino, 1993). It might therefore be sensible to expect some relationship between SLA and long-term SOC turnover estimates.

As noted following linear regression analysis of SLA as a driver of modelled pool output, there was no explanatory power derived from SLA. This suggests that there is a fundamental disconnect between the quality related

indices derived from SLA and the turnover of long residence-time C. This proposes that the intrinsic properties of present-day vegetation are not directly related to turnover of the derived SOC, but this conclusion is likely clouded by the relative resolutions concerned. SLA values are a high resolution attribute, in that the value is very informative about a particular vegetation community. But long residence time C turnover is concerned with C which is so far transformed from the parent litter input, that the subtle differences is SLA values are 'blurred' by the transformation and stabilisation processes that occur in soil. This disconnect was noted in a number of studies focussing on short-term decomposition studies of plant litter in relation to SLA (Cornelissen, 1996, Cortez *et al.*, 2007, Schadler *et al.*, 2003). Data from Cortez (2007) has been re-drawn in figure 8.4.1 and shows the initial high correlation between SLA and decomposition rate, but the rapid fall in this relationship over the duration of the incubation (836 days) leads to the conclusion that the SLA-decomposition relationship cannot be expected to hold in more long term studies of SOC turnover. This supports the situation found in the current study, and aids in the suggestion that a more broad categorisation of litter quality inputs might be more useful in fitting in with the range of turnover times estimated from radiocarbon modelling. More woody and generally nutrient poor systems are also likely to employ strategies associated with reduced decomposition (high lignin content, greater concentrations of phenolics, tannins and the employment of hairs, spines and waxes (Cornelissen, 1996)) which might be less correlated with SLA, but more important in terms of influencing the fate of litter-derived SOC in terms of chemical recalcitrance. This suggests that the general life strategy of a plant might be more informative for driving long-term C storage than some other characteristics of vegetation type or class. However, the relationships seen in the current study between woodland dominated systems and resultant MRT/pool allocation suggest the converse. It therefore must be considered that 1. Woody species do not create a uniformly 'woody' litter, i.e. they tend to produce leaves as a major litter input rather than woody mass, and 2. Litter quality might be too far removed from the nature of SOC studied to be of direct relevance.

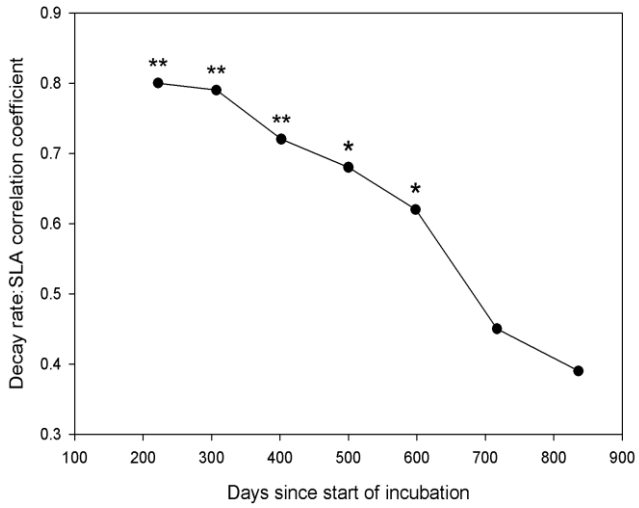

Figure 8.4.1 Decay rate of litter correlated (Pearson) with SLA over 836 days from the start of litter incubation. Significance levels (p=<0.01, p=<0.05) denoted by ** and * respectively. Data redrawn from Cortez (2007).

Soil texture will undoubtedly play a role in the stabilisation mechanisms that contribute towards driving the SOC pool size and fractions observed in this study. Utilising soil texture and soil type as potential classification options was a major research question, and as this information was collected during CS 2007, the same strategy was used as for the AVC approach. As shown in Figures 8.3.22 and 8.3.23, both soil texture and soil type failed to adequately provide any significant different groups when considered in light of modelled output. A number of issues may surround this finding. Soil type is an objective approach to classifying soils which relies on assessment of a profile rather than a distinct component of the soil. In this respect, attributes which define the soil type may be less relevant when investigating the storage of SOC in near-surface soils. A more simple approach may yield better results, focussing more on the functional characteristics of soil classes, e.g. grouping into peats, organo-mineral, and mineral soils may be more appropriate. Soil textural analysis output was given a classified name in CS 2007. Whilst this does allow for some broad comment to be made about the dominant textural component, a more quantitative approach (i.e. % sand, silt and clay) may be a better method for relating textural properties to modelled pools.

8.5 Conclusion.

Generally, there was a large variability in modelled MRT and size of slow and passive turnover pools of SOC across British habitats. Some broad differences were revealed by comparing turnover data to vegetation classification, specifically in terms of the subtle difference in passive-pool input and subsequent impact on total C stock. Weak climatic effects were detected across the range of data, mainly expressed as function of temperature, and this is expected to be mostly related to subsequent NPP and the resulting quantity and quality of substrate production. However, the best available metric for litter quality failed to have any significant explanatory power over modelled output. If litter quality and quantity do act to modify SOC turnover and stabilisation on longer timescales, the attributes of interest appear likely to related more to chemical recalcitrance than physical properties.

Soil characteristics had some explanatory power over observed turnover rates, with mineral content and total C pool appearing to correlate with longer residence time. This suggests mineral protection of SOC might act as a major determinant in longer term storage of SOC and as a mechanism for increasing recalcitrance. Although when used as a classification approach, soil texture and type failed to provide a sensible strategy for exploring modelled output.

Given the assumptions made about vegetation classes coupled with the possible sources of error associated with obtaining a single representative radiocarbon value, it is very encouraging that distinctions were made between modelled data and vegetation classes. This situation would no doubt be improved by further work which investigated the spatial and vertical variation of radiocarbon content and turnover times. Further exploration of these concepts will give a fuller understanding of the relationships between vegetation, decomposer community and soil mineralogy when considering longer-term SOC turnover. As the link between longer term storage of C and the small input to the passive pool is clear, it follows that focus should be

placed on identifying what constitutes this longer-turnover pool, and how sensitive it is to environmental perturbations. This is especially relevant given current methods to study C exchange and cycling are unable to specifically detect losses from particular pools, and that it is these pools which define the C-stock. The relationship between passive pool size and C-stock also presents notable potential as a framework for modelling, allowing estimation of slow:passive ratio of total SOC.

Chapter 9.
Conclusions and outlook.

9.1 Drivers of Soil respiration and GHG production across a range of spatial scales

As a key ecosystem process, and the main route by which C is lost from terrestrial systems, understanding the dynamics and drivers of soil respiration is central to terrestrial biogeochemistry. This study considered the variation in soil respiration at the plot scale in response to climate manipulation, at a larger spatial scale by the comparison of two similar ecosystem types, and at the national scale by measurement of collected soils from a national soil-survey. Soil temperature (Davidson *et al.*, 1998a, Lloyd & Taylor, 1994, Reichstein *et al.*, 2005a) and soil moisture (Harper *et al.*, 2005, Huang & Fu, 2000, Smith, 2005, Sowerby *et al.*, 2008) are routinely shown in the literature as the main drivers of soil respiration, and for the current study, soil temperature was indeed a significant controlling variable. The relationship between soil temperature and soil respiration is complex when considered in-situ, and due to the multi-compartment nature of soil respiration, the stimulation of each component source cannot immediately be quantified. Taking soil respiration as a whole ecosystem process, this study supported the role played by soil temperature. However, the greater driving of respiration during key phenological periods of the year underpin the likely situation that the majority of soil respiration is either directly due to autotrophic activity (root respiration) or due to the effect of rhizosphere processes on the respiration of heterotrophic components.

The attempt to split rooted and non-rooted components was not entirely successful, and led to no firm conclusion about the relative contributions. There was evidence of some decomposition processes having taken place in extracted root-free cores when compared to intact soil, suggesting that, due to the general slow-rate of decomposition, upland organic soils would require significant time to reach a true root-free state using this approach.

The stimulation of soil respiration by warming as part of a long-term manipulation experiment (Emmett *et al.*, 2004) suggests that even modest warming of less than one degree Celsius can result in a ~15% extra efflux of

C from soil. Like the general observation of temperature stimulation during key phenological periods, the treatment effect of warming was significant during the early summer (April – June). As the majority of soil respiration during the autumn would likely be a result of decomposition of fresh plant residue, the absence of a significant stimulation at this point would suggest the autotrophic components of soil respiration are more affected by the treatment.

Like soil temperature, the availability (be it limitation or excess) of soil water can influence soil respiration. Reducing throughfall to a typical wet upland soil during the summer and into autumn (usually May – Nov) caused a substantial increase in soil respiration compared to control plots, with the significant treatment effect falling in the May – Aug period. Reducing the moisture excess will also allow for a greater metabolic rate in response to temperature increases, and this was observed under throughfall exclusion, with a substantial increase in temperature sensitivity in agreement with findings by Sowerby *et al* (2008). Unlike the warming and control plots, throughfall exclusion remained temperature sensitive during summer months. This suggests the interactive effects of drought and increased temperature are likely to exert a greater effect on soil respiration than warming alone, especially during key periods of the year such as the summer growing period.

The losses of C in soil respiration due to the single or possible interactive effects of warming and moisture reduction need to be contextualised by obtaining information about source compartments, but also in light of photosynthetic activity. The net ecosystem C balance is key to understanding the true impact of climate on such systems, and it is in this direction in which this study could be extended.

At a larger spatial scale, the comparison of two contrasting heathland systems suggested that the controls and dynamics of CO_2, N_2O and CH_4 production vary markedly. The dynamic between soil temperature and CO_2 and CH_4 efflux suggest that the C-form will be temperature dependent, with

CH_4 being the dominant efflux product at lower temperatures, and CO_2 at increasing temperature. This finding opens up a focus on the identification of controls on the metabolic path by which C is cycled in upland systems. Differences in mean flux rates between the two sites also suggests that ecosystem estimates of expected gas-fluxes should incorporate vegetation type and subtle differences in soil type also, as it is expected that a portion of the between-site differences observed may be due to the substrate availability as influenced by soil textural properties.

Taking soil respiration measurements on ~700 soils collected as part of the Countryside Survey 2007 soils collection provided insight into the controls of respiration on a national scale. Across the samples, total SOC content was the most important explanatory variable, suggesting that when conditions are standardised, substrate content becomes the dominant controlling variable across all systems. The similarity of fluxes between systems when flux was expressed per unit of SOC suggests that GB soils can be split into two or three groups of flux in relations to mineralisation efficiency. On interpretation of this could be that this is a reflection on SOC quality between the groups, and that GB soils are more similar than would perhaps be thought. This would be further elucidated by actual chemical and physical analysis of the SOC components and subsequent comparison with the observed fluxes. Climatic drivers also provided some explanatory power, with growing degree days and precipitation tending to explain some flux estimates. This compares with the smaller spatial scales, with precipitation input and the favourability of growing conditions linking to processes governing the accumulation of organic matter, and therefore substrate availability during core-incubations. These links support the differential control of production and decomposition on a national scale.

Estimates of soil nutrient status failed to offer significant explanatory power, whereas vegetation groupings provided a suitable framework to categorise samples. Whilst distinct ecosystem types will arise as an interaction of climate, soils and management, the fertility of soils will play a major role. Linking the role of fertility to decomposition processes could be better

estimated with future approaches considering analysis of the available forms of soil nutrients. Textural properties of soil will also play a large role, and whilst this data was not available, bulk density having a degree of explanatory power suggests that future studies should make more a focus of soil physical properties.

9.2 C turnover of longer-MRT C and links to respiration.

Radiocarbon modelling of surface soils allowed estimation of mean residence times of SOC and the fraction of SOC turned over in a 20 year turnover pool and 1000 year turnover pool. The size of the 1000 year-turnover (passive) pool was strongly correlated to the total C-stock of top soils, indicating that it is the size (and therefore input to) this pool which controls the stock of C. Input to this pool is small, and amounting to less than 7gC/m^2/yr is likely to be a component of input which is difficult to identify. Making physical fractions within soils based on degrees of mineral protection (Poirier *et al.*, 2005, Sohi *et al.*, 2005) and making radiocarbon-based assessment of turnover (Gaudinski *et al.*, 2000) may go some way to identifying those components of SOC which make up the longer-MRT pool. The role of vegetation in these observations suggests that there is considerable variation in the turnover dynamics of longer residence time C across ecosystem types. Specifically, systems which would be expected to accumulate C for long periods of time, such as woodlands, actually have relatively short residence times in comparison grass lands and shrubs.

Climatic drivers were poor at explaining the output of this approach, suggesting that whilst climatic variables are useful for explaining variation in respiration fluxes at the plot and national scale, the longer-term stabilisation of SOC is less influenced by the variability in short-term processes. The small contribution of input to the more stable forms of SOC, and the poor link between classic drivers and the output of radiocarbon modelling suggest that factors which act to vary short-term processes such as soil respiration may not influence whole-soil C-stock. Only through modification of these input

rates via a dramatic alteration of the decomposition dynamics would the longer residence time pools be affected.

Overall, this study highlighted the variable nature on the driving of soil respiration by edaphic and climatic factors routinely reported in the literature. However, for the first time on a national scale, the importance of simple measures such as SOM content and bulk density in explaining the majority of variation in flux estimates was supported. Coupled with the observation of vegetation-type driving longer turnover SOM, these observations suggest that much of these processes are driven at the ecosystem scale. The broad features which define ecosystems, rather than the more discrete variables of a site offer more power in exploring functional measures at larger spatial scales.

9.3 Outlook

The need to continue monitoring of soil respiration at a range of spatial and temporal scales is evident, however the need to focus on interactive factors, rather than to retain single-drivers, is pressing. Increasing the temporal resolution of such measurements will improve understanding of short-term fluctuations in meteorological events and soil respiration, and also aid in investigating links between climate manipulations and seasonal changes to respiration. This is particularly crucial given alterations to growing season length, phonological change and changes in snow cover and associated freeze-thaw/dry-rewet behaviour under a changing climate. Compartmentalisation of soil respiration using tested methods has not been successful here, however by taking advantage of isotopic methods such as $^{14}CO_2$ dating or stable isotope tracers, the relative contributions to respiration could be further investigated.

The key move forward though is to integrate the monitoring of soil respiration and ecosystem processes with the stabilisation mechanisms and drivers that might control the turnover of SOC on decadal and millennial timescales. It is

these pools which ultimately define the C-stock, and it is these pools to which alteration from climate and management would result in actual SOC loss. Linking any such approach with one that defines the role of substrate quality in a physical and chemical sense would also vastly increase the ability to understand SOC turnover in a general sense, but also in light of predicted climate change or management-induced land disturbance.

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Appendix 1. Filling technique for Gas Chromatography vials.

A1.1 Aim and method

This experiment was carried out to assess the degree of error inherent in the procedure for evacuating and filling G.C vials with sample gas. As the vials would be routinely used both in the field and in the laboratory, it was neccessary to find a sensible procedure which included the lowest possible error, without causing a logistically difficult process to be built in to the sampling technique.

Based on the procedures in place at the time (two evacuations, two fills), the experiment aimed to test approaches which fell either side of the accpeted approach. The techniques are summarised in Table A1.1. Each vial was new and freshly capped with unused seals and aluminium caps. Evacuations involved the insertion of a 23 guage hypodermic needle into the seal and withdawal of one 20ml syringe of gas. After a withdrawal, the plunger was held in place whilst the needle was removed. In the case of subsequant withdrawals where there was likely to be little gas remaining, the maintenance of a vaccuum pressure by holding firmly the plunger was needed. A fill consisted of the injection of 20ml of calibration gas. Unlike the evacuations, to reduce build up of pressure in the vial, after the second injection, the syringe was removed from the needle whilst the needle is left in the seal. This allows for immediate pressure equilibration, and the needle is removed after the audible component of this equilibration has ceased.

After preparing each of the vials according to the filling technique, the vials were arranged randomly on the sampling carousel for analysis using a Perkin Elmer Clarus 500 Gas Chromatograph (GC) equipped with a Porapaq QS (80-100 mesh) analytical column. Samples were auto-analysed using a turbomatrix 40 headspace auto-analyser. N_2O was detected using ECD (at 400°C, sample oven at 40°C), CH_4 was detected using FID (at 375°C,

sample oven at 40°C) equipped with a methaniser. Carrier gas pressure was 20 PSI, and injection pressure 23.2 PSI, all other controls were as Perkin Elmer standard setup.

Sample concentrations for each vial were expressed as a percentage error for the standard calibration gas (table A1.2) and expressed for each gas against the filling techniques (figures A1.1 – A1.4).

Table A1.1 Evacuations and vial fills for each of the filling techniques.

Technique	Evacuations	Fills
1	3	2
2	3	1
3	2	2
4	2	1
5	1	2
6	1	1
7	0	2
8	0	1

A1.2 Results and Discussion

Measured gas concentrations for each individual sample are shown in Table A1.2. These raw values were expressed as a percentage error (% difference in measured value against expected standard value) are are shown in Figure A1.1 – A1.3). Immediately clear is that the error increased in both the CO_2 and the N_2O tests as the technique number increased. This pattern was not repeated for CH_4 however, and the percntage error fluctuated throughout the range of techniques. Combining the three gases to give an average percentage error indicated that despite the variability in CH_4, the error still generally increased with technique number.

Figures A1.5 and A1.6 show the tight relationship between CO_2 and N_2O error, as well as the poor fit between CH_4 and CO_2. This situation is difficult to explain, as it is counterintuative to observe more thorough filling procedures to strongly infleunce the accuracy of two measured gases, but completely fail to influence the accuracy of another. This result may in some way relte to the detection limits or accuracy of the GC, or problems associated with intial calibrating of the GC. This could be circular, as the calibration procedure utilises the vial filling appraoch 1, and so there is an inherent erro prior to analysis which should be considered.

Despite these issues and the inability to fully explain the discrepencies with CH_4, it remains that the more thorough filling techniques provided the most accurate method. Given the logistical constraints of both the lab and the field, it is recommended that technique 1 be adopted for labortaory work. Where time or logistiocal constarints operate, technique 3 can be used without any significant scarifice of accuracy.

Table A1.2 Measured gas concentrations for replicates of vials under each filling technique.

Technique	CH_4 (ppm)	CO_2 (ppm)	N_2O (ppm)
1	4.31	970.94	0.96
1	4.42	964.40	0.97
1	4.36	997.00	0.98
2	4.29	876.38	0.86
2	4.07	885.46	0.88
2	4.52	968.24	0.94
3	4.36	932.36	0.91
3	3.99	939.05	0.93
3	4.36	950.55	0.95
4	4.42	971.26	0.94
4	4.53	870.66	0.84
4	4.57	910.57	0.89
5	4.25	889.13	0.87
5	4.44	878.68	0.87
5	4.45	889.09	0.88
6	4.43	900.79	0.84
6	4.47	948.79	0.89
6	4.62	935.76	0.90
7	4.65	865.65	0.84
7	4.48	866.68	0.85
7	4.03	844.41	0.82
8	4.09	710.07	0.70
8	4.30	750.02	0.71
8	4.16	716.61	0.68

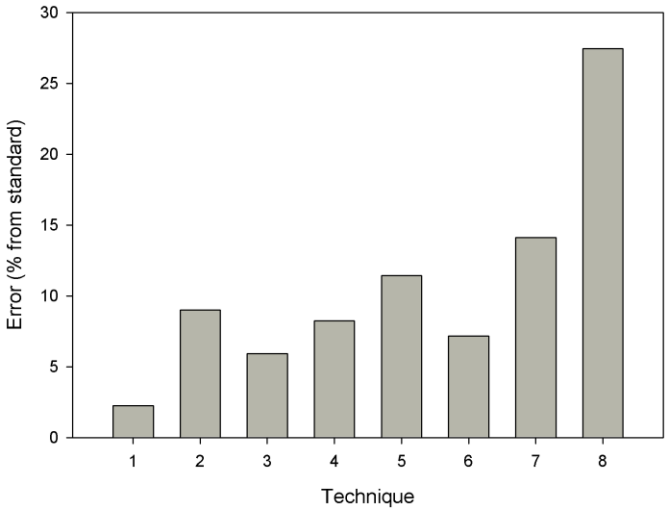

Figure A1.1 percentage error in the measurement of CO_2 against the calibrated standard over the eight filling techniques.

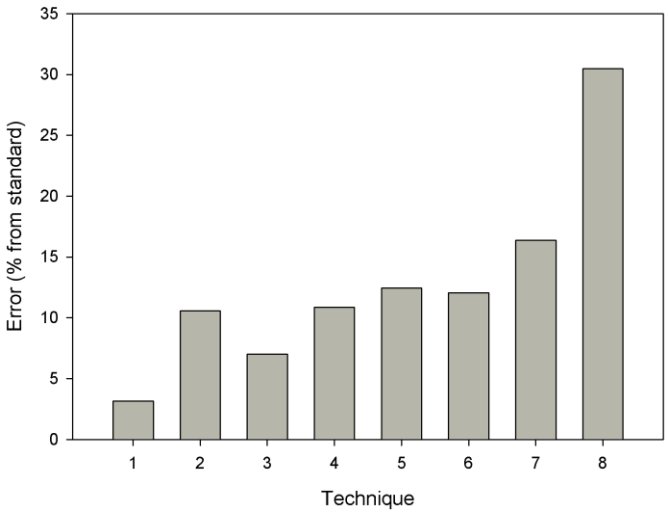

Figure A1.2 percentage error in the measurement of N_2O against the calibrated standard over the eight filling techniques.

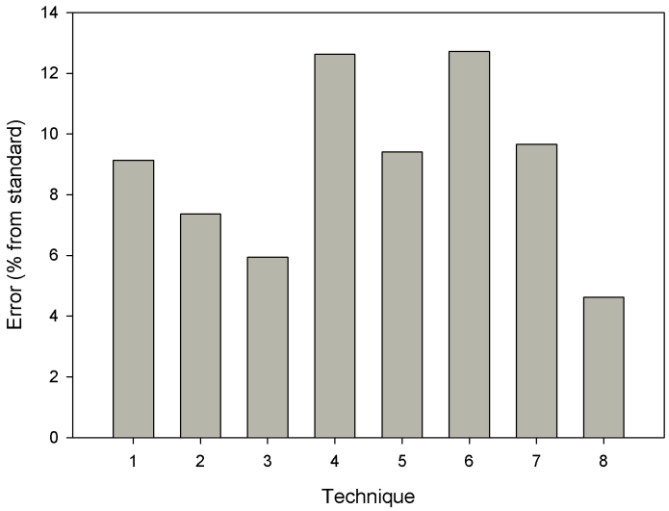

Figure A1.3 percentage error in the measurement of CH_4 against the calibrated standard over the eight filling techniques.

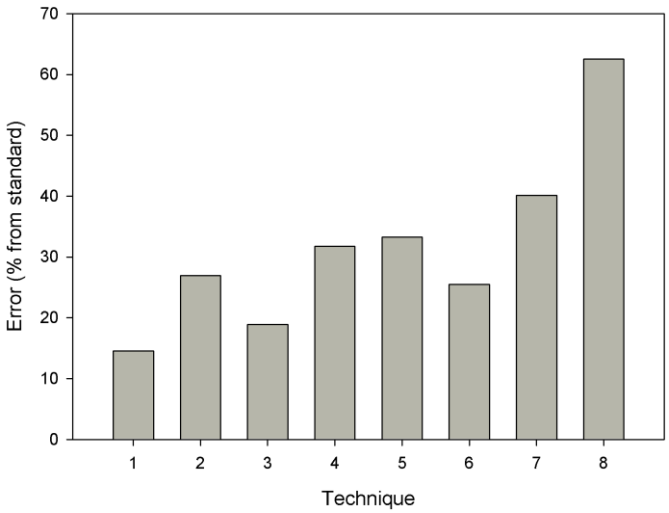

Figure A1.4 percentage total error in the measurement of all three gases against the calibrated standard over the eight filling techniques.

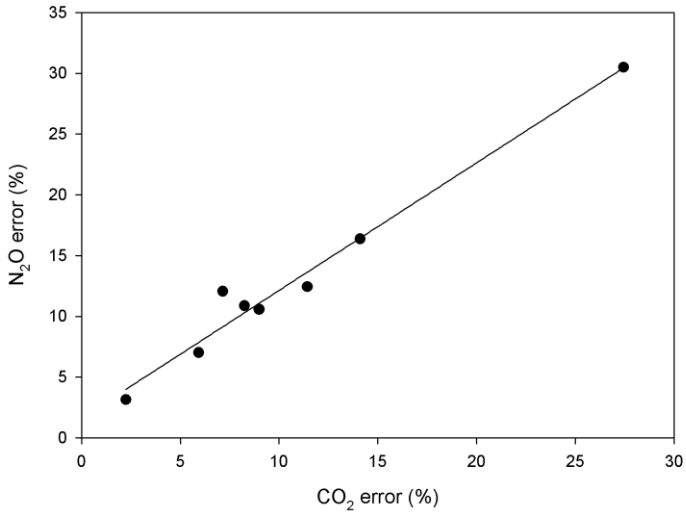

Figure A1.5 CO_2 error against N_2O error over the eight filling techniques. Linear regression gives r^2 of 0.97, $p < 0.001$.

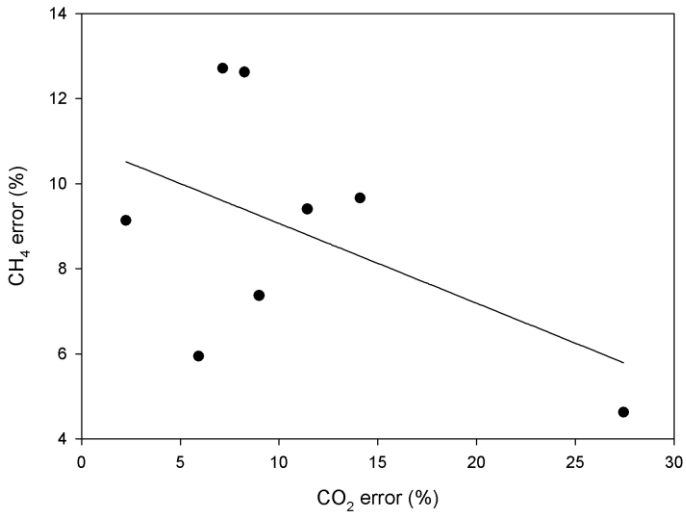

Figure A1.6 CO_2 error against CH_4 error over the eight filling techniques. Linear regression gives r^2 of 0.24, $p = 0.21$.

Appendix 2. Model output for MRT and two-pool models used in Chapter 8.

Sample ID	AVC	^{14}C content (% Abs. Mod.)	MRT (years)	Slow Input (g C/m^2)	Slow Size (g C/m^2)	Passive Input (g C/m^2)	Passive Size (g C/m^2)
1020X1	8	110.08	82.79	385.32	7706.41	3.03	3028.26
1020X4	8	122.17	26.89	237.96	4759.28	0	0
1075X3	6	108.93	95.49	322.93	6458.68	3.09	3088.19
1125X1	8	101.11	275.66	198.16	3963.28	6.11	6105.45
1125X3	8	107.48	114.85	211.56	4231.17	2.55	2551.69
1125X4	8	104.94	160.48	336.54	6730.76	5.92	5916.48
1148X3	8	90.82	966.18	20.79	415.81	18.97	18967.6
1149X4	7	98.79	388.09	205.19	4103.87	9.14	9143.4
1184X2	7	83.87	1627.71	0	0	1.63	1627.71
121x1	3	106.53	129.78	228.81	4576.28	3.18	3184.06
152x3	4	103.86	186.36	117.68	2353.63	2.42	2421.05
15x2	4	107.23	118.54	229.56	4591.11	2.88	2875.22
15x5	4	109.88	84.92	276.15	5522.95	2.25	2249.8
164x4	5	103.05	208.7	83.09	1661.84	1.92	1921.47
179x1	3	102.97	211.06	166.6	3331.92	3.9	3896.82
230x2	7	87.71	1255.83	0	0	5.9	5902.03
270x5	5	105.88	141.39	242.21	4844.28	3.71	3711.07
273x2	3	105.76	143.75	281.9	5638	4.4	4399.02
273X5	3	107.21	118.79	238.68	4773.55	3	2996.76
294x4	7	106.52	129.96	179.28	3585.55	2.5	2498.82
317x3	4	104.4	172.93	176.18	3523.59	3.35	3351.79
317x4	3	96.9	484.57	70.11	1402.25	4.41	4411.63
355x1	5	109.04	94.26	221.01	4420.19	2.08	2077.19
402x1	5	107.79	110.39	202.46	4049.22	2.33	2327.48
467X5	5	107.62	112.82	186.9	3738.06	2.21	2206.27
487x1	4	107.32	117.12	190.29	3805.74	2.35	2349.49
507x2	3	100.95	282.09	140.93	2818.69	4.45	4447.91
518x2	4	107.98	107.68	232.24	4644.79	2.59	2589.4
521x5	3	69.96	3643.79	0	0	7.51	7509.86
543x5	3	88.81	1096.42	0	0	6.86	6863.29

563x5	3	95.51	573.66	76.88	1537.7	6.51	6511.95
587X3	7	60.63	5065.76	0	0	9.9	9897.86
602x1	7	100.5	301.55	116.14	2322.72	3.93	3931.77
604x1	3	82.72	1764.43	0	0	7.31	7311.38
631x2	3	99.28	360.95	159.75	3195.02	6.57	6565.93
657x1	4	103.64	192.01	178.42	3568.33	3.79	3786.05
673x3	7	96.15	546.84	79.63	1592.63	5.84	5843.26
679x3	6	102.03	241.48	233.66	4673.28	6.28	6276.6
6X1	8	105.37	151.38	301.46	6029.28	4.98	4977.38
701x1	4	109.45	89.54	274.14	5482.83	2.4	2404.39

Sample ID	AVC	^{14}C content (% Abs. Mod.)	MRT (years)	Slow Input (g C/m^2)	Slow Size (g C/m^2)	Passive Input (g C/m^2)	Passive Size (g C/m^2)
704x1	3	94.5	674.12	72.43	1448.65	7.92	7922.68
724X2	7	93.85	717.48	82.92	1658.38	11.01	11011.79
769x4	6	106.96	122.75	162.81	3256.19	2.12	2124.61
770x1	6	98.63	393.89	126.76	2535.22	5.81	5811.46
796x3	4	107.46	115.12	209.59	4191.79	2.53	2534.93
819X4	4	89.94	996.91	0	0	9.02	9021.75
826x3	4	98.71	392.81	89.57	1791.36	4.05	4046.1
835x2	7	98.84	385.03	77.32	1546.46	3.42	3415.51
843X4	7	105.19	155.22	126.89	2537.72	2.15	2152.32
86x1	5	111.89	65.84	213.59	4271.86	1.18	1180.05
86x2	4	95.12	618	85.74	1714.84	7.97	7970.57
931X2	7	105.27	153.45	389.47	7789.48	6.53	6525.54
935X5	6	119.62	26.89	357.68	7153.56	0	0
951X4	8	110.98	73.98	252.72	5054.43	1.68	1681.07
955X1	8	84.15	1571.96	0	0	12.13	12125.73
979X5	7	93.41	738.87	38.45	768.92	5.92	5916.86
995X2	8	108.24	104.2	295.87	5917.36	3.17	3165.88
995x5	8	93.66	715.02	57.1	1141.9	8.07	8066.23