Oxidation state of a peatland

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Abstract

The oxidative ratio [OR_{terra}] is the amount of O_2 released relative to the CO_2 sequestered by the terrestrial biosphere and can be used to assess the magnitude of the terrestrial carbon [C] sink. The Intergovernmental Panel on Climate Change [IPCC] use a value of 1.10±0.05 for the OR_{terra}; this value is from one study [Severinghaus 1995]. The value of the OR_{terra} is hence imperative in the calculation of carbon flux to land; an overestimation of OR would result in an underestimation of C flux to land. Peatlands represent the most important terrestrial C store and are predicted to be amongst the ecosystems worst affected by climate change; predicted impacts include lowering of water tables and wildfires. Recent research has found the accepted value of the OR_{terra} to be higher than the value measured in several ecosystems [e.g., Worrall et al. 2013]. The accuracy of the use of 1.10±0.05 for peatland ecosystems and the effects of wildfire on peat soils is assessed here.

An outline of the current understanding of the OR_{terra} and the C sink nature of peatland ecosystems is given in Chapter 1. Gaseous flux analysis of the OR of a field peatland ecosystem is performed in Chapter 2. Contributions towards overcoming difficulties in measurement of OR by gaseous flux analysis identified in Chapter 2 are made by measuring OR of an artificial peatland regularly by the same method and by elemental analysis in Chapter 3. Variation in OR with depth and location of Austrian peatlands is analysed in Chapter 4. The effects of wildfire on oxidation state and composition of peat soils from Swineshaw moorland, UK is assessed in Chapter 5.

This study finds a significant difference in OR measured by gaseous flux analysis and elemental analysis. The method of gaseous flux measurement of OR was limited by the detection

limit of the apparatus and this approach would require long measurement times. Measurement of gas fluxes under dark conditions prior to light conditions increases the rate of photosynthesis. OR measurement by gaseous flux analysis would be best focused on times and locations with high photosynthesis. The accepted value of OR_{terra} is found to be at the maximum extent of values measured by this study and is not representative of the range of values measured in peatland ecosystems. Use of the IPCC's value for OR_{terra} may be resulting in an underestimation of the global terrestrial C sink. Change in OR with depth and location of peatland ecosystems, and burnt status is found to show significant and complex variation in the samples analysed.

Increase in the degree of unsaturation [Ω] and decrease in H/C with depth in peat soils is a result of condensation reactions which occur with burial. Changes to these compositional indicators, and others e.g., C/N in peat soils affected by wildfire, are suggested to be more appropriate for assessing the C-sink nature of peatland ecosystems than the oxidation state or OR.

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Finally, thanks to my friends and family for their invaluable support and encouragement.

Declaration and Copyright

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

- Jennifer Ruth Wilcox, September 2019

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Table of contents

List of Figures

List of Tables

1.0 Introduction

1.1 Terrestrial carbon sink

Increasing global atmospheric carbon dioxide [CO_2] concentrations as a result of anthropogenic fossil fuel burning has long been recognised [Hansen et al. 1981]. The increase in greenhouse gas emissions is associated with a rise in global temperatures [e.g., Arrhenius 1896]. Increasing greenhouse gas concentrations in the atmosphere as a result of human activities are also known to be affecting the radiative energy balance in the atmosphere [IPCC 2007]. CO_2 in the atmosphere is in equilibrium with oceanic and land ecosystems, with both currently acting as carbon sinks [Le Quéré et al. 2009]. Cox et al. [2000] predicted that the terrestrial biosphere will continue to act as an overall carbon [C] sink until about 2050, when it will become a source; the source predicted by the model largely results from a 'widespread climate-driven loss of soil C'.

To predict future changes in atmospheric CO_2 concentration it is necessary to gain an understanding of the exchange of the gas between the atmosphere and the terrestrial biosphere [Gifford 2003]. Prediction of changes in the terrestrial C balance is also key to development of policies and legislation to minimise and revoke climate change. To understand the links between the C cycle and Earth's climate systems it is necessary to perform long-term studies of ecosystem CO_2 exchange [Lafleur et al. 2003].

Gross primary productivity [GPP] is defined as the rate at which C is fixed into an ecosystem by the plants present there. Net ecosystem exchange [NEE] is the balance between the photosynthetic flux fixing CO_2 into an ecosystem and the combined autotrophic and heterotrophic respiratory flux releasing CO_2 to the atmosphere. Primary productivity in terrestrial ecosystems is known to remove significant quantities of C from the atmosphere. Piao et al. [2009] found that in the 1980s and 1990s terrestrial ecosystems in China absorbed 28-37% of cumulated C emissions here. For peatlands, Worrall et al. [2003] showed that the primary productivity is more important than fluvial C flux in estimating the C budget of an ecosystem. The terrestrial GPP has previously been found to constitute the largest global land carbon flux [Beer et al. 2010]. By convention, positive values of NEE indicate a net fixation of carbon; negative ones represent a loss of CO_2 to the atmosphere. A negative value of NEE represents a respiratory flux greater than that resulting from photosynthesis. As a result of variations in the value of the two fluxes, the net ecosystem exchange of CO_2 can show considerable interannual variability [Schimel et al. 2001]. The flux of CO_2 into or out of an ecosystem has been shown to depend on soil process variability to the same extent as plant productivity [Valentini et al. 2000; Bubier et al. 2003], hence it is necessary to gain an understanding of how both factors affect CO_2 exchange between the atmosphere and the terrestrial biosphere. The oxidative ratio [see below] describes CO_2 flux between an ecosystem and the atmosphere and is often associated with the NEE [Masiello et al. 2008].

1.2 Oxidative ratio and carbon oxidation state

1.2.1 Oxidative ratio

The oxidative ratio [OR] is defined as the amount of CO_2 sequestered in the terrestrial biosphere for each mole of O_2 produced during photosynthesis [Seibt et al. 2004]. It can hence be calculated as:

$$OR = \frac{O_2\ flux}{CO_2\ flux} \qquad \text{[Equation 1.1]}$$

A lower value of OR represents a higher CO_2 sequestration potential of an environment. The value of OR strongly effects O_2 mixing ratios in the atmosphere and hence is widely used to track the environmental fate of fossil fuel CO_2 [Masiello et al. 2008; Worrall et al. 2015]. As well as being a valuable tracer of biosphere-atmosphere CO_2 exchange, the OR is useful in assessing organic matter synthesis and destruction within the C sinks [Clay et al. 2018]. The organic matter tracing capabilities of the OR occur because terrestrial biosphere organic matter plays a fundamental role in moderating the exchange of CO_2 between the atmosphere and the biosphere [Clay and Worrall 2015a].

The terrestrial ecosystem is considered by the Intergovernmental Panel on Climate Change [IPCC] to have a global-wide OR value of 1.1±0.05 [IPCC 2007; Clay and Worrall 2015a]. This value is based upon a single study performed by Severinghaus [1995] utilising gas flow through a steady-state soil-containing chamber. Severinghaus [1995] acknowledged that the usefulness of extrapolation of results was limited due to the great heterogeneity of soils: "the sample size of soils measured is clearly too small to draw general conclusions about global soils".

Many studies have used this OR value of the terrestrial biosphere of 1.1 to calculate C fluxes using Equation 1.2 [e.g., Battle et al. 2000; Steinbach et al. 2011].

$$f_{land} = -\frac{OR_{ff}}{OR_{terra}} f_{fuel} + \frac{1}{4.8 \times 0.471 \, x \, OR_{terra}} \frac{d[\frac{O_2}{N_2}]}{dt} \qquad \text{[Equation 1.2]}$$

Where f_{fuel} is the flux of CO_2 due to fossil fuel combustion, $\frac{d[\frac{O_2}{N_2}]}{dt}$ is the rate of change of molar ratio atmospheric O_2 and N_2, OR_{ff} is the combustion stoichiometry; OR_{terra} is the oxidative ratio of the terrestrial biosphere.

The value of 1.1 assigned to the OR has, in recent years, received considerable attention from the scientific community. Worrall et al. [2013] report a global terrestrial OR value of 1.04 based upon a meta-analysis of studies of soil organic matter. A value of OR_{terra} of 1.04 would mean that the sink of C to the land has been underestimated by up to 14% by use of the IPCC value. Clay and Worrall [2015a] calculated a global OR_{terra} of 1.056 based upon a range of peats and mineral soils across the UK.

Worrall et al. [2013] identified several soil orders and global biomes for which the value of OR had not been calculated or insufficient sampling had been performed. Permanent wetlands, shrublands and savannahs as well as urban biomes had all been left out of previous studies into global terrestrial OR. Clay and Worrall [2015b] identified a lack of studies which had sampled more than one carbon pool at the same site i.e. vegetation and its underlying soil. To overcome this they measured OR of Southern African soils, vegetation and litter and updated the global OR_{terra} estimate to 1.06±0.06. An even lower OR ratio between 0.96 and 0.99 was calculated by Worrall et al. [2017] based on a complete peatland ecosystem flux estimation which took into account biomass, litter, peat soil profile, particulate organic matter (POM), and dissolved organic matter (DOM) fluxes from a peat-covered catchment.

Gallagher et al. [2014] measured an OR of 1.058 in US agricultural crops in 2010 and extrapolations show that this has increased from 1.040 in 1930. The increase in OR was thought to result from shifts in agricultural use with soybean acreage increasing and oat acreage decreasing. This study also found OR to vary between vegetation groups i.e. legumes versus grass crops. Gallagher et al. [2017] found that it is the plant species present in an ecosystem, not the climate, which controls the OR of aboveground biomass in deciduous and coniferous ecosystems. The OR of leaf litter in these two environments was significantly different; measured at 1.102 ± 0.022 in coniferous forest and 1.045 ± 0.011 in deciduous forest. Hockaday et al. [2015] found that the OR of net primary production was not affected by changes in atmospheric CO_2, however, the estimated OR for soil respiration increased from 1.006 at ambient CO_2 to 1.054 at elevated CO_2. Hence, a disequilibrium in ecosystem OR may result from environmental changes.

The uncritical use of a single OR value may result in the miscalculation of global carbon fluxes. For example, Resplandy et al. [2018] used an OR value of 1.05±0.05, following the recommendation of Randerson et al. [2006], to quantify ocean heat uptake from changes in atmospheric O_2 and CO_2 composition. This contribution, originally published in Nature, was later withdrawn partially as a result of the uncertainty in the land OR on the APO budget. Understanding of the value of OR, it's variation and controls there of needs to improve if accurate estimation of carbon flux to land and ocean is to be achieved.

1.2.2 Carbon oxidation state

The oxidation state of carbon [C_{ox}] within an ecosystem describes the arrangement of C atoms in the organic matter present. It ranges from -4 at the most reduced [i.e. methane, CH_4] to +4 at the most oxidised [i.e. carbon dioxide, CO_2]. Masiello et al. [2008] reported that the C_{ox} of organic matter, and hence an environment or ecosystem, can be determined from its elemental composition using the equation:

$$C_{ox} = \frac{2[O]-[H]+3[N]}{[C]} \qquad \text{[Equation 1.3]}$$

Where [X] = molar concentration of C, N, H and O. Sulphur is not included in this equation as it is assumed to represent less than 0.25% of the total biomass [Clay and Worrall 2015b; Charlson et al. 2000]. Description of the chemistry of organic species in terms of their C_{ox} was found by Kroll et al. [2011] to be useful for describing complex reactive systems within ecosystems. C_{ox} reflects the synthesis and decomposition of natural organic matter and is a fundamental property of the carbon cycle. From C_{ox} values it is possible to draw conclusions about organism and ecosystem biogeochemistry, tissue composition and environmental conditions.

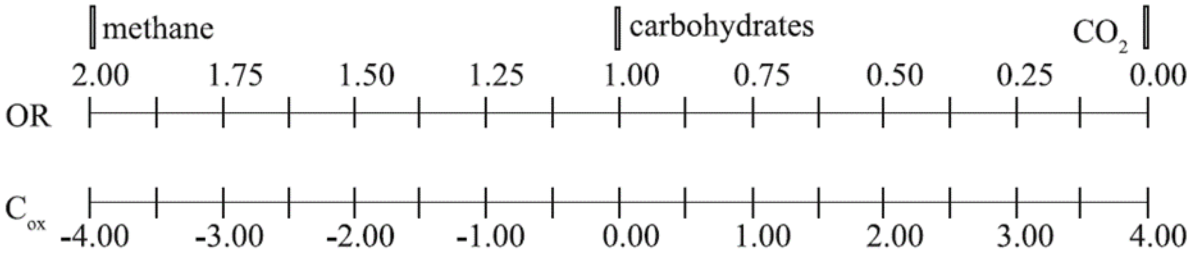
1.2.3 Oxidation state of organic matter

Since C_{ox} and OR_{terra} are related through the balancing of organic matter synthesis, a quantitative linear relationship exists between the two; defined by Eq. 1.4 and shown schematically in Figure 1.1.

$$OR = 1 - \left(\frac{C_{ox}}{4}\right) + \frac{3[N]}{4[C]} \qquad \text{[Equation 1.4]}$$

Equation 1.4 assumes that the ultimate source of nitrogen in carbon fixation is atmospheric nitrogen [N_2] [Clay et al. 2018]. N_2, nitrate [NO_3^-] or ammonium [NH_4^+] as ecosystem N sources can be used to calculate OR and the equation changes accordingly; the source which should be chosen is the form of N that crosses the boundaries of the ecosystem being measured. In ecosystems where the majority of nitrogen is received through N fixation, such as peatlands and forests, the assumption that N_2 is the ecosystem N source generates minor errors (up to 0.01 OR units) if the ecosystems are receiving 20% of their N as NO_3^- [Gallagher et al. 2017]. It is also assumed that S and P do not contribute to C_{ox}. Hockaday et al. [2009] have shown that the error in the OR of this assumption is only ±0.002. The values of OR and carbon oxidation state [C_{ox}] are increasingly used to estimate global sinks of fossil fuel emissions in the atmosphere and the biosphere [Keeling et al. 1996]; hence establishment of correct values is imperative [Masiello et al. 2008].

Figure 1.1: Scale of oxidative ratio [OR] and carbon oxidation state [C_{ox}] of organic matter showing approximate values of key compounds mentioned in this thesis. Edited from Masiello et al. [2008].



The conclusions drawn by recent research finding that interaction between the terrestrial biosphere and the atmosphere is occurring at a lower OR than previously thought would suggest a lower oxidation state of the ecosystems in which these processes occur. The differences in measured values of OR_{terra} indicate that the C fluxes to land may have been miscalculated by assuming the IPCC's value which is too high and does not allow for natural variation. Worrall et al. [2013] suggested a considerable underestimation of anthropogenic carbon flux to land, up to 14%, has resulted from the assumed validity of this OR value of 1.1. The variation in OR values measured globally and in different ecosystems means that at our current level of understanding of OR it is difficult to predict the underestimation of C flux to land, but as understanding improves a more accurate value may be estimated.

1.3 Measurement of the oxidative ratio

Previous studies have returned values of C_{ox} and OR utilising a range of measurement techniques. Accuracy and ease of measurement using each technique varies.

1.3.1 CHNO analysis

CHNO elemental analysis is used to provide molar concentrations of carbon [C], hydrogen [H], nitrogen [N] and oxygen [O] which are then used to calculate C_{ox} using Equation 1.3 and OR using equation 1.4. This method has been used by studies such as Keeling [1988], where the composition of wood was used to estimate a terrestrial OR of 1.05. Since the composition of wood is different from that of other organic matter types, more recent studies have attempted to provide values of OR representative of other carbon sinks. Clay and Worrall [2015b] used this technique to estimate a global OR_{terra} of 1.06±0.06 and more recently Clay et al. [2018] used CHNO analysis to show that OR increases with latitude in Fennoscandian ecosystems. Although the chemical composition of organic matter changes throughout the year, Clay et al. [2018] suggest that because C is fixed over a limited period of time, assuming that ecosystems act as closed systems, the OR gained by elemental analysis is representative of the flux of formation. Masiello et al. [2008] found that the CHNO elemental analysis technique yielded more accurate values of C_{ox} and hence OR than the process of calorimetry [see Section 1.3.2].

1.3.2 Calorimetry

C_{ox} can be calculated by bomb calorimetric measurement of heat of combustion [ΔH_c] coupled with weight percent carbon [%C] measurements. C_{ox} is then calculated by the approximation shown by Equation 1.5.

$$C_{ox} = 4 - \frac{1.6}{EA_c}[0.06968\Delta H_c - 0.065] \quad \text{[Equation 1.5]}$$

Where EA_c is the %C results from an elemental analyser. Measurements of C_{ox} made by calorimetry and corresponding calculated OR values [using Equation 1.4] have previously been shown to be less accurate but more precise when used for a single compound than values obtained by elemental analysis [Masiello et al. 2008].

1.3.3 ^{13}C NMR

^{13}C Nuclear Magnetic Resonance (^{13}C NMR) allows the investigation of mechanisms controlling soil carbon oxidation state and oxidative ratio. The chemistry of organic materials can be assessed by solid state ^{13}C NMR, hence it can be used for estimating OR of fluxes resulting from disturbances such as fire and land use change [Hockaday et al. 2009].

1.3.4 Gaseous flux

Since the OR is defined by Equation 1.1, its value should be calculable by measuring the flux of CO_2 and O_2 between the atmosphere and the terrestrial biosphere. Despite this, studies into the OR using this technique are lacking. Previously, accurate direct measurements of the oxidation state of an environment by gaseous flux analysis have been largely unattainable due to logistics and expense. Recent advances in technology have made it possible to measure the simultaneous exchange of CO_2 and O_2 between the soil and atmosphere and hence calculate the oxidative ratio of an environment. Other problems relating to the gaseous flux measurement of the oxidative ratio have been identified in previous studies. In a study attempting to constrain the subsoil C source to cave-air CO_2, Bergel et al. [2017] found that measurements of OR are affected by additional belowground processes like gas-water exchange and diffusion which offset O_2 and CO_2 concentrations. In the recent study by Brecheisen et al. [2019] developments in the construction and use of Field Portable Gas Analysers (FPGAs) were suggested to provide a cost-effective, light-weight, compact and reliable method for monitoring dynamic soil gases in-situ in the field which may present a novel way of measuring OR.

Micrometeorological measurements of gaseous C flux in a range of ecosystems have previously been used to estimate the carbon balance of the corresponding terrestrial environments. Pioneering studies utilised ‘the chamber technique’ by which a clear chamber equipped with a fan and temperature probe is placed on a gas collar in the soil to measure rate of change of CO_2 in the air [e.g., Whiting 1994; Bubier et al. 1998; Alm et al. 1999]. A need for longer-term flux measurements to analyse total C exchange in peatland ecosystems resulted in an increase in studies performed using eddy covariance techniques [e.g., Neumann et al. 1994; Aurela et al. 2001; Lafleur et al. 2003]. These measure long-term [periods of years] CO_2 fluxes, heat and water vapour of an ecosystem using a closed path infrared gas analyser and three-dimensional sonic anemometer. In the study by Severinghaus [1995], which returned the OR of 1.1, a steady-state chamber experiment was used to measure O_2 and CO_2 fluxes between soils and the atmosphere at a range of localities.

Previous studies have shown that decomposition causes organic matter to become more reduced relative to the initial biomass [Baldock et al. 2004]. Reduction of organic matter has been proposed to result from the loss of oxidised biomolecules such as carbohydrates and polysaccharides during the initial stages of decomposition [Worrall et al. 2017]. Studies which have measured atmospheric gaseous fluxes have returned ecosystem OR values as low as 0.86 [Ishidoya et al. 2015] and 0.89 [van der Laan et al. 2014]. Hence, measuring OR of an ecosystem based on its elemental composition may not be completely reliable for gaseous exchange and C balance purposes as the effects of organic matter decomposition on oxidation state may increase the measured value of OR. Moore et al. [2002] also found that direct measurement of micrometeorological CO_2 exchange yields a more accurate estimate of NEE than biomass compositional analysis. Williams and Robertson [1991] also suggested that a reliable method for measuring the OR of an ecosystem is to chemically determine gross O_2 and CO_2 production and consumption.

1.4 Variation in OR

Variation in the value of OR temporally and spatially is reported in the literature. The value of OR varies depending on the timescale over which it is monitored. Over short periods, OR varies substantially depending on terrestrial assimilation and respiration, however, over longer time periods the OR of accumulated organic material should represent the O_2:CO_2 exchange ratio of the terrestrial ecosystem.

O_2 and CO_2 exchange ratios are known to vary with the composition of and chemical reactions taking place in organic matter [Keeling and Shertz 1992]. Randerson et al. [2006] suggest that increased disturbance of the biosphere, largely as a result of human activity, is favouring plant functional types with lower ORs resulting in increased oxidation of the terrestrial biosphere. Worrall et al. [2013] identified several gaps in the understanding of the global OR, including a lack of measured values for entire soil groups and biomes.

The oxidation state of organic matter has also been observed to change with latitude [Clay et al. 2018]; this has been suggested to result from differences in climate or land-use. As would be expected, variation in the water level of an environment effects its oxidation state. It has been found by many studies [e.g., Roulet et al. 1993; Moore and Knowles 1989; Yavitt et al. 1988] that oxidation potential in the unsaturated and aerobic layers above the water table is higher than in the saturated and anaerobic layers below.

C_{ox}, and by inference OR, has been found to depend on levels of disturbance occurring in biomes [Randerson et al. 2006]. Clay et al. [2018] suggested that an increased disturbance to the terrestrial biosphere would cause a decrease in OR_{terra}. Findings of Gallagher et al. [2014] that the OR of US agricultural crops has increased since 1930 relating to the type of crop grown suggests that variation in OR depends on the type of disturbance occurring. Hockaday et al. [2009] suggested that episodic flux disturbances like fires may cause substantially different ORs from ecosystem respiration fluxes.

1.5 Other compositional indicators

Compositional indicators which do not directly relate to the oxidation state of organic matter have previously been shown to be useful for assessing chemical changes within ecosystems. The degree of unsaturation [Ω] can be calculated from elemental molar concentrations using Equation 1.6.

$$\Omega = \mathrm{C} - \frac{H}{2} - \frac{N}{2} + 1 \qquad \text{[Equation 1.6]}$$

Where C, H and N represent the moles of carbon, hydrogen and nitrogen respectively. The Ω is a parameter used to quantify the number of rings and π-bonds within a molecule where a $\Omega = 0$ represents a pure alkane and $\Omega = 4$ represents benzene [McMurray 2004]. Increase in the Ω of litter relative to vegetation and with depth in a peat profile has been observed in previous studies [e.g., Worrall et al. 2016]. The increase in Ω is thought to result from condensation reactions that form C-C double bonds and remove substituents, often H and O. The results of Clay et al. [2018] showed that litter had a higher Ω than soils, in disagreement with previous studies.

Three other compositional indicators are often calculated in assessments of the state or composition of organic matter pools: the C/N, H/C and O/C molar ratios. Clay and Worrall [2015b] used O/C and H/C elemental ratios to suggest that organic matter material types varied amongst sites in South African soils and vegetation. The C/N ratio of peat soils was used by Worrall et al. [2012] to infer the depth of the acrotelm/catotelm boundary between 40 and 50cm. The compositional indicators can be used in combination with OR and C_{ox} to provide more accurate interpretations of biochemical changes and processes occurring in organic matter pools. Worrall et al. [2016] suggested that an increase in both C_{ox} and Ω and simultaneous decrease in C/N with depth in peat soils represents a relative loss of H and formation of carbonyl groups. Clay et al. [2018] found that, based upon a partial regression analysis, the OR is most closely related to the variation in the O/C ratio, followed by the H/C ratio and then the C/N ratio, although all these ratios were found to vary significantly with OR.

1.6 Peatland ecosystems

1.6.1 Peatland carbon balance

Within the terrestrial biosphere, peatlands are the most important C store [Loisel et al. 2014; Worrall et al. 2018]. Despite occupying only 3-5% of the total global land area [Schindler 1999; Rydin and Jelgum 2013] there is estimated to be a total C content of 500 Pg [1 Pg = $1x10^{15}g$] in northern peatlands [Gorham 1991]. This large reserve is a result of primary productivity which traps C in vegetation, and is then converted to peat by burial and incomplete decomposition. The C sequestered in a peat bog is a balance between that fixed by gross primary production [NPP] and burial and that lost from the system by decay [Lafleur et al. 2001]. C accumulation since the last ice age [around 10,000 years] has resulted in the large reserves observed today, which represent up to one-third of the total terrestrial soil C [Lafleur et al. 2003].

Despite being a considerable C reserve, it has been suggested that some present-day peatlands are sources of C, resulting in its release into the atmosphere, as opposed to sinks taking C out of the atmosphere [Waddington and Roulet, 1996; Worrall et al. 2003]. Billett et al. [2004], however, showed that UK peatlands currently operate as C sinks unless they are affected by management or climatic pressures. It has been proposed from records preserved in peat cores that C accumulation rates may be reduced relative to the last 150 years. Alterations in accumulation rate may relate to changes in the state of the plant community which Panikov and Dedysh [2000] found to strongly influence CO_2 exchange in peat bogs.

It has been estimated that the UK holds around 13% of the global blanket bog resource [Ratcliffe and Oswald 1988] and that 15% of UK land is peat-covered [Billett et al. 2010]. Identification of a missing sink of anthropogenic CO_2 in the northern hemisphere [Keeling et al. 1996; Houghton et al. 1998] has led to the hypothesis that northern land biota remove ~30% of fossil fuel CO_2 emissions [Gorham 1991]. Estimation of an accurate value of OR_{terra} and understanding of its global variation has the potential to make calculation of C fluxes to land easier, and hence make assessment of this missing northern hemisphere sink possible.

Changes in OR and C_{ox} with organic matter types and soil depth in peatland ecosystems have been documented by previous studies. Worrall et al. [2013] found that no significant change in OR or C_{ox} with depth occurred in peat soil cores from Moor House National Nature Reserve [NNR], UK. Lack of OR variation with depth in UK peatlands was later supported by the results of Clay and Worrall [2015a] and Worrall et al. [2018]. Significant variation in OR between organic matter types within individual ecosystems is reported. Worrall et al. [2013] found "very little difference between bulk soil and bulk vegetation values", however this was later contradicted by Clay and Worrall [2015a] which found vegetation and litter to have significantly lower ORs than underling soil samples. Clay and Worrall [2015b] found that soils had the lowest OR values, which disagrees with results of previous studies.

1.6.2 Environmental controls on the peatland C balance

A range of climatic factors are known to effect the C balance of peat soils [e.g., Davidson and Janssens 2006]. Photosynthetic and respiratory processes involve enzyme-controlled chemical reactions which are temperature dependent. A common perspective exists that the dominant limiting factor in respiration is temperature whereas multiple limiting factors are key to photosynthetic rate, including temperature, light intensity, CO_2 concentration, nutrient availability and water stress [Woodwell et al. 1998]. It has been shown that as the water table within a peat catchment rises, methane [CH_4] emissions rise while CO_2 emissions fall [Best and Jacobs 1997]. An increase in CH_4 release has been suggested to result from a thinning of the aerobic zone which results in a reduction in O_2 availability and aerobic enzymatic processes [e.g., Bubier et al. 2003]. The position of the water table below a peatland also effects the distribution, biomass and productivity of plant species growing there which can have an impact on C exchange [Moore et al. 2002].

Peatland ecosystems occur predominantly in high latitude and altitude environments with high annual rainfall. These regions are predicted to undergo considerable climatic changes as a result of human-induced global warming [IPCC, 1996]. As stores of large quantities of C, interest in how environmental factors affect C exchange in peatlands has increased over the past few decades.

1.6.3 Wildfires in peatland ecosystems

Organic soils are vulnerable to wildfires [Turetsky et al. 2004; Benscoter et al. 2011]. Extent and severity of peatland wildfires can be substantial [Shelter et al. 2008] and have been predicted to increase in the near future as a result of global warming [Field et al. 2007]. The increased occurrence of peatland wildfires is predicted to result partially from drought conditions which will lower water tables. A type of flameless combustion called smouldering dominates in wildfires in peatland ecosystems [Turetsky et al. 2014]. Smouldering is a slow, low temperature [peak ~600°C] combustion of organic matter, which can persist for weeks or months [Rein et al. 2008; Hadden et al. 2013].

The effects of peat fires on the physical and ecological structure of peat soils are significant and include damage to seedbanks, changes to hydrophobicity and pH increases [Davies et al. 2013]. Previous studies have identified a significant loss of soil C as a result of peatland burning. Effects of wildfires on composition of peat soils are, however, lacking and little is known about the effects of fires on C stabilization in soils [González-Pérez et al. 2004]. Episodic flux disturbances like fires may cause substantially different ORs from ecosystem respiration fluxes [Hockaday et al. 2009]. Understanding of how the OR of the terrestrial biosphere responds to wildfire is lacking. To our knowledge, only one previous study has looked into the effect of burning on the OR of soils; this was by Hockaday et al. [2009] and found burnt soil residues were substantially oxidised in comparison to unburnt horizons. Flux of C from ecosystems as a result of fire has been proposed by Schimel [1995] to be as important as natural ecosystem respiration in removing C from the biosphere. The nature of burn events makes estimation of OR by gaseous flux analysis difficult, hence other methods such as compositional analysis must be employed.

1.7 Aims of this study

This study aims to measure the OR of peatland environments as a contribution to the current effort being made to assess the accuracy and global synchronicity of the IPCC value of 1.1±0.05. Variation of OR in peatland environments and the accuracy of the accepted IPCC value and more recent estimates will be assessed. Whether a single value is appropriate for use as global terrestrial OR or if individual values relating to environment and location would be more more effective will be assessed.

Previously, OR and CO_2 exchange in peatlands have largely been viewed as separate fields of study. Recent advances in technology have enabled simultaneous measurement of CO_2 and O_2 flux between an ecosystem and the atmosphere. The literature surrounding terrestrial C balance identifies a lack of long-term measurement of C exchange; the present study hopes to utilise the recent advances to measure fluxes in both a field and laboratory environment which can be used to calculate peatland OR and contribute to overcoming this flaw. The study also aims to develop the method of OR measurement by gaseous flux analysis.

Measurement of the OR of vegetation and peat samples from a range of locations by CHNO elemental analysis will also be performed to gain an understanding of variation in OR results with measurement technique. A disparity between results of studies which have used gaseous flux analysis and elemental analysis to measure OR was identified in Section 1.3.3. Investigation of this disparity will be made by measuring OR by both techniques. Assessment and comparison of the current techniques used to measure the OR will be performed. It is hoped that by using the most up to date scientific technology, comment will be made on the most reliable method of measuring OR.

Previous studies have identified a potential reduction [increase in OR] of organic matter relative to the O_2:CO_2 exchange ratio of an ecosystem. By measuring OR and C_{ox} in vegetation and peat from different depths, changes in oxidation state between organic matter types will be assessed. This study will add to the database of values of OR and contribute to understanding of variation in oxidation state within peat soils. Variation in other compositional indicators [Ω, C/N, H/C, O/C] between peat soils at different locations and depths will also be used to assess chemical changes which occur in this organic carbon pool. Measurement of the OR of peat cores taken from a peatland affected by wildfire will also be performed. By measuring OR by elemental analysis of soils affected by wildfire it is hoped that the effects of burning on OR and other compositional indicators will be identified. Quantification of changes in oxidation state and other chemical parameters as a result of wildfires may reduce uncertainties of the effects of wildfire on global C budget.

2.0 Oxidative ratio of a peatland ecosystem from gaseous flux analysis

2.1 Introduction

Chapter 1 summarised the conclusions made in the scientific literature regarding the oxidative ratio [OR] of the global terrestrial biosphere, with a focus on peatland ecosystems. In the literature review, note was made of the potential increased reliability of gaseous flux measurements relative to elemental analysis in quantifying the OR of organic matter which is likely to be subject to decomposition and hence return a more reduced value [greater positive value] of OR. To assess the reliability of gaseous analysis for measuring OR, this chapter seeks to gain field values of oxygen [O_2] and carbon dioxide [CO_2] fluxes in a well-constrained peatland environment. From these values a direct measurement of OR will be calculated. The feasibility of OR measurement by gaseous flux analysis will be assessed.

2.2 Aims and objectives

This chapter aims to measure the oxidative ratio of a peatland environment by gaseous flux analysis. For this aim, several objectives were identified:

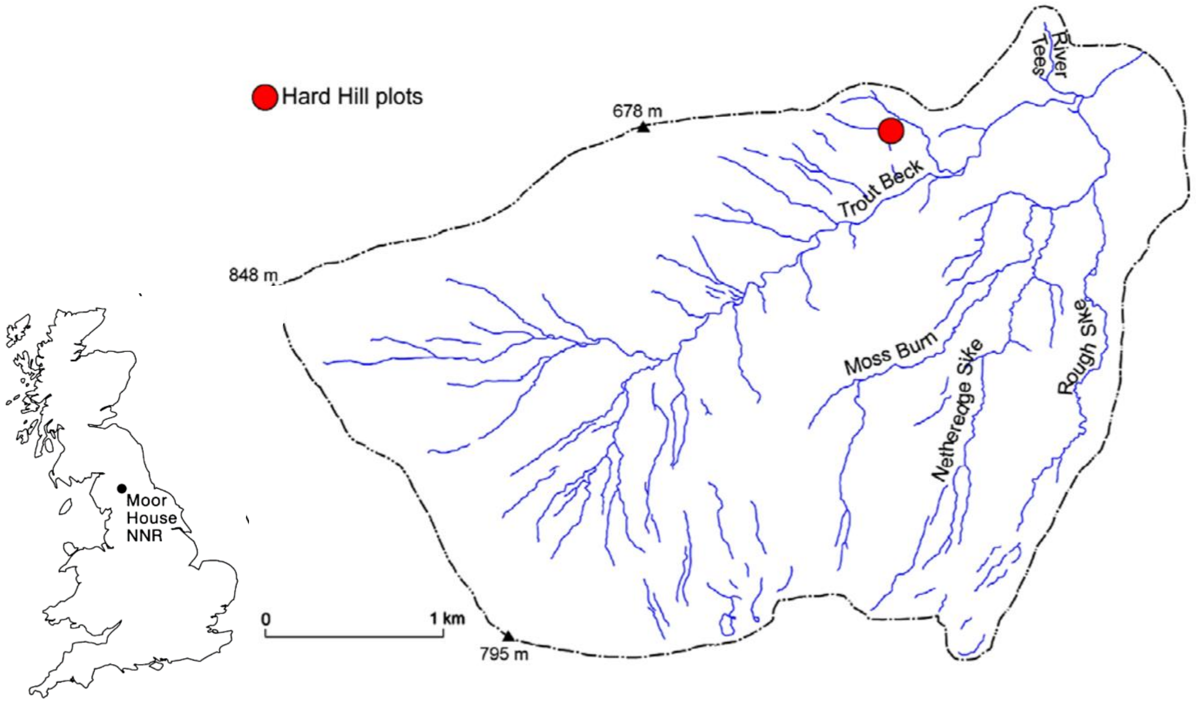
1. Field measurements of O_2 and CO_2 gaseous flux will be made across a 12-month study period to avoid minor short-term variations relating to terrestrial assimilation and water table variations.
2. OR of the peatland ecosystem will be calculated assuming it’s value equates to the gaseous flux ratio of O_2 to CO_2.
3. The feasibility and accuracy of OR values obtained by direct measurement of O_2 and CO_2 flux will be assessed.

2.3 Materials and Methods

2.3.1 Study site

The Hard Hill Plots are situated in the Moor House National Nature Reserve [NNR] in Upper Teesdale in the North Pennine region of the UK [National grid ref. NY 756326, Figure 2.1]. The Moor House NNR is a terrestrial and freshwater site within the UK Environmental Change Network [ECN]. Altitude of the reserve ranges from 300-850 m above sea level. Moor House is the most extensively studied of the UK peatlands [e.g., Billett et al. 2010, Worrall et al. 2017]. The Moor House NNR contains the Trout Beck catchment which is an 11.4 km^2 blanket peat catchment in the headwater of the River Tees. Underlying geology belongs to the main Yoredale Series of the Carboniferous, consisting of alternating layers of limestones, sandstones and shales with intrusions of the doleritic whin sill. Periglacial solifluction deposits of drift and head largely obscure the bedrock, especially on gentler slopes. The Moor House NNR is covered in blanket bog of ombrotrophic peat formed as a result of impeded drainage from glacial till during the mid to late Holocene [Johnson and Dunham, 1963]. The blanket peat ranges in thickness from 0.4 to 5 m.

Figure 2.1: Location of the Hard Hill Plots within Moor House NNR, UK.



Holden and Rose [2011] performed a study of climatic conditions at the Moor House Site between 1991-2006. Holden and Rose [2011] reported that the mean temperature during this period was 5.81°C, an average of 99 air frosts per year occurred and the mean number of snow lying days was 41. The mean annual total precipitation at the site for the periods of 1953-1980 and 1991-2006 was 2012 mm.

Eddy et al. [1968] performed a complete assessment of the vegetation covering the reserve; the dominant plants established in the Hard Hill plots are: Eriophorum sp. [cotton grass], Calluna vulgaris [heather] and Sphagnum sp [moss]. Previous studies on the Moor House NNR provide established budgets of C, N and P for the site [e.g., Worrall et al. 2012] and effective oxidation states [Worrall et al. 2017] which make the site ideal for direct OR measurement. Worrall et al. [2015] found no significant change in C_{ox} or OR with depth in peat cores from Moor House. Worrall et al. [2003] found that the study catchment is a net sink of carbon of ~12.9 $gC/m^2/yr$ based on an input and output model taking into account dissolved and particulate organic carbon [DOC and POC]; inorganic carbon; wet and dry deposition; methane [CH_4] and CO_2 exchange.

In 1954, Dr R.J. Elliot set up plots at Hard Hill within the Moor House site to study vegetation change under burning and grazing management: one of these plots [plot A] was used for this study. The plot consists of six sub-plots, three of which are fenced off to prevent grazing whilst the adjacent three are unfenced and therefore lightly grazed. Each set of three plots consists of three randomly allocated vegetation types determined by prescribed burning rotations of no burning, a 10-year burn period and a 20-year burn period [Lee et al. 2013].

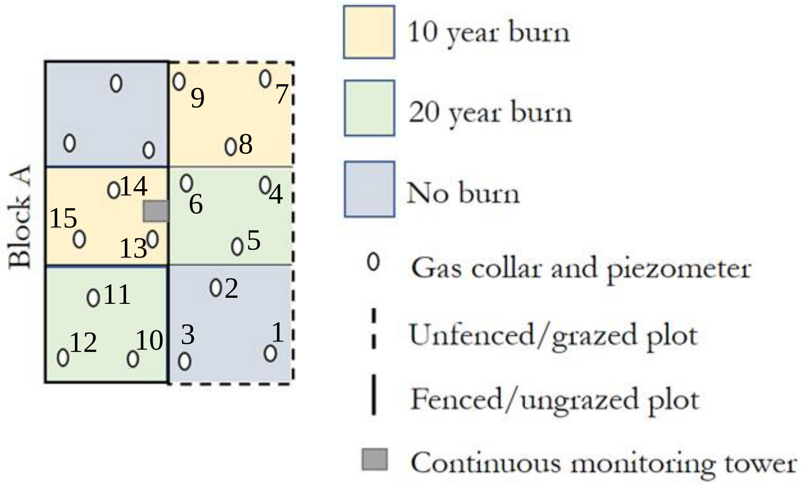
2.3.2 Experimental design

2.3.2.1 Sampling

Hard Hill Plot A was selected for this study for ease of access [Figure 2.2]. 18 gas collars of 15 cm diameter were installed in Hard Hill Plot A. The gas collars were inserted firmly into intact soil to make a rough seal. Each gas collar was placed on top of intact vegetation to ensure photosynthetic and respiratory activity would be recorded. Within each sub-plot, 3 gas collars were installed in the vegetation of each height, both in the grazed and ungrazed sections. Within 50 cm of each gas collar, a piezometer was installed in the peat. Gas collars and piezometers were installed at least 2 weeks prior to any measurements being made to minimise effects of ecosystem disturbance.

Due to the location of the field site and adverse weather conditions, flux analysis was not performed in the months from December 2018 to April 2019. This lack of access was a serious limitation of the study as short-term variations in gaseous flux and OR over winter and early-spring could not be determined. Time restrictions of visits to the Moor House peatland meant that only 5 of the six sub-plots in Plot A could be analysed and no gaseous flux analyses were performed in the ungrazed/no-burn sub-plot.

Figure 2.2: Hard Hill Plot A at Moor House NNR showing burn rotations and grazing regimes. Each square plot is 30mx30m within a rectangular block of six plots. Numbers represent the ordering and labelling system of gas collar plots used in taking measurements.



2.3.2.2 Gaseous flux analysis

CO_2 and O_2 flux were measured on 08/11/2018, 29/11/2018, 15/05/2019 and 14/06/2019. Gaseous fluxes were measured using an infrared gas analyser or IRGA [PP-systems EGM-5] connected to a closed chamber [PP-systems canopy assimilation chamber CPY-5, dimensions 145mm x 146mm]. The CPY-5 includes sensors for measurement of air temperature and photosynthetically active radiation [PAR].

The CPY-5 was installed on each gas collar, ensuring a tight fit. A steady state was thus created, in which gas flows through a chamber over the soil and the upstream and downstream gas concentrations are compared. The CPY-5 was flushed in air prior to measurement, then left to measure O_2 and CO_2 flux and PAR intensity. To measure gaseous flux under light conditions the CPY-5 chamber was left uncovered. To measure flux under dark conditions an opaque shroud was placed over the CPY chamber to eliminate light, this shroud enabled measurement of dark ecosystem respiration [autotrophic and heterotrophic]. Flow rate through the IRGA occurred at a rate of 300 cm^3/min. Computer software, “Gas Analysis Software [GAS]” version

3.11 was used to read and record results from the EGM-5. In the first month of measurements [November 2018], a recording period of 5 minutes under light conditions followed by 5 minutes under dark conditions was used. On later field excursions, a longer period of measurement of CO_2 and O_2 flux was adopted to overcome a lower precision of O_2 measurement. On 15/05/2019 the period of measurement used for the EGM-5 software was 40 minutes under dark conditions followed by 40 minutes under light conditions. On 14/06/2019, a 30 minute recording time was used under each light condition. All measurements on the 14/06/2019, except the second measurement at Plot 8 [see Figure 2.2], were taken with the dark recording first. A summary of field measurements is shown in Table 2.1.

The flux of gaseous O_2 and CO_2 was calculated by the same method and over the same time period to reduce error. Gaseous flux was calculated assuming the ideal gas laws were obeyed within the CPY-5 system using Equation 2.1:

$$Gas\ flux = \frac{\left(\frac{(\Delta[X])}{22.4} * V\right) * 10^6}{At} \qquad \text{[Equation 2.1]}$$

Where gas flux = change in concentration of the gas per unit area per second [in μmol m^{-2} s^{-1}], $\Delta[X]$ = change in concentration of the gas [X] = CO_2 or O_2 [in %], V = volume of the CPY-5 chamber [litres], A = area of the soil in contact with the chamber [in m^2] and t=period of measurement of flux in seconds. The constant 22.4 L is the volume of air occupied by one mole of an ideal gas [Kolb 1978].

Table 2.1: Summary of field OR measurements and recording conditions throughout the year.

Date	Number of OR measurements	Weather conditions	Duration of light/dark measurement	Light measurement at start or end	Comments
08/11/2018	13	Light rain, moderate wind, 5-12°C, PAR 45-320µmol m^{-2} s^{-1}.	5 minutes/5 minutes	start	Waether conditions worsened throughout day.
29/11/2018	2	Heavy rain, strong wind, cold, <10°C, PAR 60-70µmol m^{-2} s^{-1}.	5 minutes/5 minutes	start	Equipment failed as result of poor weather.
15/05/2019	4	Dry, light wind, ~20-25°C, PAR 300-1300µmol m^{-2} s^{-1}.	40 minutes/40 minutes	end	Fewer measurments could be made as a result of longer recording time.
14/06/2019	5	Dry, light wind, ~25-30°C, PAR 500-1100µmol m^{-2} s^{-1}.	30 minutes/30 minutes	4 at end, 1 at start	Fewer measurments could be made as a result of longer recording time.

2.3.2.3 Groundwater level

At the time of measurement of gas flux, a water table depth measurement was taken from the piezometer that had been co-located with the gas collar using a PP-systems tape measure.

2.3.2.4 Oxidative Ratio

O_2 flux corresponding to oxygen released into the atmosphere as a result of photosynthetic activity was inferred to be equal to the difference between oxygen fluxes under light and dark conditions. The CO_2 flux sequestered by the terrestrial biosphere by photosynthesis was calculated as the difference between light and dark condition fluxes. The OR was calculated from the total CO_2 and O_2 flux differences using Equation 1.1. This was performed for each gas collar using the measurements made upon field visitation each month.

2.3.2.5 Statistical analysis

This experiment was designed to test how the OR of a peat bog ecosystem varied with changing environmental parameters. To answer this question, a linear regression model was performed to assess the statistical significance of photosynthetically active radiation [PAR] levels and the water table depth [wtd] in determining the OR measured by gaseous flux analysis. The OR response variable was tested for normality prior to regression using the Anderson-Darling test [Anderson and Darling, 1952]. If the dataset failed the normality test [i.e. Anderson-Darling [AD] statistic > 5.0 or dataset without linear trend on the normality plot] the outlier OR measurements were removed from further statistical analysis. Following removal of the outliers that dataset was retested using the AD test to ensure normality

2.4 Results

2.4.1 Measurements under light conditions

2.4.1i 08/11/2018

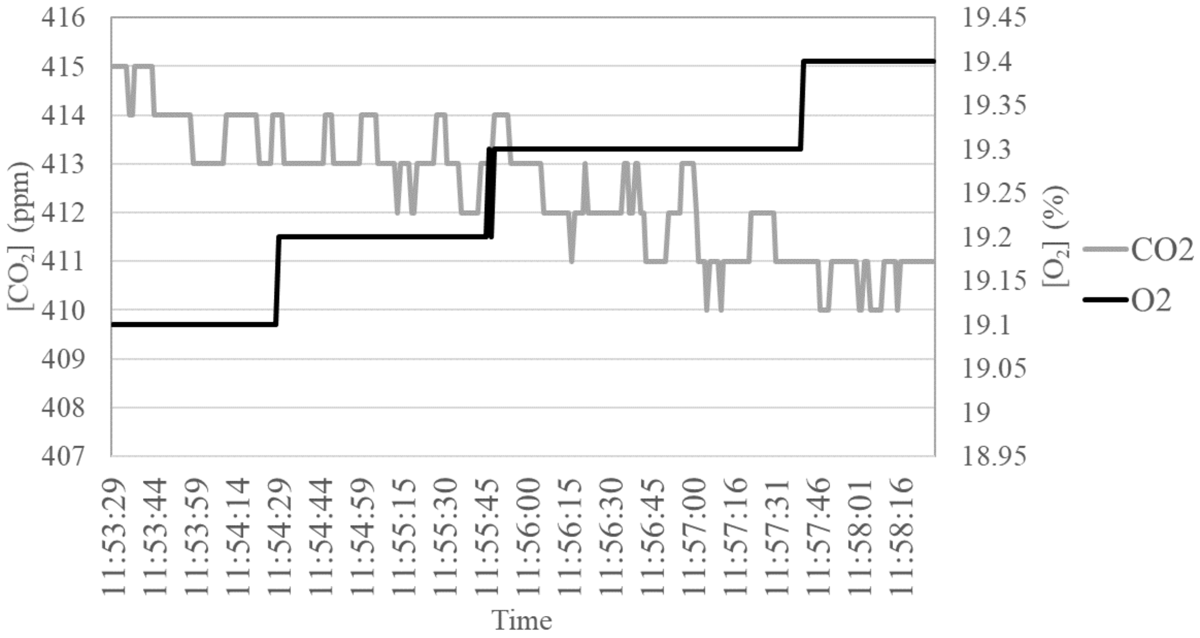
On this day it was possible to make 13 measurements of gas flux under light conditions. Under light conditions, O_2 concentration within the CPY-5 chamber was observed to increase [upto 0.3%] or remain constant in 11 of the 13 measurements made over a 5 minute recording period [Table 2.2]. The increase in O_2 concentration observed at Plot 1 was steady throughout the 5 minute record [Figure 2.3]. On this first day of flux measurement, the concentration of O_2 in the chamber was observed to decrease by 0.1% over the 5 minute recording period at two of the plots [Plots 2 and 10] under light conditions.

When exposed to light, CO_2 concentration within the chamber was observed to decrease in 7 of the 13 5-minute monitoring periods [Table 2.2]. On the first monitoring day, change in CO_2 in a 5-minute monitoring period under light conditions ranged from an increase of 5 ppm to a decrease of 10 ppm [ppm is parts per million volume]. Under constant light conditions at Plot 1, CO_2 concentration showed a continuous steady decrease in concentration with minor fluctuations from linear [Figure 2.3].

Table 2.2: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under light conditions on 08/11/2018. Negative values represent a fall in the concentration of the gas in the chamber. On all occasions the light measurement was made immediately before the dark measurement and the recording period used was 5 minutes.

Plot	mean PAR	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
1	313	0.3	-0.0005	64.88	-0.11
2	238	-0.1	0.0003	-21.63	0.06
3	293	0.1	-0.0007	21.63	-0.15
4	220	0	-0.0010	0.00	-0.22
5	275	0.3	0.0002	64.88	0.04
6	262	0	-0.0003	0.00	-0.06
7	105	0	-0.0004	0.00	-0.09
8	89	0.2	-0.0005	43.25	-0.11
9	106	0	-0.0003	0.00	-0.06
10	93	-0.1	0.0005	-21.63	0.11
11	88	0.1	0.0004	21.63	0.09
12	46	0.2	0.0003	43.25	0.06
13	47	0.1	0.0005	21.63	0.11

Figure 2.3: Concentration of O_2 and CO_2 in the CYP-5 chamber over 5-minute recording interval as measured on 08/11/2018 at Plot 1 under light conditions.



Due to the lower precision of measurement of O_2 relative to CO_2, observed changes in concentration of O_2 within the chamber were less frequent [Figure 2.3, 2.4]. Mean O_2 flux over a five-minute recording interval on the 08/11/2018 returned values ranging from -21.63 to 64.88 µmol m^{-2} s^{-1} [Table 2.2]. Calculated CO_2 flux ranged from -0.22 to 0.11 µmol m^{-2} s^{-1}.

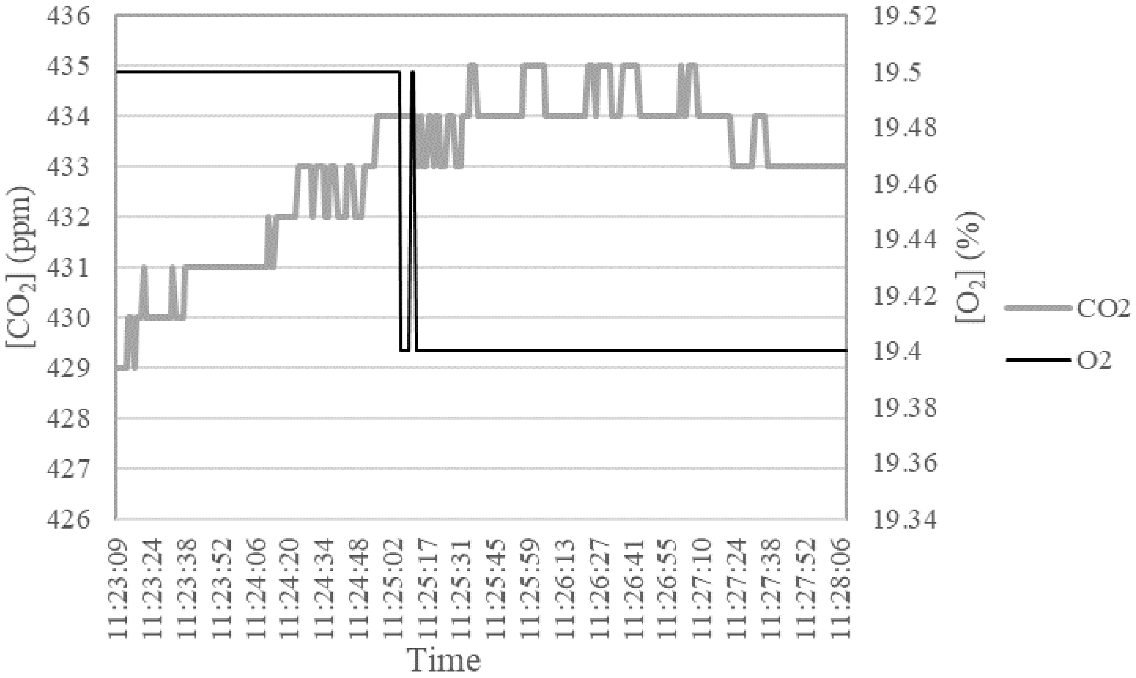
2.4.1ii 29/11/2018

On this day, the EGM-5 function was lost as a result of poor weather conditions and therefore it was possible to make only 2 measurements of gas flux under light conditions. Under light conditions on 29/11/2018, the O_2 concentration in the CPY-5 chamber was observed to fall by 0.1% at Plot 4 and remain constant at Plot 5 [Table 2.3]. CO_2 concentration in the chamber increased during both 5-minute light condition measurements [Figure 2.4]. At Plot 4, the concentration of CO_2 in the CPY-5 chamber increased steadily from 429 ppm to 434 ppm over the first 2 minutes of recording then settled out at this level for the remaining measurement. It should be noted that average light intensity was low on this day, both measurements being made under mean PARs of less than 70 µmol m^{-2} s^{-1}.

Table 2.3: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under light conditions on 29/11/2018. Negative values represent a fall in the concentration of the gas in the chamber. On all occasions the light measurement was made first and the measurement period used was 5 minutes.

Plot	mean PAR	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
4	69	-0.1	0.0004	-21.63	0.09
5	64	0	0.0002	0.00	0.04

Figure 2.4: CO_2 and O_2 concentration in the CPY-5 chamber over 5 minute recording interval under light conditions at Plot 4 on 29/11/2018.



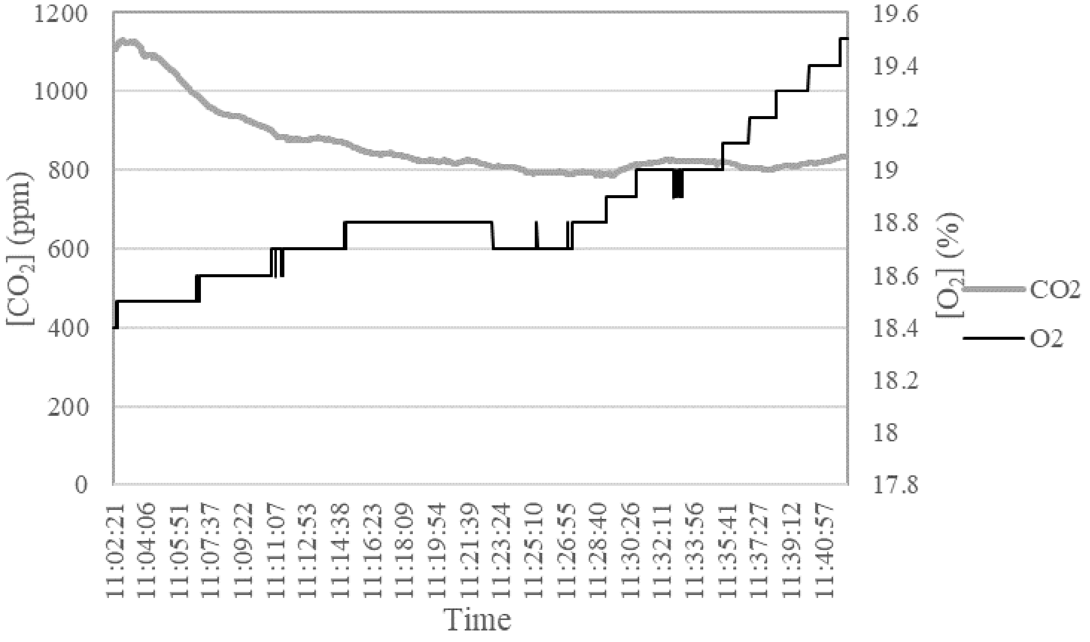
2.4.1iii 15/05/2019

On this day it was possible to make 4 measurements of gaseous flux under light conditions; this was less than performed on 08/11/2019 as a result of the longer recording period used in May measurements. Change in O_2 concentration in the CPY-5 chamber on 15/05/2019 under light conditions over a 40 minute recording interval varied from a decrease of 0.2% to an increase of 1.1%. CO_2 concentration decreased by a value between 0.0249% and 0.0282% [Table 2.4]. The observed decrease in CO_2 concentration under light conditions was fast when photosynthetically active radiation [PAR] initially entered the CPY-5 and gas collar system, then gradually declined to a slower rate of fall with some fluctuation in concentration [Figure 2.5]. At the Plots 3 and 13, O_2 concentration showed an almost linear increase over the recording interval.

Table 2.4: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under light conditions on 15/05/2019. Negative values represent a fall in the concentration of the gas in the chamber. On all occasions the light measurement was made immediately following the dark measurement and the measurement period was 40 minutes.

Plot	mean PAR	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
3	1258	1.1	-0.0278	29.74	-0.75
8	434	-0.2	-0.0249	-5.41	-0.67
13	441	0.1	-0.0258	2.70	-0.70
12	349	-0.1	-0.0282	-2.70	-0.76

Figure 2.5: CO_2 and O_2 concentration in the CPY-5 chamber over 40 minute recording interval under light conditions at Plot 3 on 15/05/2019.



2.4.1iv 14/06/2019

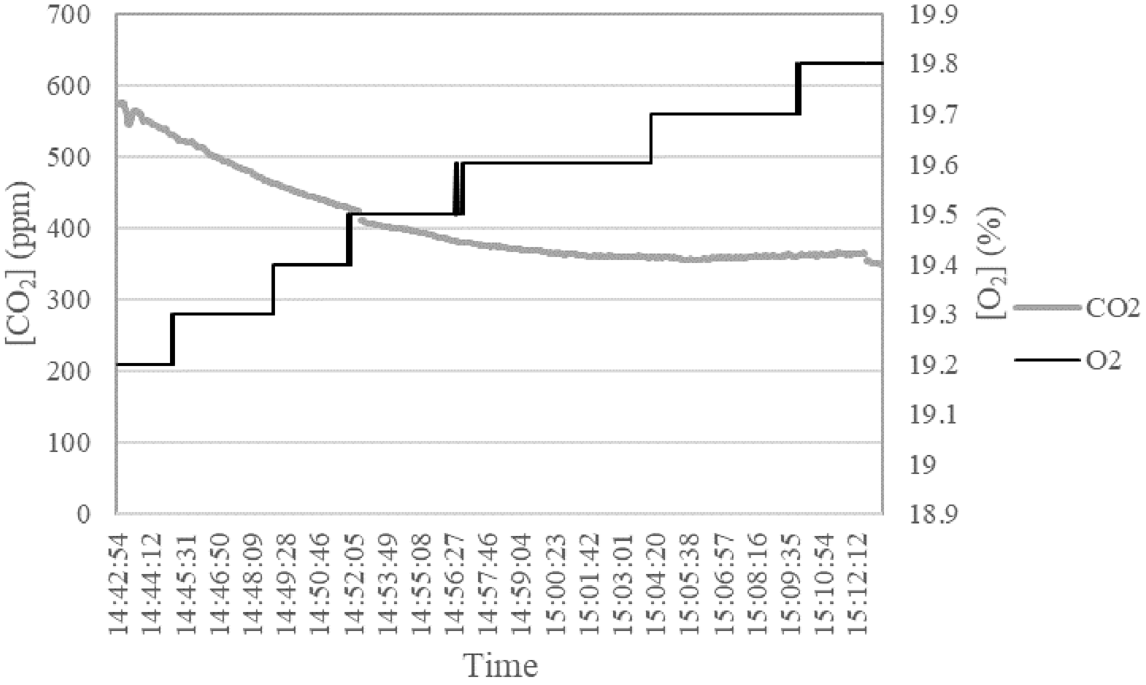
Under light conditions on 14/06/2019, the O_2 flux measured over a 30 minute recording period ranged from -21.63 to 21.63 μmol m^{-2} s^{-1}. Four of the five O_2 flux measurements were positive, showing an increase in the O_2 concentration in the CPY-5 chamber, resulting from a net outflux from the peat soil. CO_2 flux was negative in all five measurements made under light conditions, representing a decrease in the concentration in the chamber and a net flow into the peat soil. CO_2 flux varied from -0.80 μmol m^{-2} s^{-1} to -1.43 μmol m^{-2} s^{-1} [Table 2.5].

Table 2.5: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under light conditions on 14/06/2019. Negative values represent a fall in the concentration of the gas in the chamber. The light measurement was made immediately following the dark measurement, except the second measurement at Plot 8 where the light recording was first. The measurement period was 30 minutes.

Plot	mean PAR	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
3	827	-0.6	-0.0396	-21.63	-1.43
8	517	0.3	-0.0072	10.81	-0.26
8	517	0.3	-0.0072	10.81	-0.26
6	1078	0.6	-0.0062	21.63	-0.22
13	578	0.6	-0.0218	21.63	-0.80

Increase in O_2 observed in 4 of the 5 light measurements was linear throughout the recording period [Figure 2.6]. Decrease in CO_2 concentration was greatest at the start of the recording period under light conditions, when PAR initially entered the system [e.g., Figure 2.6].

Figure 2.6: CO_2 and O_2 concentration in the CPY-5 chamber over 30 minute recording interval under light conditions at Plot 13 on 14/06/2019.



2.4.2 Measurements under dark conditions

2.4.2i 08/11/2018

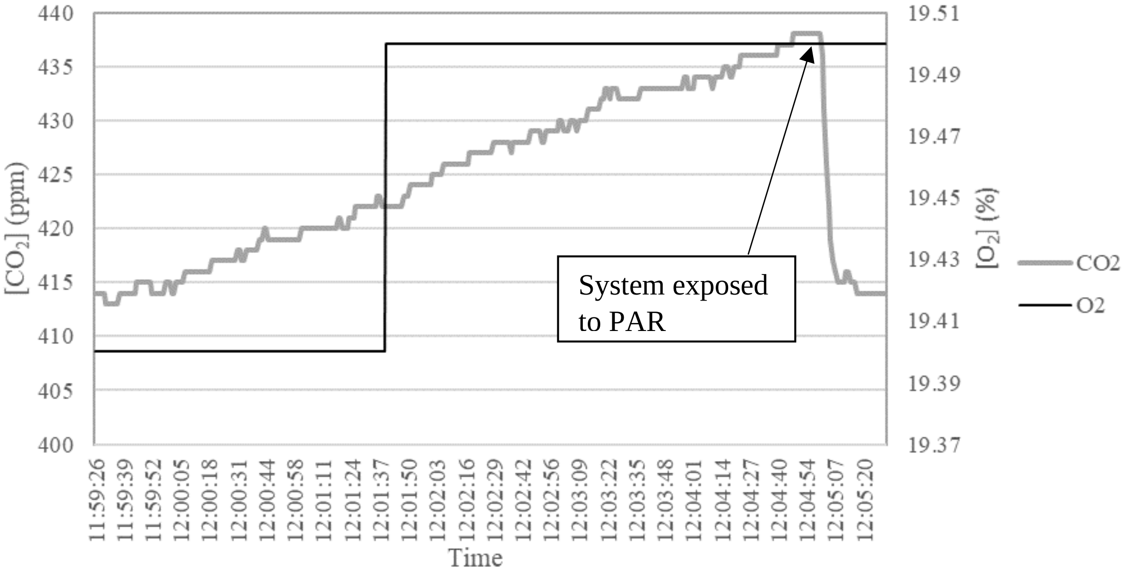
On 08/11/2018, under dark conditions the concentration of O_2 in the chamber over the 5-minute recording period was observed to remain constant at three plots and increase by 0.1% at six plots out of the 13 analysed [Table 2.6, Figure 2.7]. At two of the plots the concentration of O_2 in the chamber decreased by 0.1% and at Plot 10 the concentration of O_2 increased by 0.3%. CO_2 concentration in the CPY-5 chamber increased in 12 of the 13 measurements made. The change in CO_2 concentration in the CPY-5 chamber ranged from -0.0001% to 0.0029%.

Table 2.6: Change in concentration and corresponding flux of O_2 and CO_2 in CYP-5 chamber at each plot as measured under dark conditions over 5 minute period on 08/11/2018. Positive values represent an increase in the gas concentration in the chamber.

Plot	mean PAR	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
1	8	0.1	0.0024	21.63	0.52
2	5	0	0.0016	0.00	0.35
3	9	0	0.0003	0.00	0.06
4	1	-0.1	0.0008	-21.63	0.17
5	8	0.1	0.0003	21.63	0.06
6	7	0.1	0.0003	21.63	0.06
7	3	-0.1	-0.0001	-21.63	-0.02
8	1	0.1	0.0001	21.63	0.02
9	3	-0.2	0.0004	-43.25	0.09
10	4	0.3	0.0005	64.88	0.11
11	3	0	0.0029	0.00	0.63
12	0	0.1	0.0008	21.63	0.17
13	0	0.1	0.0015	21.63	0.32

At Plot 1 on 08/11/2018, CO_2 concentration in the CPY-5 chamber increased steadily over the 5-minute dark recording period. When the system was exposed to light at the end of the dark-chamber measurement, the concentration of CO_2 decreased rapidly to levels close to pre-dark chamber concentrations [Figure 2.7].

Figure 2.7: Concentration of O_2 and CO_2 in the CPY-5 chamber over 5-minute recording interval as measured on 08/11/2018 at Plot 1 under dark conditions.


System exposed to PAR

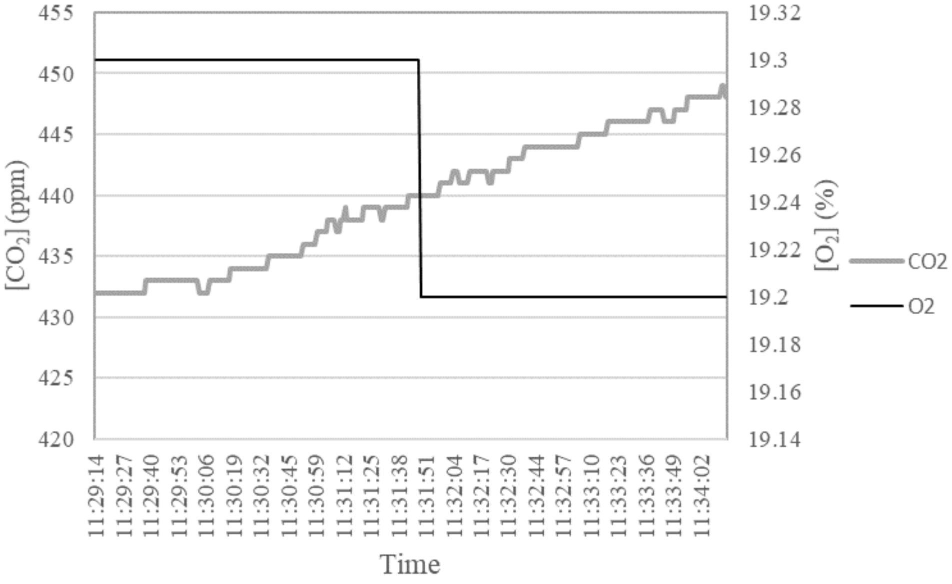
2.4.2ii 29/11/2018

Only two dark measurements could be made on this day. Under dark conditions on 29/05/2019, the O_2 concentration in the CPY-5 chamber over a 5-minute recording period remained constant or decreased by 0.1% [Table. 2.7]. CO_2 concentration increased during both dark-chamber measurements [Figure 2.8]. The lower precision of measurement of O_2 concentration made comparison of fluxes difficult when the recording period was 5-minutes as change in O_2 concentration was often less than 0.1% [below the detection limit].

Table 2.7: Change in concentration and corresponding flux of O_2 and CO_2 in CYP-5 chamber at each plot as measured under dark conditions over 5 minute period on 29/11/2018.

Plot	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
4	-0.1	0.0016	-21.63	0.35
5	0	0.0001	0.00	0.02

Figure 2.8: CO_2 and O_2 concentration in the CPY-5 chamber over 5 minute recording interval under dark conditions at Plot 4 on 29/11/2018.



2.4.2iii 15/05/2019

Two of the four measurements made under dark conditions on 15/05/2019 showed positive O_2 fluxes [i.e. O_2 concentration entering the chamber from the soil]. The other two O_2 flux measurements made were negative [Table 2.8]. All dark-system measurements showed positive CO_2 fluxes [ranging from 0.70 to 1.86µmol m^{-2} s^{-1}], representing an increase in the CO_2 concentration in the CPY-5 chamber.

Table 2.8: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under dark conditions on 15/05/2019. On all occasions the dark measurement was made immediately before the light measurement and the recording period was 40 minutes.

Plot	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
3	0.8	0.0688	21.63	1.86
8	0.4	0.0260	10.81	0.70
13	-0.1	0.0584	-2.70	1.58
12	-0.4	0.0340	-10.81	0.92

Rate of increase of CO_2 concentration in the CPY-5 chamber was highest at the start of the recording period, then settled to a slower rate as the recording period continued [Figure 2.09, 2.10]. Trends in change in O_2 concentration varied between plots. At Plot 3, a 0.2% fall in O_2 concentration in the initial 10 minutes of recording was followed by a steady increase of 1.0% over the final 30 minutes. At Plot 12, a steady fall in the O_2 concentration in the CPY-5 chamber of 0.4% was observed during the 40 minute record.

Figure 2.9: CO_2 and O_2 concentration in CPY-5 chamber at Plot 3 over 40 minute recording period under dark conditions on 15/05/2019.

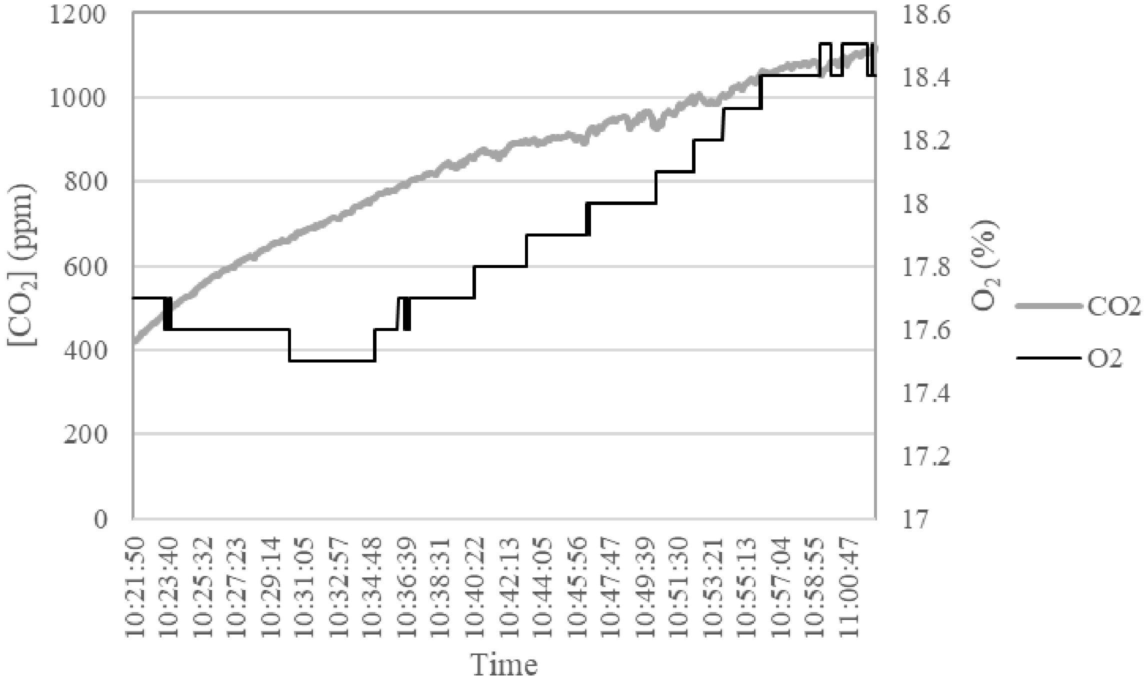
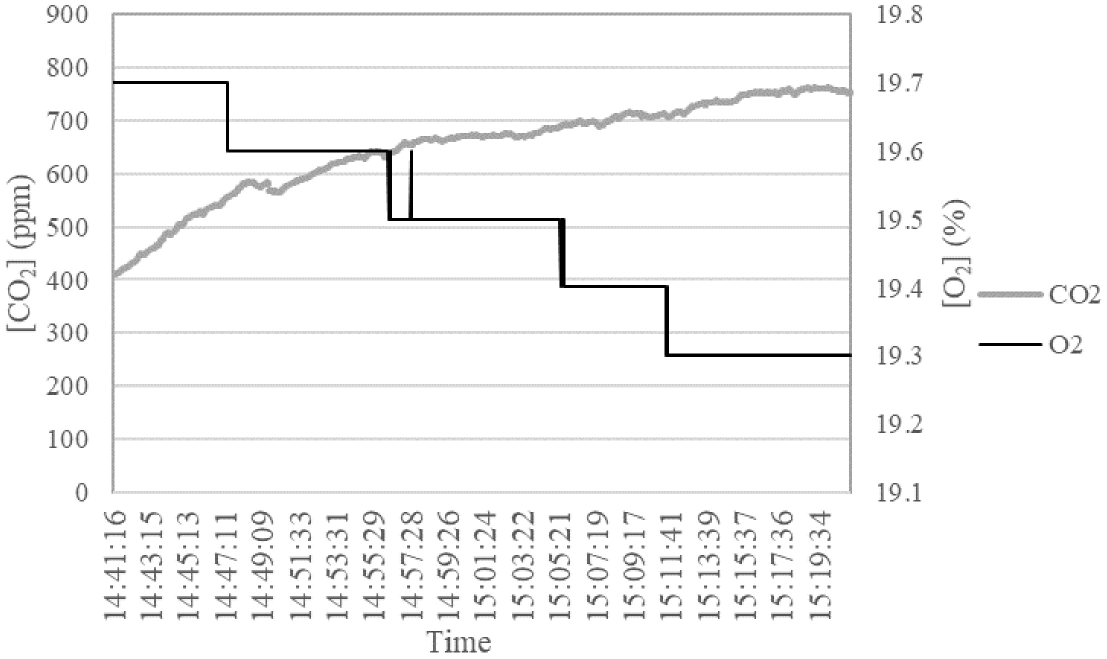


Figure 2.10: CO_2 and O_2 concentration in CPY-5 chamber at Plot 12 over 40 minute recording period under dark conditions on 15/05/2019.



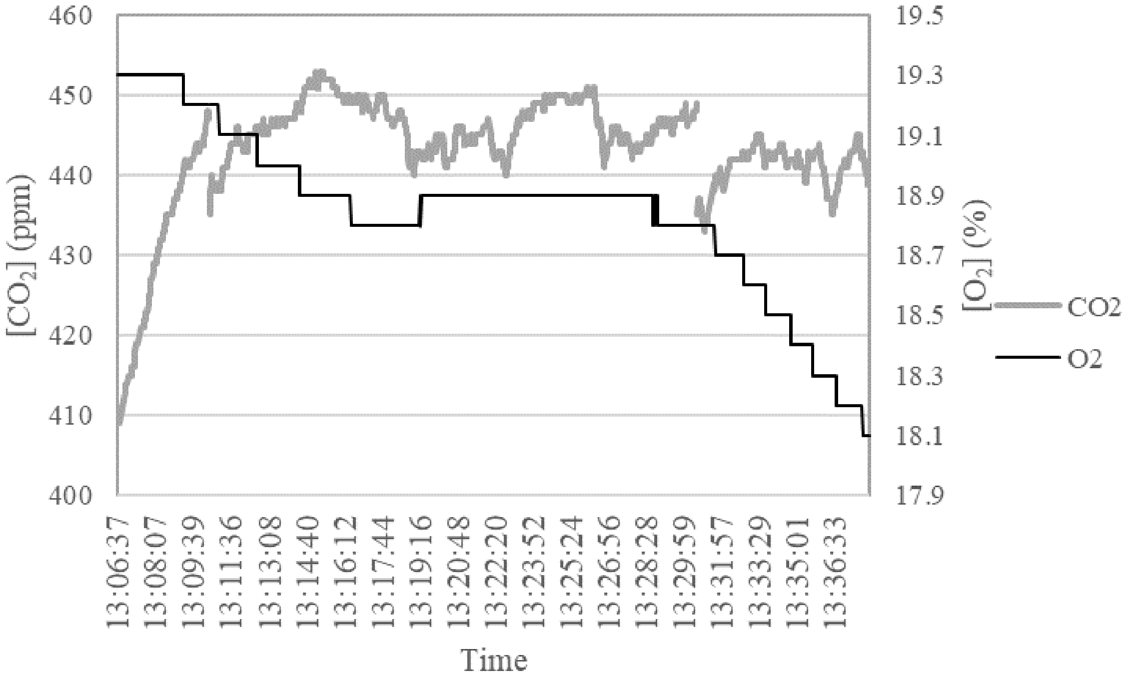
2.4.2iv 14/06/2019

The mean O_2 flux across the 30 minute recording period was negative in three of the five dark recording intervals on 14/06/2019 [Table 2.9], showing a net flow of O_2 into the soil from the CPY-5 chamber. The CO_2 flux was positive in all 5 measurements, showing net flow into the chamber. As observed on 15/05/2019, the rate of increase of CO_2 concentration was greatest at the start of the recording period [Figure 2.11].

Table 2.9: Change in concentration and corresponding fluxes of O_2 and CO_2 in CYP-5 chamber at each plot as measured under dark conditions on 14/06/2019. On all occasions except the second measurement at Plot 8, the dark measurement was made immediately before the light measurement. The second measurement at Plot 8 was made with the light reading immediately before the dark. The recording period used was 30 minutes.

Plot	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
3	-0.7	0.0294	-25.23	1.06
8	0.9	0.0034	32.44	0.12
8	-0.4	0.0152	-14.42	0.55
6	-1.0	0.0027	-36.04	0.10
13	0.4	0.0155	14.42	0.56

Figure 2.11: CO_2 and O_2 concentration in the CPY-5 chamber over 30 minute recording interval under dark conditions at Plot 6 on 14/06/2019.



2.4.3 Oxidative Ratio

Between November 2018 and June 2019, 24 OR measurements were made using the direct gaseous flux measurement method at Moor House NNR. By subtracting the value of flux under dark conditions, the change in concentration as a result of respiration is removed from the light measurements. Hence the values of O_2 flux and CO_2 flux calculated by this method represent the photosynthetic fluxes with changes resulting from respiration removed. O_2 released during photosynthesis had a mean value of 8.64 µmol m^{-2} s^{-1} and a range of -86.51 µmol m^{-2} s^{-1} to 57.67 µmol m^{-2} s^{-1}. CO_2 sequestered during photosynthesis had a mean value of 0.68 µmol m^{-2} s^{-1} and ranged from -0.02 µmol m^{-2} s^{-1} to 2.61 µmol m^{-2} s^{-1}.

Table 2.10: O_2 and CO_2 flux resulting from photosynthetic activity as measured on 08/11/2018. The Oxidative Ratio [OR] is calculated as O_2 flux/CO_2 flux.

Plot	O_2 released (μmol m^{-2} s^{-1})	CO_2 sequestered (μmol m^{-2} s^{-1})	Oxidative Ratio
1	43.25	0.63	68.97
2	-21.63	0.28	-76.92
3	21.63	0.22	100.00
4	21.63	0.39	55.56
5	43.25	0.02	2000.00
6	-21.63	0.13	-166.67
7	21.63	0.06	333.33
8	21.63	0.13	166.67
9	43.25	0.15	285.71
10	-86.51	0.00	0.00
11	21.63	0.54	40.00
12	21.63	0.11	200.00
13	0.00	0.22	0.00

Table 2.11: O_2 and CO_2 flux resulting from photosynthetic activity as measured on 29/11/2018. The OR is calculated as O_2 flux/CO_2 flux.

Plot	O_2 released (μmol m^{-2} s^{-1})	CO_2 sequestered (μmol m^{-2} s^{-1})	Oxidative Ratio
4	0.00	0.26	0.00
5	0.00	-0.02	0.00

Mean OR of the measurements made in November was 200.44 with a range of -166.67 to 2000. This OR value is positive as expected. Three of the O_2 flux measurements were negative [Tables 2.10 and 2.11], suggesting net flux into the peat soil during photosynthesis. The five-minute recording period limited the variation in O_2 concentration which could be observed in the chamber. The lower precision of measurement of O_2 concentration of the EGM-5 meant that in 3 of 15 measurements no change in O_2 concentration was observed and hence an O_2 flux of 0.00 µmol m^{-2} s^{-1} was calculated.

To overcome the low precision of the O_2 flux measurements, a longer recording period was used in May and June 2019. A mean OR of -0.37 was calculated based on a 40 minute recording period in May 2019, OR results ranged from -11.79 to 4.82 [Table 2.12]. Mean OR was 32.24 [range of -56.60 to 179.78] for June 2019 from a 30-minute recording period [Table 2.13]. On both the May and June measurement day one of the ORs calculate was negative, resulting from a negative O_2 flux, suggestion O_2 flow into the peat soil from the CPY-5 chamber during photosynthesis.

Table 2.12: O_2 and CO_2 flux resulting from photosynthetic activity as measured on 15/05/2019. The OR is calculated as O_2 flux/CO_2 flux.

Plot	O_2 released (µmol m^{-2} s^{-1})	CO_2 sequestered (µmol m^{-2} s^{-1})	Oxidative Ratio
3	8.11	2.61	3.11
8	-16.22	1.38	-11.79
13	5.41	2.28	2.38
12	8.11	1.68	4.82

Table 2.13: O_2 and CO_2 flux resulting from photosynthetic activity as measured on 14/06/2019. The OR is calculated as O_2 flux/CO_2 flux.

Plot	O_2 released (µmol m^{-2} s^{-1})	CO_2 sequestered (µmol m^{-2} s^{-1})	Oxidative Ratio
3	3.60	2.49	1.45
8	-21.63	0.38	-56.60
8	25.23	0.81	31.25
6	57.67	0.32	179.78
13	7.21	1.36	5.32

2.4.4 Statistical analysis

The measurement of OR made at Plot 5 on 08/11/2018 was removed from further statistical analysis based on the results of the Anderson-Darling normality test [Figure 2.12]. Results of the linear regression model show that PAR did not cause a significant change in OR measured [i.e. $p>0.05$]. There was also no significant change in OR with water table depth. The mean OR, after removal of 4% of the data, was 50.71 and results ranged from -166.67μmol m^{-2} s^{-1} to 333.33μmol m^{-2} s^{-1}. The mean OR calculated in each month when measurements could be made is shown in Table 2.14.

Figure 2.12: Results of the Anderson-Darling normality test on the growth tent OR measurements. (a) Shows the AD-test prior to removal of outliers, this AD test failed based on the non-linearity of the data points. (b) Shows the AD-test following removal of 1 outlier resulting in an AD statistic = 1.278.

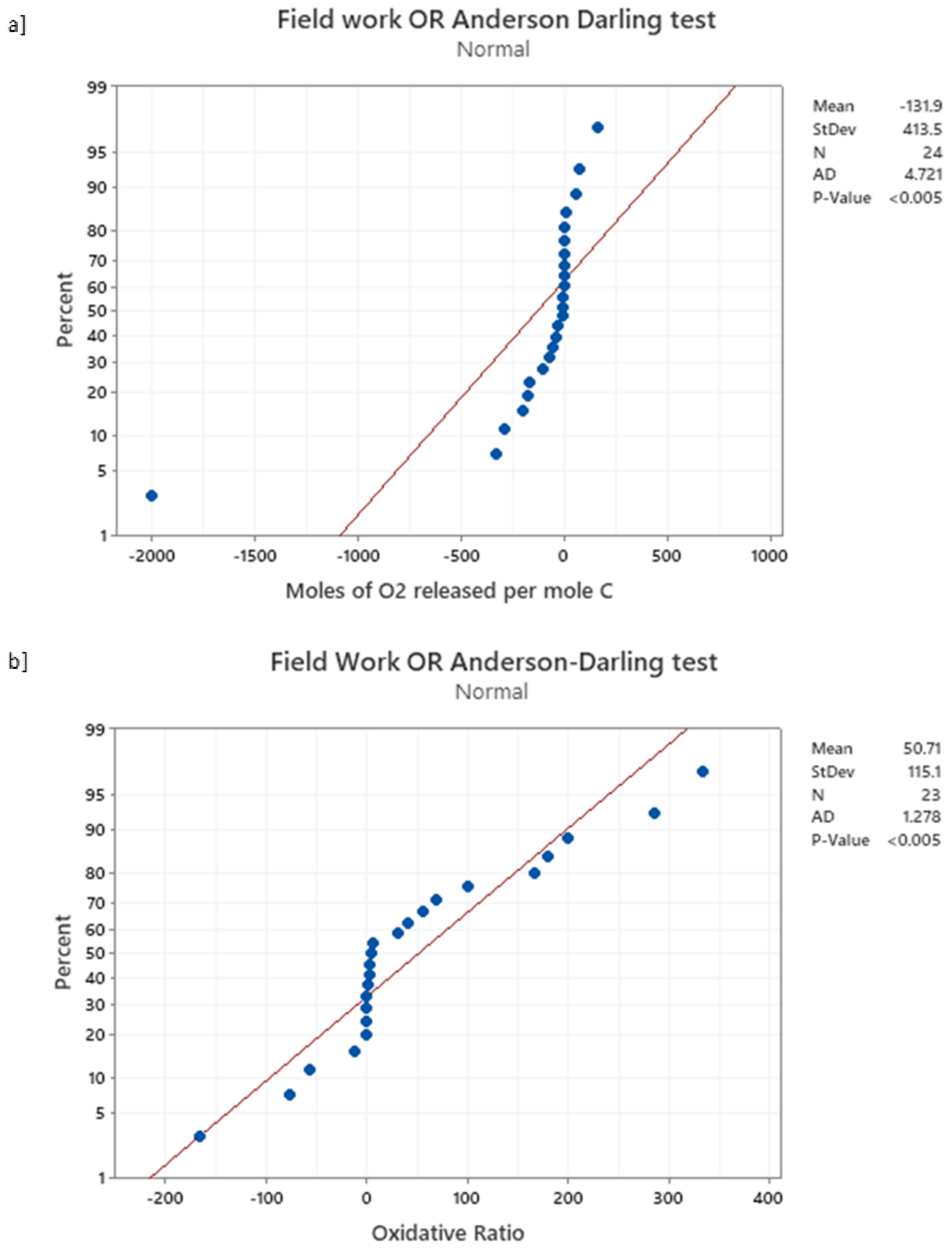


Table 2.14: Mean OR calculated for each month of measurement.

Month	Average OR
November 2018	71.9
May 2019	-0.37
June 2019	32.24

2.5 Discussion

2.5.1 Oxidative ratio of a peatland ecosystem

This Chapter has measured the OR of a peatland ecosystem to be 50.71 by gaseous flux analysis. By definition, the OR reflects the O_2 released into the atmosphere relative to the CO_2 sequestered by the terrestrial biosphere during photosynthesis, hence the positive value is expected.

In a biogeochemical system where photosynthetic activity is the dominant process over respiratory activity, atmospheric O_2 concentration is expected to increase and CO_2 concentration is expected to fall, assuming the well-known photosynthetic reaction equation:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \qquad \text{[Equation 2.2]}$$

Under light conditions, O_2 concentration was observed to increase in 13 of 24 measurements and CO_2 decreased in 16 of 24 measurements. Under dark conditions, when photosynthesis was inhibited by a lack of photosynthetically active radiation [PAR], the concentration of CO_2 in the CPY-5 chamber increased in 23 out of 24 flux measurements. Under dark conditions, the O_2 concentration decreased in 10 and remained constant in a further 4 of the 24 flux measurements. The effects of photosynthesis on gaseous concentration were, therefore, evident in the majority of results of gaseous flux analysis in the EGM-5 and CPY-5 system.

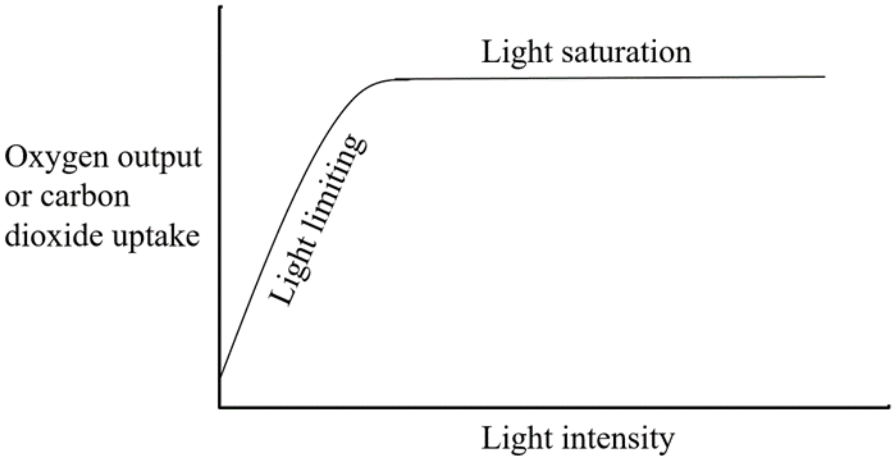
Measurements of CO_2 concentration show that under dark conditions, the rate of increase in concentration was highest at the start of the measurement period. When the dark shroud was removed from the CPY-5 chamber, the fall in concentration of CO_2 was highest at first and fell as the time of recording increased. These findings agree with those of Severinghaus [1995] and other previous incubation studies. The rapid initial increase in CO_2 concentration under dark conditions has previously been attributed to the movement of CO_2 out of the soil water down a concentration gradient as pCO_2 in soil air falls due to the initiation of flushing [Severinghaus 1995]. The reduction in rate of increase of CO_2 with time under dark conditions could be attributed to a true respiratory decrease, where the rate of oxidation of carbohydrate to CO_2 and H_2O [by the reverse of Equation 2.1] fell.

When the system had been in darkness for 5 minutes and was then exposed to light a rapid drop in CO_2 concentration occurred [Figure 2.7]. CO_2 concentration, which had been increasing steadily over the 5-minute period, fell suddenly back to its original sunlight value. The rapid change in concentration is thought to represent a sudden increase in productivity of the system. This sudden increase in rate of photosynthesis was a result of build-up of CO_2 in the system, which could then be synthesised to glucose rapidly when PAR was no longer a limiting factor [Fogg 1968]. This produces the asymmetric pattern seen in CO_2 concentration at the end of dark flux measurement.

The calculated value of OR [50.71] falls outside the theoretical range of 0-2 predicted by Masiello et al. [2008]. The mean change in O_2 concentration under light conditions across the measurement period was 0.1%. The mean change in CO_2 concentration under light conditions was 0.0079%. Hence, measured concentration change differed by a factor of 100. As a result of this difference, the OR calculated by Equation 1.1 was orders of magnitude greater than values within the range predicted by Masiello et al. [2008]. The limitations of the measurement technique used, as discussed in section 2.5.2, mean that the values of OR measured in this study should be treated with caution. The technique used is flawed and requires development and analytical error may exist relating to the conditions of measurement and the equipment used.

The linear regression model showed that the measured value of OR did not vary significantly with PAR levels or water table depth. The lack of significant change in OR with PAR is explained by considering the effect of an increased light intensity on photochemical reactions taking place during photosynthesis [Figure 2.13]. Increased light intensity results in an increased rate of photosynthesis, which is defined by the reaction shown in Equation 2.2. An increased rate of photosynthesis results in a simultaneous increase in the rate of O_2 output and CO_2 uptake. Although the concentration of both gases shows an increased change and the gaseous fluxes are higher under increased PAR, the calculated OR remains unaffected by the light intensity.

Figure 2.13: The effect of light intensity on O_2 output or CO_2 input to the terrestrial biosphere. Edited from Fogg et al. 1968.



2.5.2 Limitations

As a result of adverse weather conditions, the field site could not be visited between December 2018 and April 2019, hence OR could not be measured at the field site during this time. Since previous C flux measurements have often been carried out in Spring and Summer months, measurement over the Winter period would have contributed to advancements in the measurements of gaseous fluxes. Adverse weather limited the efficiency and working capabilities of the EGM-5 CPY-5 system, hence measurement of OR by this method is likely to continue to be affected during winter months. As field measurements could only be made during 3 months, the reliability of this study as a measure of OR over a 12-month period is difficult to assess.

The method of gaseous flux analysis, using an EGM-5 and CPY-5, was limited by the difference in measurement precision of CO_2 and O_2 gases. Since CO_2 is measured in parts per million [ppm] and O_2 in percentage [%] by the IRGA, calculation of comparable gaseous fluxes was often not possible and retuned OR values outside the range of accepted values.

2.5.3 Development of field gaseous flux measurement technique

Despite limitations, this study has developed the measurement technique of gaseous fluxes in a field environment using the EGM-5 and CPY-5 system. The initial method used a measurement period of 5 minutes. Under light conditions when photosynthesis in plant tissues is enabled, an increase in the concentration of O_2 and a fall in concentration of CO_2 in the CPY-5 chamber was expected. However, in November, 5 minute recordings made under light conditions showed an increase in O_2 concentration in only 7 of the 15 measurements. CO_2 concentration was also only observed to decrease in 7 of the 15 5-minute recoding intervals. When the recording period increased to 40 minutes, O_2 concentration was observed to increase in 2 of the 4 light measurements. However, CO_2 concentration decreased in all of the 40 minute light-recording intervals. When a recording interval of 30 minutes was used in June, under light conditions, O_2 increased in 4 of the 5 measurements made, and CO_2 concentration increased in all of the measurements. It is proposed therefore that the effects of photosynthesis are observed under recording intervals greater than 30 minutes under light conditions. The May and June light gaseous flux measurements were made under higher levels of PAR [see Tables 2.3 and 2.4] hence higher rates of photosynthesis were enabled. It is suggested therefore that the optimum measurement of OR by gaseous flux analysis is over long time periods [>30 minutes] in a highly photosynthetically active system.

It was also found that the effects of photosynthesis on gaseous flux were more evident when the dark-chamber measurements were made first. A build-up of CO_2 in the CPY-5 system under dark conditions enables photosynthesis to occur at a high rate when PAR initially enters the system. This rate falls as the concentration of CO_2 falls.

2.6 Conclusions

This chapter has attempted to measure the OR of the Moor House peatland by direct gaseous flux analysis over a 12 month study period. The value of OR calculated by this method [50.71] is outside the range proposed by any previous studies, resulting from a high-magnitude difference in the measured fluxes of CO_2 and O_2. The measurements were limited by different precisions of the CO_2 and O_2 measurement. As a result of the limitations of the measurement procedures used in this study, it is suggested that the results should be treated with caution and may not be comparable to those reported in other studies. Despite these findings, development has been made to the method of measurement of gaseous fluxes in a field environment using the CPY-5 EGM-5 system. Periods of measurement longer than 30 minutes allow changes in concentration high enough to overcome the low measurement precision of O_2. This study found that PAR and water table depth did not cause significant variation in the value of OR measured by gaseous flux analysis, however as this method of OR measurement requires further improvement and significantly more data is required, the correlation between environmental variables and OR cannot be concluded from this study.

3.0 Oxidative ratio of laboratory grown peat

3.1 Introduction

Chapter 2 identified challenges in measuring peatland Oxidative Ratio [OR] by direct gaseous flux analysis in a field environment. This chapter aims to overcome some of these difficulties by creating an artificial peatland environment where gaseous flux can be measured over long time periods on a regular basis. It is hoped that the findings of this chapter will contribute to the development of the method of OR calculation by direct gaseous flux measurement. Elemental analysis of the peat samples performed at the end of the growing period allows the OR to be measured by another well-established means for comparison of results.

3.2 Aims and objectives

The aim of this chapter was to gain an understanding of the OR of peat grown in a laboratory and develop the method of OR measurement by gaseous flux analysis. To meet these aims several objectives were established:

1. Growth of peat soil and vegetation under growth-focussed laboratory conditions.
2. Measure carbon dioxide [CO_2] and oxygen [O_2] flux between the peat soil and the atmosphere regularly over a 3-month period.
3. Calculate the OR using Equation 1.1.
4. Analyse peat samples from 2 cm depth increments in the cores and the dominant vegetation following growth in the laboratory and calculation of C_{ox} and OR.
5. Comparison of OR values returned by gaseous flux calculations and elemental analysis.
6. Development of the method of direct gaseous flux measurement of OR.

3.3 Materials and Methods

3.3.1 Sphagnum and peat sampling

Six cores of sphagnum and peat ~30 cm deep were taken from Waldridge Fell, County Durham, UK [National grid ref. NZ 2490 4971, Figure 3.1] on 17/01/2019. The cores were collected by inserting a gas collar into the bog soil and digging this out. The gas collars containing soil and sphagnum were then bagged and taken to the Environmental Geochemistry Laboratory, Durham University Earth Science Department.

Figure 3.1: Location of field site at Waldridge Fell. Images taken from Google Earth 2019.

3.3.2 Sphagnum and peat growth

The cores were removed from bags and placed, still in gas collars into a 58 cm x 58 cm plastic tray 7 cm deep [Figure 3.2]. The tray was placed in a Holland Hydroponics BAY6 75cm x 75cm x 130cm Propagation Tent [Figure 3.3]. The tent contained ventilation windows to allow circulation of O_2 and CO_2 between the tent and the laboratory. Conditions in the tent were controlled. A dual spectrum hps 250W lamp was on at full power between 6 am and 10 pm daily. This lamp provides PAR of mean intensity 240 μmol m^{-2} s^{-1} with a standard deviation of 2.11. An artificial water table was created by filling the plastic tray to ~4cm with deionized water – deionized water was used as its ionic composition and strength is similar to that of rainwater. Temperature and humidity inside the tent were monitored by a Large Display Hygro/Thermo. The six cores were numbered 1-6 [Figure 3.2].

Figure 3.2: Sphagnum and peat cores in gas collars placed in tray on 17/01/2019. Sample numbering system shown.

3.3.3i Gaseous flux measurement of OR

The sphagnum and peat cores were left to become established in the growth tent for a week prior to any analysis. In Chapter 2, it was found that when the EGM-5 runs in CPY-5 mode, an analysis time of 5 minutes puts a limit on the change in concentration of CO_2 and O_2 which can be measured. Practicality of field measurements were also limited by adverse weather conditions; short light days; and the remote location of the Moor House NNR. Gaseous flux analysis over longer time periods [exceeding 25 minutes] on peat samples grown in the laboratory enabled some of these issues to be overcome.

The core on which the measurement of gaseous flux was made was varied and recorded each time to ensure all samples were analysed equally and any difference in conditions in the tent could be identified by analysing samples in different positions. The period of measurement of flux was varied so that variation in OR with time of monitoring was understood. Analysis was performed at least twice weekly from 24/01/2019 to 01/05/2019.

Under full light conditions the CPY-5 was flushed in air and then placed onto a gas collar ensuring a tight fit [Figure 3.3a]. The growth tent was closed with the EGM-5 left outside [Figure 3.3b]. A recording period between 24 minutes to 3 hours was set for the EGM-5 and CPY-5 system to measure CO_2 and O_2 concentration in the CPY-5 chamber.

Figure 3.3[a]: Inside the growth tent during gaseous flux measurement under light conditions. CPY-5 is fitted to Core 3 here.

Figure 3.3[b]: Growth tent closed for measurement of gaseous flux under light conditions as shown in [a]. EGM-5 remains on outside of tent connected to CPY-5 on inside.

Immediately after the light record was performed, the 250W dual spectrum hps light was switched off. The CPY-5 chamber was left on the same peat sample. The growth tent was closed and the CPY-5 and EGM-5 system recorded the concentration of CO_2 and O_2 in the CPY-5 chamber for the same length of time as was recorded under light conditions. On some analyses, the light in the growth tent was switched on following the measurements under dark conditions to enable OR to be measured under conditions changing from light to dark and also from dark to light.

The fluxes of O_2 and CO_2 between the CPY-5 chamber and the peat samples were calculated over the recording period on each day of measurement. Flux calculation was performed for light and dark measurements and all fluxes were converted to μmol m^{-2} s^{-1} using Equation 2.1 [See Chapter 2, Section 2.3.2.2]. The difference between the O_2 flux in light and dark conditions was calculated. The difference between CO_2 flux under light and dark conditions was also calculated. Oxidative ratio was then calculated using Equation 1.1 [See Chapter 1, Section 1.2.1] using the flux differences calculated. The flux difference represents the flux resulting from photosynthetic activity, hence the ratio of O_2 and CO_2 flux measured in this way represents the OR.

3.3.3ii Statistical analysis

The period of time the peat samples had been growing in the growth tent; the peat core on which the measurement was made; the period of measurement of flux; and whether flux was monitored under light or dark conditions initially were all factors recorded. To assess the statistical significance of these factors in the controlling OR, analysis of variance [ANOVA] was performed. The normality of the OR dataset was first assessed using the Anderson-Darling normality test [Anderson and Darling 1952]. If the dataset failed the normality test [i.e. Anderson-Darling [AD] statistic <5.0] outliers were removed before further statistical analysis – log transformation. After removal of outliers the data series was re-tested to ensure normality [i.e. Anderson-Darling statistic < 5.0]. The ANOVA was then performed to determine the statistical significance of the experimental factors. In the ANOVA model the peat core analysed was considered a factor with 6 levels, the number of days in the growth tent was a factor with 37 levels and the order of light conditions [pre- or post- dark conditions] was a factor with 2 levels. Time of measurement of gaseous flux was considered in the ANOVA model as a covariate. The response factor considered was the calculated oxidative ratio [OR]. The Tukey *post-hoc* analysis test at 95% level was used to determine which levels of any factor showed significant differences.

3.3.4i Elemental analysis

Once all gaseous flux measurements were made, the peat cores were left to dry in their gas collars for 3 weeks. The samples were then removed from the collars and Cores 2, 4 and 6 were divided into vegetation and 2 cm depth increments to 8cm. To ensure the samples were completely dry they were left in an oven at 60°C for 48 hours. The vegetation and peat samples were all ground using a Spex Sample Prep 6770 Freezer Mill.

The ground samples [vegetation and 2 cm depth intervals] were analysed for their carbon, hydrogen, nitrogen [CHN] and separately for their oxygen [O] concentrations on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler. Computer software used was EAS Clarity [DataApex Ltd, Prague, Czech Republic]. For both CHN setup and the separate O setup calibration curves with $r^2>0.999$ were created using an acetanilide standard. Each sample was analysed in triplicate i.e. 3 times on the CHN set up and a further three times on the O set up, and a mean calculated for C, H, N and O. Samples of acetanilide were included within each run as unknown samples to act as internal quality control checks. A total of 3 vegetation and 12 peat samples were analysed for their elemental concentrations.

CHNO weight percentages were converted to molar concentrations using equation 3.1.

$$n = \frac{m}{M} \qquad \text{[Equation 3.1]}$$

where n= the molar concentration of C, H, N or O, m= the weight percentage of the element and M= the molar mass of the element. Molar concentrations were then used to calculate the carbon oxidative state [C_{ox}] using Equation 1.3 [see Chapter 1, Section 1.2.2 of this thesis]. The molar concentrations were used along with the values of C_{ox} calculated for each sample to determine the OR using Equation 1.4 [Section 1.2.3]. The degree of unsaturation [Ω] was then calculated from the molar concentrations using Equation 1.6 [Section 1.5].

3.3.4ii Statistical analysis

The core and the depth of the peat sample were two factors which had potential to cause variation in OR. A two-way ANOVA was used to determine the statistical significance of the factors – core number and peat depth. The normality of data was first assessed using the Anderson-Darling normality test [Anderson and Darling 1952]. All datasets analysed had an AD value <5 and so did not need to be transformed prior to analysis. Response variables considered were OR, C_{ox}, Ω and the elemental ratios C/N, H/C and O/C. Least mean squares of the core and depth factors with respect to each derived variable were calculated in software Minitab 18. The least squares method approximates a mean solution of overdetermined systems. Tukey pairwise comparison at the 95% confidence level was used to assess significant differences between the levels of any factor. The samples were compared with standard samples of lignin [Aldrich, CAS 8068-05-1], cellulose [Whatman, CAS 9004-36-4], humic acid [Alfa-Aesar, CAS 1415-93-6] and gluten compositions. The lignin and cellulose present two of the largest components of plants found in a peatland ecosystem [McDermitt and Loomis, 1981].

3.4 Results

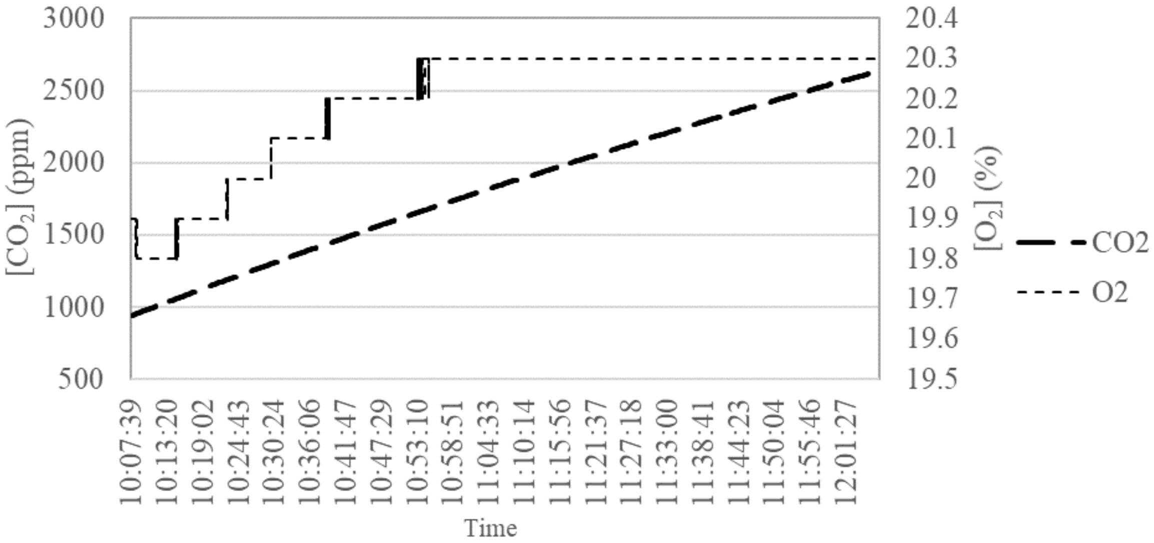
3.4.1 Gaseous flux analysis results

Over the 3 month period between 24/01/2019 to 30/04/2019, 90 measurements of O_2 and CO_2 flux were made under light conditions and 72 under dark conditions. The period of measurement ranged from 24 minutes to 3 hours. It should be noted that over the course of the measurements, the dominant vegetation types growing in the peat soil changed [Figures 3.2 and 3.4]. The abundance and size of vegetation increased over the 3-month growth period. Two plant species in particular can be noted as growing: Hydrocotyle vulgaris [marsh pennywort] and Galium saxatile [heath bedstraw] [Fitter et al., 1978].

Figure 3.4: Peat samples in the growth tent at the end of the growth period on 23/04/2019. Orientation and core numbering system as in Figure 3.2.

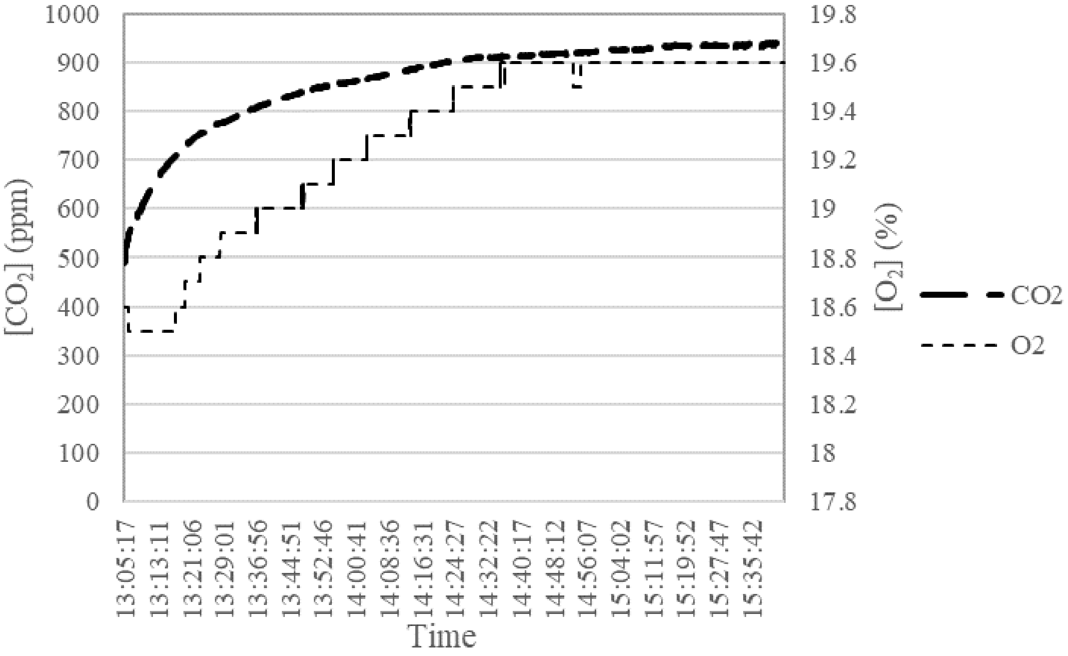
The pattern of changes in CO_2 and O_2 concentration under light conditions in the CPY-5 chamber varied across the 3-month growth-period. This section presents examples of the observed CO_2 and O_2 concentration behaviour. Measurements made under light conditions after a week of growth under the conditions described in section 3.3.2 showed an increase in the concentration of O_2 in the CPY-5 chamber [Figure 3.5]. Over a 2-hour measurement period on 06/02/2019, O_2 concentration increased by 0.4% and CO_2 concentration increased by 0.15% when the CPY-5 chamber was fitted on Core 3 in the growth tent. The increase in O_2 concentration was observed in the first 55 minutes of recording; concentration then settled out and remained constant at 20.3% for the remainder of the 2 hour recording period. CO_2 concentration showed an almost linear increase through the 2 hour recording period.

Figure 3.5: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 3 under light conditions on 24/01/2019.



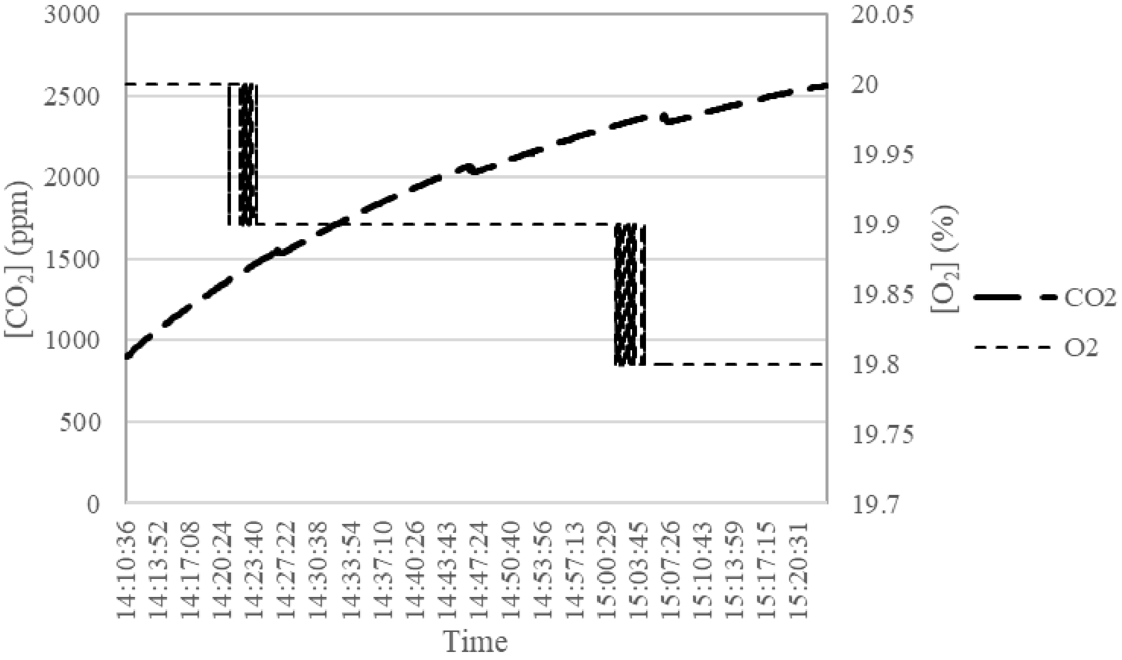
When the samples of peat had been left in the growth tent for 3 weeks, the pattern of change in concentration of CO_2 in the CPY-5 chamber under light conditions changed. Instead of a linear increase, as observed in Figure 3.5, rate of increase of CO_2 concentration in the CPY-5 chamber was observed to fall with time of recording [Figure 3.6]. Reduction in rate of CO_2 increase or decrease with time of recording was a common trend. Increase in concentration of CO_2 observed under light conditions decreased in magnitude when the samples had been growing in the growth tent for a longer time period [Table 3.2].

Figure 3.6: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 2 under light conditions on 21/02/2019.



When the measurements under light conditions followed dark conditions, CO_2 concentration in the CPY-5 chamber was observed to decrease in 100% of recordings [e.g., Figure 3.8]. During the majority of light measurements, O_2 concentration was observed to increase at the start of the recording period and then reach a maximum value [e.g., Fig 3.5, 3.6].

Figure 3.7: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 6 under light conditions on 24/04/2019.



Under light conditions, the O_2 flux between the peat samples and CPY-5 chamber was positive in 79 of the 90 measurements, indicating a net flux of O_2 from the biosphere into the atmosphere. Exceptions to this rule are two negative fluxes measured in the first month of analysis at Core 2 [Table 3.1]. In 9 measurements no net flux of O_2 into or out of the peat sample was recorded. The highest O_2 flux measured under light conditions was 16.22 µmol m^{-2} s^{-1} at Core 4 on 25/04/2019 and the lowest was -6.55 µmol m^{-2} s^{-1} on 18/02/2019 at Core 2.

A total of 54 of the 90 measurements had negative CO_2 fluxes. At the start of the growth period, in January and February, CO_2 flux was found to be positive in 6 of the 9 measurements made under light conditions, indicating a net flux of CO_2 into the CPY-5 chamber. Of the 21 measurements made in March, 12 CO_2 fluxes were positive, indicating a shift to flow of CO_2 into the peat soil from the CPY-5 chamber as the samples had been growing for longer. The rate of rise or fall in concentration of CO_2 was highest at the start of the recording period under light conditions and declined throughout the recording [Figure 3.8]. All CO_2 fluxes measured under light conditions immediately following dark conditions were negative [Table 3.2, 3.3]. CO_2 flux measured under light conditions ranged from 1.54 to -3.9 µmol m^{-2} s^{-1}.

Figure 3.8: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 3 under light conditions on 26/04/2019.

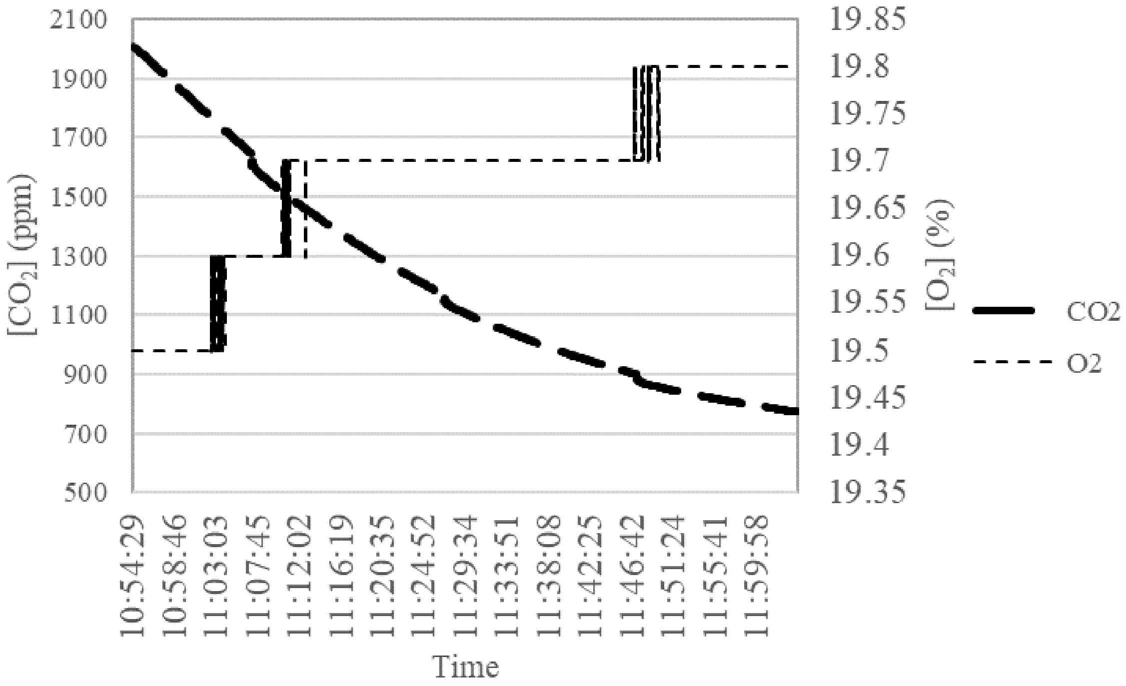


Table 3.1: Growth tent EGM-5 measurements made under light conditions in January and February 2019. On all occasions the light measurement was made first.

Date	Core	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
24/01/2019	3	119	0.4	0.1699	3.63	1.54
28/01/2019	2	105	-0.5	-0.0027	-5.15	-0.03
01/02/2019	5	120	1.0	0.0028	9.01	0.03
06/02/2019	6	78	0.4	0.009	5.55	0.12
12/02/2019	1	180	0.7	0.0153	4.21	0.09
18/02/2019	2	33	-0.2	0.0066	-6.55	0.22
21/02/2019	2	120	1.0	0.0437	9.01	0.39
25/02/2019	1	60	0.6	-0.0058	10.81	-0.10
26/02/2019	4	60	0.6	-0.0001	10.81	0.00

Table 3.2: Growth tent EGM-5 measurements made under light conditions in March 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Order of conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
01/03/2019	5	S	60	0.6	0.0017	10.81	0.03
04/03/2019	3	S	120	0.6	0.0445	5.41	0.40
07/03/2019	6	S	120	1.4	0.009	12.62	0.08
08/03/2019	5	S	120	0.4	0.004	3.60	0.04
11/03/2019	3	S	25	0.2	0.0089	8.65	0.38
12/03/2019	5	S	100	1.0	0.009	10.81	0.10
13/03/2019	4	S	70	0.3	-0.0062	4.63	-0.10
14/03/2019	2	S	100	0.4	0.0416	4.33	0.45
15/03/2019	1	S	90	0.1	-0.0081	1.20	-0.10
18/03/2019	4	S	80	0.2	0.0223	2.70	0.30
18/03/2019	4	I	80	0.2	-0.1642	2.70	-2.22
19/03/2019	2	S	120	0.1	0.0479	0.90	0.43
19/03/2019	2	I	120	0.8	-0.174	7.21	-1.57
20/03/2019	6	S	90	0.3	0.0262	3.60	0.31
20/03/2019	6	I	90	0.7	-0.324	8.41	-3.89
21/03/2019	5	S	75	0.6	0.0094	8.65	0.14
21/03/2019	5	I	75	0.1	-0.0414	1.44	-0.60
29/03/2019	1	S	60	0.2	0.0018	3.60	0.03
29/03/2019	1	I	60	0.2	-0.1473	3.60	-2.65
29/03/2019	6	S	25	0.0	-0.0062	0.00	-0.27
29/03/2019	6	I	25	0.1	-0.0766	4.33	-3.31

Table 3.3: Growth tent EGM-5 measurements made under light conditions in April 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Order of conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
02/04/2019	2	S	39	0.2	0.0121	5.55	0.34
02/04/2019	2	I	39	0.1	-0.0736	2.77	-2.04
02/04/2019	3	S	55	0.4	0.0033	7.86	0.06
02/04/2019	3	I	55	0.3	-0.1593	5.90	-3.13
03/04/2019	1	S	40	0.3	-0.0074	8.11	-0.20
03/04/2019	1	I	40	0.1	-0.0975	2.70	-2.64
04/04/2019	5	S	50	0.5	-0.0018	10.81	-0.04
04/04/2019	5	I	50	0.0	-0.0646	0.00	-1.40
05/04/2019	2	S	30	0.4	0.0232	14.42	0.84
05/04/2019	2	I	30	0.1	-0.0532	3.60	-1.92
05/04/2019	4	S	60	0.1	-0.0893	1.80	-1.61
09/04/2019	6	S	50	0.3	0.0149	6.49	0.32
09/04/2019	6	I	50	0.1	-0.1515	2.16	-3.28
09/04/2019	2	S	60	0.0	0.0254	0.00	0.46
09/04/2019	2	I	60	0.2	-0.1188	3.60	-2.14
10/04/2019	4	S	90	0.4	0.0247	4.81	0.30
10/04/2019	4	I	90	0.2	-0.1852	2.40	-2.23
10/04/2019	4	I	120	0.3	-0.2118	2.70	-1.91
10/04/2019	4	S	50	0.2	-0.1252	4.33	-2.71
11/04/2019	1	S	110	1.0	-0.0137	9.83	-0.13
11/04/2019	1	I	60	0.1	-0.1281	1.80	-2.31
12/04/2019	3	S	90	0.2	-0.0071	2.40	-0.09
12/04/2019	3	I	60	0.2	-0.1951	3.60	-3.52
12/04/2019	3	S	45	0.2	-0.1622	4.81	-3.90
15/04/2019	6	S	75	0.7	0.0196	10.09	0.28
15/04/2019	6	I	70	0.3	-0.1914	4.63	-2.96
15/04/2019	6	S	70	0.3	-0.1914	4.63	-2.96
15/04/2019	6	S	90	0.3	-0.2095	3.60	-2.52
16/04/2019	4	S	40	0.5	0.0143	13.52	0.39
16/04/2019	4	I	50	0.1	-0.0781	2.16	-1.69
16/04/2019	4	S	60	0.1	-0.0875	1.80	-1.58
17/04/2019	2	S	40	0.5	0.0236	13.52	0.64
17/04/2019	2	I	40	0.3	-0.0941	8.11	-2.54
17/04/2019	5	I	60	0.1	-0.0582	1.80	-1.05
17/04/2019	5	S	50	0.1	-0.0534	2.16	-1.15
18/04/2019	5	S	59	0.8	0.0108	14.66	0.20
18/04/2019	5	I	59	0.0	-0.0639	0.00	-1.17
18/04/2019	5	S	50	0.1	-0.0274	2.16	-0.59

Table 3.3cont: Growth tent EGM-5 measurements made under light conditions in April 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Order of conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
23/04/2019	1	S	60	0.5	0.0011	9.01	0.02
23/04/2019	1	I	60	0.1	-0.0891	1.80	-1.61
23/04/2019	1	S	30	0.1	-0.0589	3.60	-2.12
23/04/2019	4	I	25	0.1	-0.0268	4.33	-1.16
23/04/2019	4	S	24	0.1	-0.0261	4.51	-1.18
23/04/2019	4	I	24	0.0	-0.0373	0.00	-1.68
24/04/2019	6	S	60	0.6	0.0082	10.81	0.15
24/04/2019	6	I	60	0.2	-0.1544	3.60	-2.78
25/04/2019	4	S	40	0.6	0.0131	16.22	0.35
25/04/2019	4	I	40	0.2	-0.0507	5.41	-1.37
25/04/2019	2	I	60	0.1	-0.1092	1.80	-1.97
26/04/2019	3	S	50	0.5	0.0071	10.81	0.15
26/04/2019	3	I	50	0.2	-0.1085	4.33	-2.35
26/04/2019	3	S	60	0.3	-0.1183	5.41	-2.13
26/04/2019	3	I	60	0.0	-0.1457	0.00	-2.63
26/04/2019	4	S	50	0.0	0.02	0.00	0.43
29/04/2019	5	S	60	0.9	0.0286	16.22	0.52
29/04/2019	5	I	60	0.0	-0.0544	0.00	-0.98
29/04/2019	4	I	40	0.0	-0.0417	0.00	-1.13
30/04/2019	1	S	60	0.8	0.0059	14.42	0.11
30/04/2019	1	I	60	0.1	-0.0904	1.80	-1.63
30/04/2019	6	I	49	0.2	-0.1249	4.41	-2.76

Under dark conditions, the concentration of CO_2 in the CPY-5 chamber changed by a greater magnitude than observed under light conditions in the majority of measurements. A CO_2 concentration increase of greater than 0.2% was observed in 14 dark measurements [Table 3.4, 3.5, 3.6]. As with change in CO_2 concentration under light conditions, early in the growth period, on 24/01/2019, the increase was close to linear throughout the recording interval [Figure 3.9]. When the peat samples had been left in the growth tent for a longer period of time [greater than 1 week], the rate of concentration change was observed to fall with time in the CPY-5 chamber during the recording interval [Figure 3.12].

O_2 concentration was observed to fall in 51 [e.g., Figure 3.9, 3.12] and remain constant in 15 [e.g., Figure 3.11] of the 72 dark chamber measurements. Exceptions to this pattern occurred on 06/02/2019 when O_2 increased by 0.3% at Core 6 over a 3.5 hour recording period [Figure 3.10].

Figure 3.9: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 3 under dark conditions on 24/01/2019.

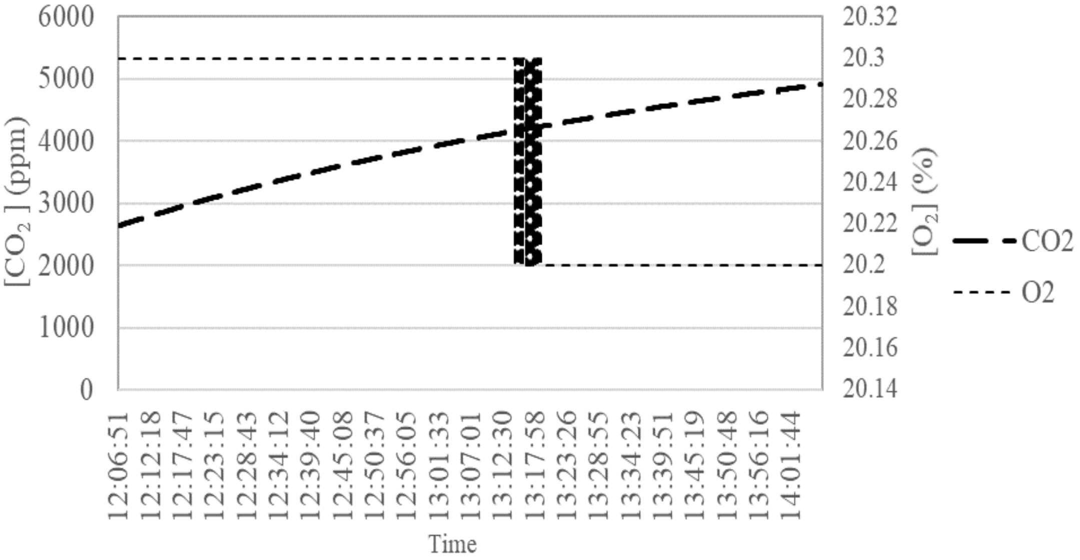


Figure 3.10: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 6 under dark conditions on 06/02/2019.

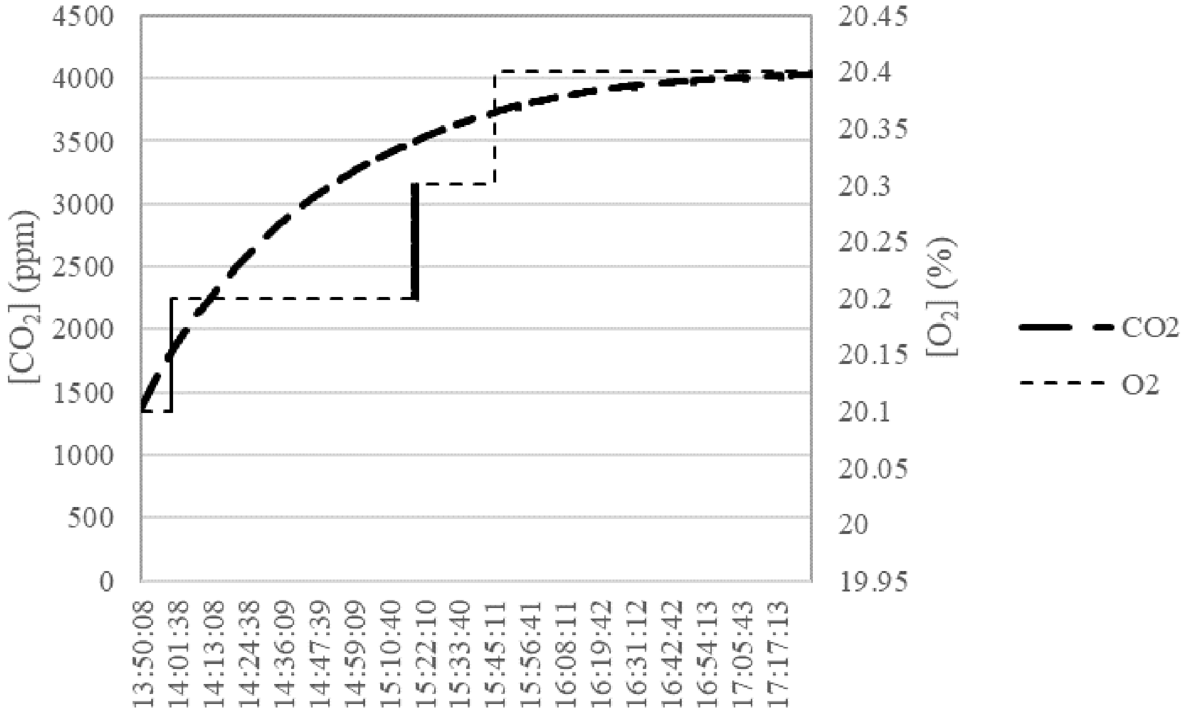


Figure 3.11: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 2 under dark conditions on 21/02/2019.

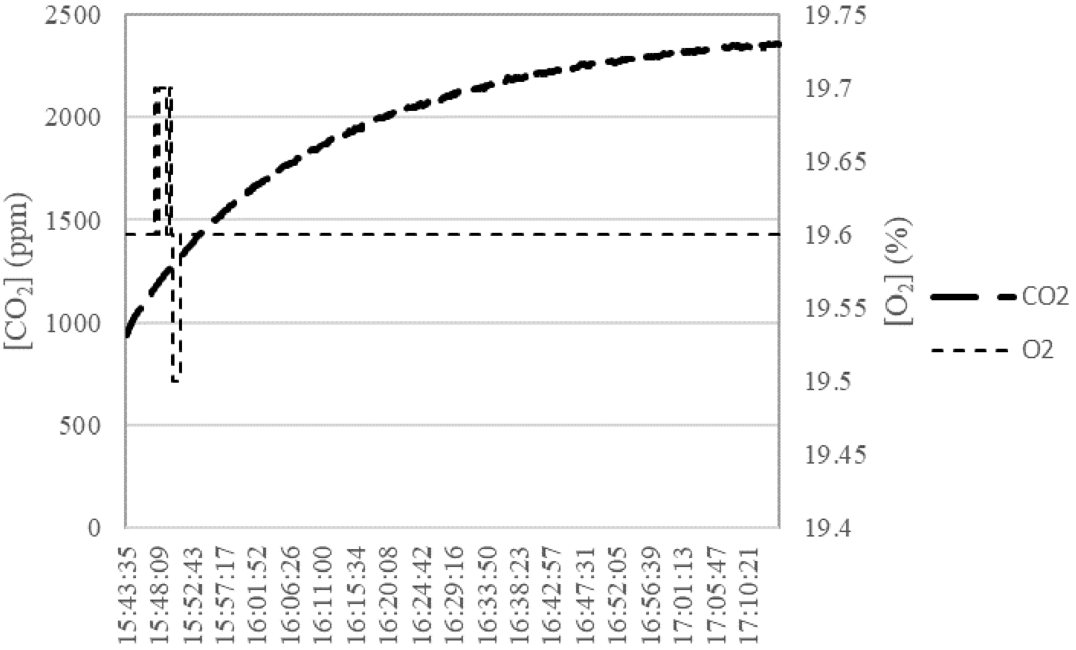
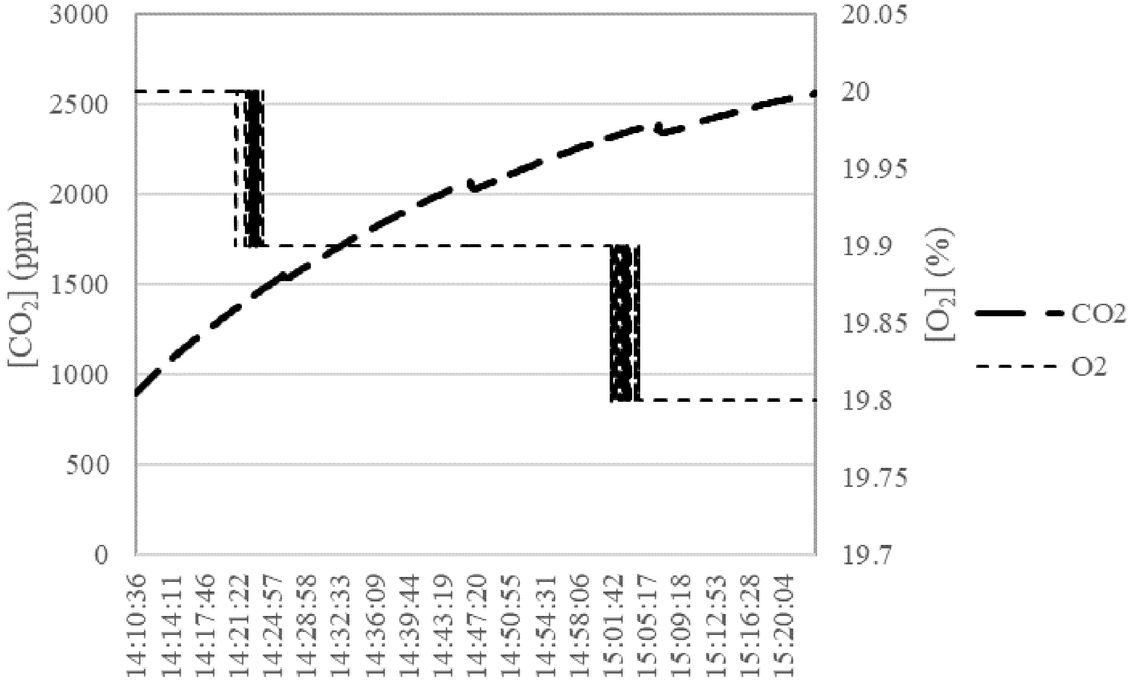


Figure 3.12: Change in concentration of CO_2 and O_2 in CPY-5 chamber at Core 6 under dark conditions on 24/04/2019.



Measurements under dark conditions showed negative O_2 fluxes in 51 of the 72 recordings [71% of recordings], representing a net flux of O_2 into the peat samples from the CPY-5 chamber. 15 [21%] of the dark chamber measurements showed no net flux of O_2 between the biosphere and atmosphere. The remaining 6 measurements [8%] record a positive flux of O_2 into the CPY-5 chamber under dark conditions. In all measurements made under dark conditions the flux of CO_2 is positive, representing a net loss of CO_2 from the peat into the CPY-5 chamber.

Table 3.4: Growth tent EGM-5 measurements made under dark conditions in January and February 2019. On all occasions the light measurement was made first.

Date	Core	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
24/01/2019	3	119	-0.1	0.226	-0.91	2.05
28/01/2019	2	105	0.0	0.03	0.00	0.31
01/02/2019	5	120	-0.2	0.1205	-1.80	1.09
06/02/2019	6	78	0.1	0.1994	1.39	2.76
12/02/2019	1	180	-1.0	0.169	-6.01	1.02
18/02/2019	2	33	-0.2	0.1271	-6.55	4.16
21/02/2019	2	120	0.0	0.1417	0.00	1.28
25/02/2019	1	60	-0.2	0.1409	-3.60	2.54
26/02/2019	4	60	0.0	0.1946	0.00	3.51

Table 3.5: Growth tent EGM-5 measurements made under dark conditions in March 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Timing of light conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
01/03/2019	5	S	60	-0.3	0.0189	-5.41	0.34
04/03/2019	3	S	120	-0.5	0.4735	-4.51	4.27
07/03/2019	6	S	120	-0.2	0.3303	-1.80	2.98
08/03/2019	5	S	120	0.0	0.1088	0.00	0.98
11/03/2019	3	S	25	-0.1	0.1055	-4.33	4.56
12/03/2019	5	S	100	-0.3	0.21	-3.24	2.27
13/03/2019	4	S	70	-0.1	0.2234	-1.54	3.45
14/03/2019	2	S	100	-0.2	0.1895	-2.16	2.05
15/03/2019	1	S	90	-0.2	0.1571	-2.40	1.89
18/03/2019	4	I	80	-0.3	0.2264	-4.05	3.06
19/03/2019	2	I	120	-0.2	0.1736	-1.80	1.56
20/03/2019	6	I	90	-0.4	0.3496	-4.81	4.20
21/03/2019	5	I	75	0.1	0.041	1.44	0.59
29/03/2019	1	I	60	-0.1	0.1541	-1.80	2.78
29/03/2019	6	S	25	-0.1	0.1145	-4.33	4.95

Table 3.6: Growth tent EGM-5 measurements made under dark conditions in April 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

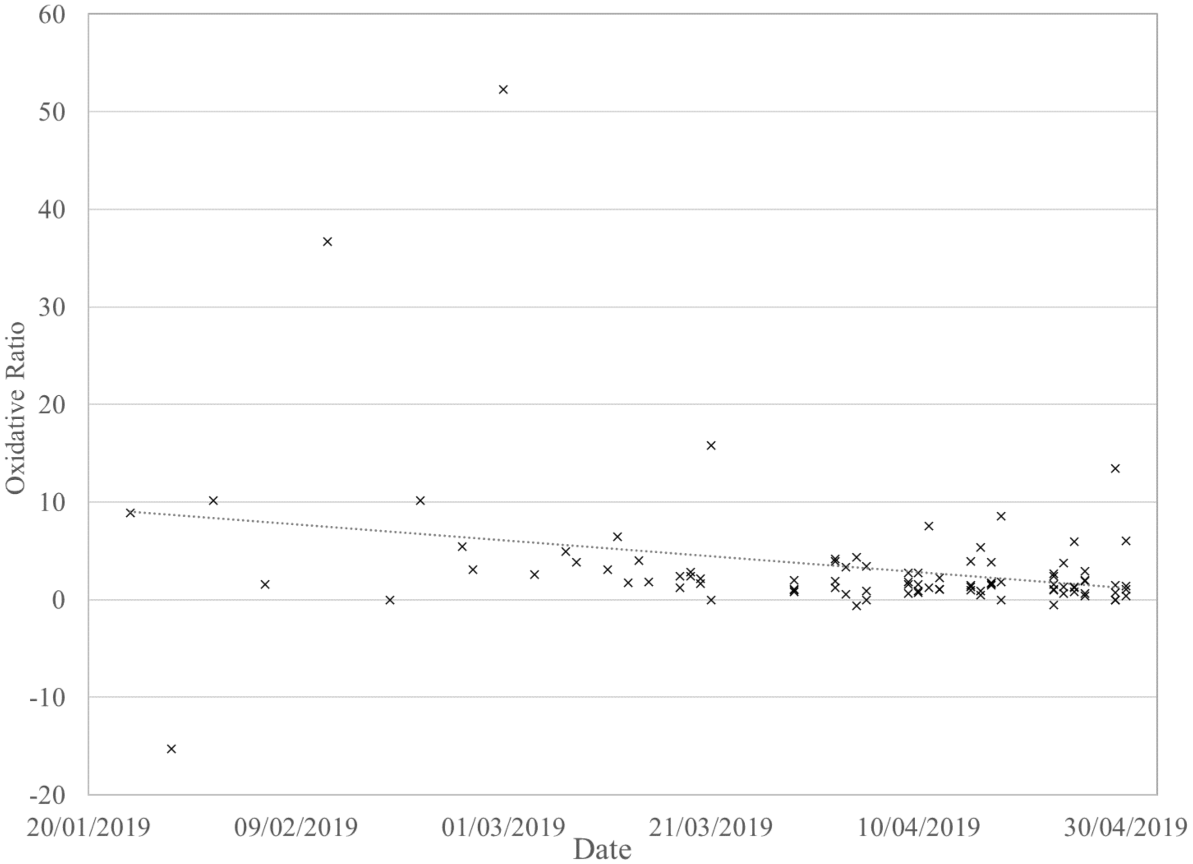
Date	Core	Timing of light conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (μmol m^{-2} s^{-1})	CO_2 flux (μmol m^{-2} s^{-1})
02/04/2019	2	S	39	-0.1	0.084	-2.77	2.33
02/04/2019	3	S	55	-0.4	0.208	-7.86	4.09
03/04/2019	1	S	40	0.0	0.0827	0.00	2.24
04/04/2019	5	S	50	0.1	0.0901	2.16	1.95
05/04/2019	2	S	30	0.1	0.1099	3.60	3.96
05/04/2019	4	S	60	-0.1	0.1229	-1.80	2.21
09/04/2019	6	S	50	-0.1	0.1608	-2.16	3.48
09/04/2019	2	S	60	-0.2	0.1341	-3.60	2.42
10/04/2019	4	S	90	-0.1	0.2038	-1.20	2.45
10/04/2019	4	I	120	-0.1	0.239	-0.90	2.15
10/04/2019	4	S	50	-0.2	0.1231	-4.33	2.66
11/04/2019	1	S	110	-0.2	0.1451	-1.97	1.43
11/04/2019	1	I	60	-0.2	0.1135	-3.60	2.05
12/04/2019	3	S	90	-0.3	0.2158	-3.60	2.59
12/04/2019	3	I	60	-0.2	0.1758	-3.60	3.17
12/04/2019	3	S	45	-0.1	0.129	-2.40	3.10
15/04/2019	6	S	75	-0.1	0.2213	-1.44	3.19
15/04/2019	6	I	70	-0.1	0.2135	-1.54	3.30
15/04/2019	6	S	70	-0.3	0.2098	-4.63	3.24
15/04/2019	6	S	90	-0.3	0.2379	-3.60	2.86
16/04/2019	4	S	40	0.0	0.1078	0.00	2.91
16/04/2019	4	I	50	0.0	0.1261	0.00	2.73
16/04/2019	4	S	60	-0.1	0.1319	-1.80	2.38
17/04/2019	2	S	40	-0.1	0.1782	-2.70	4.82
17/04/2019	2	S	40	-0.1	0.1477	-2.70	3.99
17/04/2019	5	I	60	-0.1	0.0605	-1.80	1.09
17/04/2019	5	S	50	-0.1	0.0611	-2.16	1.32
18/04/2019	5	S	59	0.0	0.1042	0.00	1.91
18/04/2019	5	S	50	-0.1	0.0826	-2.16	1.79
23/04/2019	1	S	60	0.2	0.1121	3.60	2.02
23/04/2019	1	I	60	0.2	0.1121	3.60	2.02
23/04/2019	1	S	30	-0.1	0.0675	-3.60	2.43
23/04/2019	4	I	25	0.0	0.0734	0.00	3.17
23/04/2019	4	S	24	-0.1	0.0573	-4.51	2.58
23/04/2019	4	I	24	-0.1	0.0573	-4.51	2.58
24/04/2019	6	S	60	0.0	0.1665	0.00	3.00
24/04/2019	6	I	60	0.0	0.1665	0.00	3.00
24/04/2019	6	S	60	-0.2	0.1492	-3.60	2.69

Table 3.6cont: Growth tent EGM-5 measurements made under dark conditions in April 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Timing of light conditions	Period of measurement (minutes)	Change in O_2 (%)	Change in CO_2 (%)	O_2 flux (µmol m^{-2} s^{-1})	CO_2 flux (µmol m^{-2} s^{-1})
25/04/2019	4	S	40	0.0	0.1142	0.00	3.09
25/04/2019	4	I	40	0.0	0.1142	0.00	3.09
25/04/2019	4	S	40	0.0	0.0961	0.00	2.60
25/04/2019	2	I	60	-0.1	0.1263	-1.80	2.28
26/04/2019	3	S	50	0.1	0.1433	2.16	3.10
26/04/2019	3	I	50	0.1	0.1433	2.16	3.10
26/04/2019	3	S	60	-0.2	0.1486	-3.60	2.68
26/04/2019	3	I	60	-0.2	0.1486	-3.60	2.68
26/04/2019	4	S	50	-0.2	0.1205	-4.33	2.61
29/04/2019	5	S	60	0.0	0.0954	0.00	1.72
29/04/2019	5	I	60	0.0	0.0954	0.00	1.72
29/04/2019	5	S	60	-0.2	0.0782	-3.60	1.41
29/04/2019	4	I	40	-0.1	0.0895	-2.70	2.42
29/04/2019	4	S	40	0.0	0.0717	0.00	1.94
30/04/2019	1	S	60	0.0	0.1391	0.00	2.51
30/04/2019	1	I	60	0.0	0.1391	0.00	2.51
30/04/2019	1	S	60	-0.2	0.128	-3.60	2.31
30/04/2019	6	I	49	-0.1	0.1513	-2.21	3.34

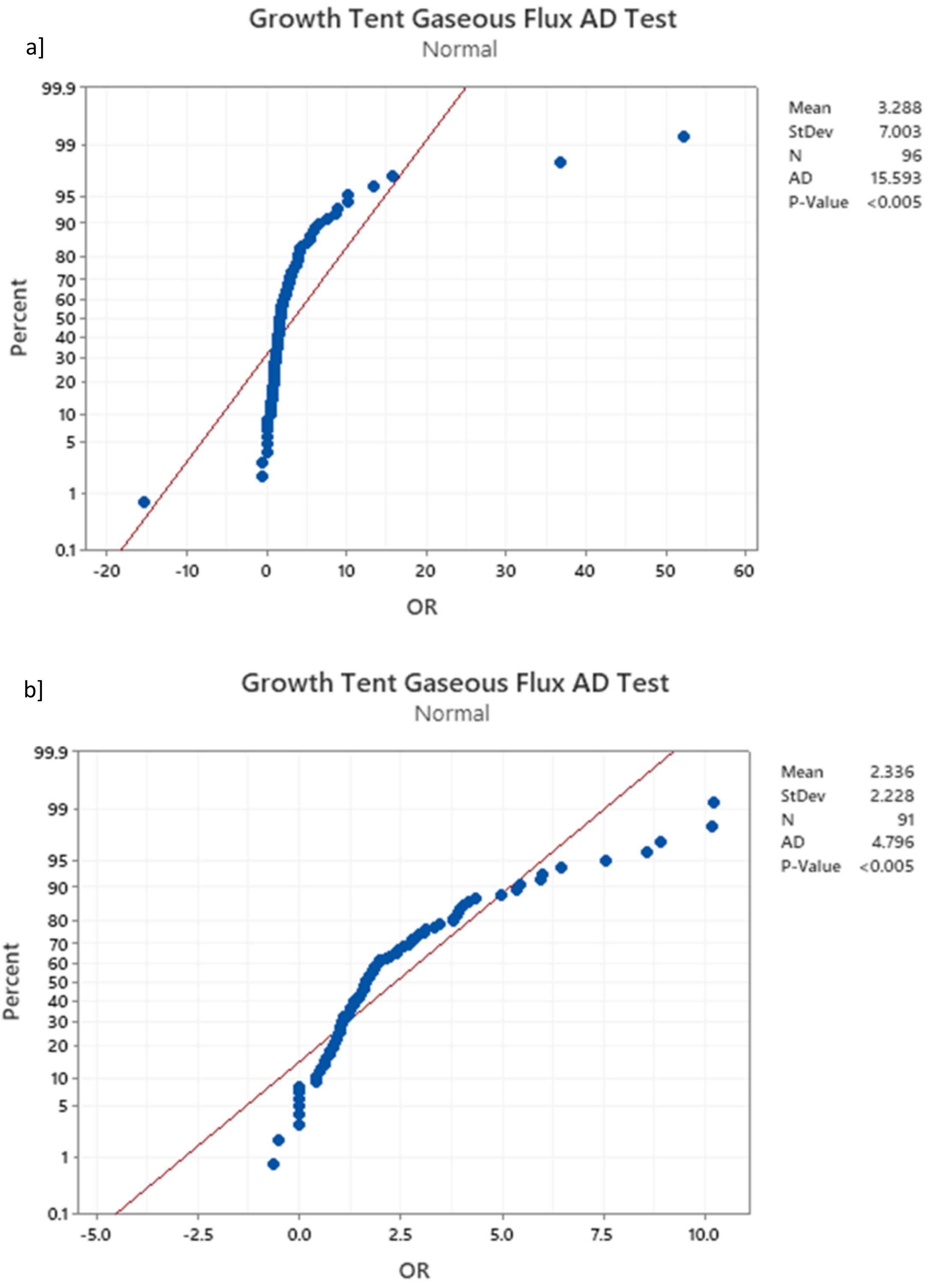
The mean OR measured by direct gaseous flux analysis in the growth tent decreased with time of growth of the peat cores. Figure 3.13 shows the OR measured on each date of measurement during the 3-month growth period, including those later identified as outliers. Distribution of OR values is wider early on in the growth-period.

Figure 3.13: Time-series plot of all OR values measured by gaseous flux analysis against date of measurement. Line of best fit is plotted.



A total of 96 ORs were calculated from the flux differences measured over the three month growth period [Table 3.8, 3.9, 3.10]. The Anderson-Darling normality test showed that 5 of the 96 OR flux ratios calculated needed to be removed prior to statistical analysis [i.e. their inclusion resulted in a dataset with AD statistic > 5.0], leaving a dataset of 91 values [Figure 3.14]. After removal of 5.2% of the data, OR values ranged from -0.65 to 10.20 with a mean value of 2.34. A positive value represents net O_2 flux into the CPY-5 chamber and net CO_2 flux into the peat sample. Since the OR is defined as the flux ratio resulting from photosynthetic activity, the positive value is expected. 83 [91%] of the flux ratios returned positive values, as expected. Two [2%] flux ratios calculated were negative and both represent a net flux of O_2 into the peat from the atmospheric chamber during photosynthesis. Six of the flux ratios calculated had values of 0.00, resulting from very small differences in O_2 flux under light and dark conditions. 55 of the calculated flux ratios fall in the range 0-2. The 3 highest flux ratios were all measured in the first month of growth [Table 3.9].

Figure 3.14: Results of the Anderson-Darling normality test on the growth tent OR measurements. (a) Shows the AD-test prior to removal of outliers, this AD test was failed i.e. AD = 15.593. (b) Shows the AD-test following removal of 5 outliers resulting in an AD statistic = 4.796.



In the ANOVA model, core and peat depth were included, but the interaction term could not be calculated. Results from ANOVA show that there were no significant differences in OR measured between the cores in the growth tent [i.e. $P < 0.05$]. The date of measurement of the gaseous fluxes and order of light conditions were shown to cause a significant difference to the calculated OR. The time of recording of flux measurements caused no significant difference in OR [Table 3.7]. The calculated OR [3.22±2.36] when the light measurement was made before the dark measurement was significantly higher than the OR measured when light conditions followed dark conditions [0.86±0.70]. Tukey *Post-hoc* analysis did not show any significant difference with date of flux measurement. The difficulties in measurement of OR by gaseous flux analysis mean that conclusions drawn from these results must be treated with caution. Further measurements and analysis of the effects of time of growth and order of light conditions will be required in future studies.

Table 3.7: Results of ANOVA for core number, timing of light conditions and days of growth with time period of measurement as a covariate.

	OR	
	df	P
Core	5	0.953
Days in growth tent	36	0.030
Order of light conditions	1	0.000
Time of measurement	1	0.417
Error	48	

Table 3.8: Growth tent Oxidative Ratio measurements made in January and February 2019. On all occasions the light measurement was made first.

Date	Core	Period of measurement (minutes)	O_2 flux difference (µmol m^{-2} s^{-1})	CO_2 flux difference (µmol m^{-2} s^{-1})	Moles of O_2 released per mole CO_2 sequestered
24/01/2019	3	119	4.54	-0.51	8.91
01/02/2019	5	120	10.81	-1.06	10.20
06/02/2019	6	78	4.16	-2.64	1.58
18/02/2019	2	33	0.00	-3.95	0.00
21/02/2019	2	120	9.01	-0.88	10.20
25/02/2019	1	60	14.42	-2.64	5.45
26/02/2019	4	60	10.81	-3.51	3.08

Table 3.9: Growth tent Oxidative Ratio measurements made in March 2019. In the timing of light conditions column, 'S' represents light conditions at the start and 'I' represents light conditions intermittent between dark conditions.

Date	Core	Timing of light conditions	Period of measurement (minutes)	O_2 flux difference (μmol m^{-2} s^{-1})	CO_2 flux difference (μmol m^{-2} s^{-1})	Moles of O_2 released per mole CO_2 sequestered
04/03/2019	3	S	120	9.91	-3.87	2.56
07/03/2019	6	S	120	14.42	-2.90	4.98
08/03/2019	5	S	120	3.60	-0.94	3.82
11/03/2019	3	S	25	12.98	-4.18	3.11
12/03/2019	5	S	100	14.06	-2.17	6.47
13/03/2019	4	S	70	6.18	-3.55	1.74
14/03/2019	2	S	100	6.49	-1.60	4.06
15/03/2019	1	S	90	3.60	-1.98	1.82
18/03/2019	4	S	80	6.76	-2.76	2.45
18/03/2019	4	I	80	6.76	-5.28	1.28
19/03/2019	2	S	120	2.70	-1.13	2.39
19/03/2019	2	I	120	9.01	-3.13	2.88
20/03/2019	6	S	90	8.41	-3.89	2.16
20/03/2019	6	I	90	13.22	-8.09	1.63
21/03/2019	5	I	75	0.00	-1.19	0.00
29/03/2019	1	S	60	5.41	-2.74	1.97
29/03/2019	1	I	60	5.41	-5.43	1.00
29/03/2019	6	S	25	4.33	-5.22	0.83
29/03/2019	6	I	25	8.65	-8.27	1.05

Table 3.10: Growth tent Oxidative Ratio measurements made in April 2019.

Date	Core	Timing of light conditions	Period of measurement (minutes)	O_2 flux difference (μmol m^{-2} s^{-1})	CO_2 flux difference (μmol m^{-2} s^{-1})	Moles of O_2 released per mole CO_2 sequestered
02/04/2019	2	S	39	8.32	-1.99	4.17
02/04/2019	2	I	39	5.55	-4.37	1.27
02/04/2019	3	S	55	15.73	-4.02	3.91
02/04/2019	3	I	55	13.76	-7.22	1.91
03/04/2019	1	S	40	8.11	-2.44	3.33
03/04/2019	1	I	40	2.70	-4.87	0.55
04/04/2019	5	S	50	8.65	-1.99	4.35
04/04/2019	5	I	50	-2.16	-3.35	-0.65
05/04/2019	2	S	30	10.81	-3.13	3.46
05/04/2019	2	I	30	0.00	-5.88	0.00
05/04/2019	4	S	60	3.60	-3.82	0.94
09/04/2019	6	S	50	8.65	-3.16	2.74
09/04/2019	6	I	50	4.33	-6.75	0.64
09/04/2019	2	S	60	3.60	-1.96	1.84
09/04/2019	2	I	60	7.21	-4.56	1.58
10/04/2019	4	S	90	6.01	-2.15	2.79
10/04/2019	4	I	90	3.60	-4.67	0.77
10/04/2019	4	I	120	3.60	-4.06	0.89
10/04/2019	4	S	50	8.65	-5.37	1.61
11/04/2019	1	S	110	11.80	-1.56	7.56
11/04/2019	1	I	60	5.41	-4.35	1.24
12/04/2019	3	S	90	6.01	-2.68	2.24
12/04/2019	3	I	60	7.21	-6.68	1.08
12/04/2019	3	S	45	7.21	-7.00	1.03
15/04/2019	6	S	75	11.53	-2.91	3.97
15/04/2019	6	I	70	6.18	-6.25	0.99
15/04/2019	6	S	70	9.27	-6.20	1.50
15/04/2019	6	S	90	7.21	-5.38	1.34
16/04/2019	4	S	40	13.52	-2.53	5.35
16/04/2019	4	I	50	2.16	-4.42	0.49
16/04/2019	4	S	60	3.60	-3.95	0.91
17/04/2019	2	S	40	16.22	-4.18	3.88
17/04/2019	2	I	40	10.81	-7.36	1.47
17/04/2019	2	S	40	10.81	-6.54	1.65
17/04/2019	5	I	60	3.60	-2.14	1.68
17/04/2019	5	S	50	4.33	-2.48	1.75

Table 3.10cont: Growth tent Oxidative Ratio measurements made in April 2019

Date	Core	Timing of light conditions	Period of measurement (minutes)	O_2 flux difference (μmol m^{-2} s^{-1})	CO_2 flux difference (μmol m^{-2} s^{-1})	Moles of O_2 released per mole CO_2 sequestered
18/04/2019	5	S	59	14.66	-1.71	8.57
18/04/2019	5	I	59	0.00	-3.08	0.00
18/04/2019	5	S	50	4.33	-2.38	1.82
23/04/2019	1	S	60	5.41	-2.00	2.70
23/04/2019	1	I	60	-1.80	-3.63	-0.50
23/04/2019	1	S	30	7.21	-4.56	1.58
23/04/2019	4	I	25	4.33	-4.33	1.00
23/04/2019	4	S	24	9.01	-3.76	2.40
23/04/2019	4	I	24	4.51	-4.26	1.06
24/04/2019	6	S	60	10.81	-2.85	3.79
24/04/2019	6	I	60	3.60	-5.78	0.62
24/04/2019	6	S	60	7.21	-5.47	1.32
25/04/2019	4	S	40	16.22	-2.73	5.93
25/04/2019	4	I	40	5.41	-4.46	1.21
25/04/2019	4	S	40	5.41	-3.97	1.36
25/04/2019	2	I	60	3.60	-4.24	0.85
26/04/2019	3	S	50	8.65	-2.95	2.94
26/04/2019	3	I	50	2.16	-5.45	0.40
26/04/2019	3	S	60	9.01	-4.81	1.87
26/04/2019	3	I	60	3.60	-5.30	0.68
26/04/2019	4	S	50	4.33	-2.17	1.99
29/04/2019	5	I	60	0.00	-2.70	0.00
29/04/2019	5	S	60	3.60	-2.39	1.51
29/04/2019	4	I	40	2.70	-3.55	0.76
29/04/2019	4	S	40	0.00	-3.07	0.00
30/04/2019	1	S	60	14.42	-2.40	6.01
30/04/2019	1	I	60	1.80	-4.14	0.44
30/04/2019	1	S	60	5.41	-3.94	1.37
30/04/2019	6	I	49	6.62	-6.10	1.09

3.4.2 Elemental analysis results

Mean OR of all the vegetation and peat samples was 1.02±0.01. None of the datasets needed transforming prior to ANOVA. Table 3.11 and 3.12 show the least mean squares of the derived variables for each core and depth interval respectively.

Table 3.11: Least mean squares ± standard error for each derived variable for the growth tent peat cores.

Core	OR	Cox	Ω
Core 2	1.03 ± 0.01	-0.04 ± 0.02	1.45 ± 0.03
Core 4	1.02 ± 0.01	-0.02 ± 0.02	1.45 ± 0.03
Core 6	1.02 ± 0.01	-0.01 ± 0.02	1.54 ± 0.03

Core	C/N	H/C	O/C
Core 2	38.87 ± 2.24	1.66 ± 0.01	0.77 ± 0.02
Core 4	44.18 ± 2.24	1.69 ± 0.01	0.80 ± 0.02
Core 6	48.31 ± 2.24	1.70 ± 0.01	0.82 ± 0.02

Table 3.12: Least mean squares ± standard error for each derived variable for the growth tent peat cores.

Depth	OR	Cox	Ω
Vegetation	1.02 ± 0.01	-0.02 ± 0.03	1.45 ± 0.03
0-2cm	1.02 ± 0.01	-0.01 ± 0.03	1.45 ± 0.03
2-4cm	1.01 ± 0.01	0.02 ± 0.03	1.54 ± 0.03
4-6cm	1.03 ± 0.01	-0.03 ± 0.03	1.55 ± 0.03
6-8cm	1.03 ± 0.01	-0.05 ± 0.03	1.62 ± 0.03

Depth	C/N	H/C	O/C
Vegetation	50.81 ± 2.89	1.72 ± 0.01	0.82 ± 0.02
0-2cm	43.96 ± 2.89	1.72 ± 0.01	0.82 ± 0.02
2-4cm	42.30 ± 2.89	1.68 ± 0.01	0.81 ± 0.02
4-6cm	46.31 ± 2.89	1.67 ± 0.01	0.79 ± 0.02
6-8cm	35.55 ± 2.89	1.63 ± 0.01	0.75 ± 0.02

The results of ANOVA performed on the derived variables with depth and core as factors are shown in Table 3.13. The interaction term could not be calculated. The OR, C_{ox} and O/C ratio did not vary significantly with core or depth. Degree of unsaturation [Ω] increased significantly with depth from 1.45±0.03 in vegetation and 0-2 cm depth samples to 1.62±0.03 at 6-8cm. Tukey pairwise comparison of the results showed that Ω was significantly different at 6-8 cm compared to vegetation and 0-2cm which is similar to *post-hoc* analysis of H/C which found significant difference at 6-8cm relative to vegetation and 0-2cm. H/C was observed to fall significantly with depth from 1.72±0.01 in vegetation and 0-2cm depth samples to 1.63±0.01 at 6-8cm. The C/N ratio is the only derived variable which showed significant variation with core number; Core 6 had the highest value [48.31±2.24] and Core 2 the lowest [38.87±2.24]. Tukey pairwise comparison of results showed Cores 2 and 6 to have significantly different C/N ratios.

Table 3.13: ANOVA for core and peat depth increments for OR, C_{ox}, Ω and elemental ratios. df = degrees of freedom, p=probability of factor being zero. Factors and interactions found to be significant [i.e. p<0.05] are highlighted in bold.

	OR		Cox		Ω	
	df	p	df	p	df	p
Depth	4	0.567	4	0.652	4	**0.007**
Core	2	0.457	2	0.649	2	0.083
Error	8		8		8	

	C/N		H/C		O/C	
	df	p	df	p	df	p
Depth	4	0.052	4	**0.005**	4	0.138
Core	2	**0.049**	2	0.051	2	0.185
Error	8		8		8	

Table 3.14: Results of the Tukey Pairwise Comparison test at 95% confidence on the C/N ratio of the three growth tent cores analysed. Means that do not share a letter are significantly different.

Core	N	Mean	Grouping	
Core 6	5	48.31	A	
Core 4	5	44.18	A	B
Core 2	5	38.87		B

Table 3.15: Results of the Tukey Pairwise Comparison test at 95% confidence on the Ω each core depth interval. Means that do not share a letter are significantly different.

Depth	N	Mean	Grouping	
6-8cm	3	1.62	A	
4-6cm	3	1.55	A	B
2-4cm	3	1.54	A	B
0-2cm	3	1.45		B
Vegetation	3	1.45		B

Table 3.16: Results of the Tukey Pairwise Comparison test at 95% confidence on the H/C ratio of each core depth interval. Means that do not share a letter are significantly different.

Depth	N	Mean	Grouping	
0-2cm	3	1.72	A	
veg	3	1.72	A	
2-4cm	3	1.68	A	B
4-6cm	3	1.67	A	B
6-8cm	3	1.63		B

3.5. Discussion

Measurement of oxidative ratio [OR] by direct gaseous flux analysis and elemental analysis [EA] returns different values. OR by gaseous flux analysis ranged from -0.50 to 10.20

with a mean value of 2.34. OR by EA showed a smaller range of 1.01 to 1.04 and a mean of 1.02. Gaseous flux analysis returned a value outside the range of values [0-2] proposed by Masiello et al. [2008], whereas all values measured by EA were within this range.

In the gaseous flux experiments under light conditions O_2 concentration increased or remained constant in the CPY-5 chamber in 97.7% of measurements. Increase in O_2 s a result of photosynthesis in vegetation growing on the established cores. Photosynthesis is also reflected in the 54 [60% of] light measurements under which CO_2 concentration fell in the CPY-5 chamber.

The effect of disturbance on the peat cores was reflected in the pattern of CO_2 concentration change in measurements made early in the 3-month growth period. Increase in CO_2 was close to linear throughout the light and dark recording intervals on the 24/01/2019. After 2 weeks of growth, the rate of change of CO_2 was highest at the start of the recording period and fell as the recording continued. This pattern of CO_2 change is in agreement with previous incubation studies including Severinghaus et al. [1995] and Chapter 2 of this thesis. The lack of this pattern in early measurements may suggest the peat cores did not become established in the growth tent immediately, hence their normal photosynthetic and respiratory processes did not occur. The number of days in the growth tent was found to cause significant difference to the calculated OR [Table 3.7, Figure 3.13], which may reflect the establishment of the cores in the growth tent later on in the growth period. The lower OR value measured with increased time in the growth tent suggests a greater CO_2 flux into the cores relative to O_2 flux out. However, Tukey post-hoc analysis did not find a significant difference between OR measured with the number of days in the growth tent.

The change and increase in dominant plant species growing on the cores as discussed in section 3.4.1 may have contributed to the change in CO_2 and O_2 flux patterns with time in the growth tent. Change in dominant plant species with time in the growth tent may therefore also have contributed to the significant change in OR with duration of growth in the growth tent. A change in OR with time resulting from a shift in the plant species growing supports the findings of Gallagher et al. [2014] and Gallagher et al. [2017]. The results of the present study disagree with those of Clay et al. [2018] and Randerson et al. [2006] which suggest that with an increased disturbance of the terrestrial biosphere, a lower OR is expected.

Consistent and rapid decrease in CO_2 [i.e. 300 parts per million volume [ppm]] in 10 minutes on 26/04/2019, see Figure 3.9] when conditions in the growth tent changed from dark to light suggest that a build up of CO_2 enabled photosynthesis at a high rate when PAR was no longer a limiting factor, in agreement with the findings of Chapter 2 of this thesis and Fogg [1968]. The order of light conditions was found to cause a significant difference to the value or OR that was measured. When light conditions followed dark conditions, a lower OR [0.86±0.70] was calculated. This lower OR results from a greater CO_2 flux difference between light and dark conditions caused by the rapid fall early in the light measurement thought to represent a high rate of photosynthetic activity.

Measurement precision of the EGM-5 and CPY-5 system was 0.1% for O_2 concentration and 1 ppm for CO_2 concentration. The differing measurement precisions of the gases made field measurement of the OR difficult [see Chapter 2] as change in the concentration of the two gases was not comparable. Change in O_2 concentration over a 5 minute recording period was found in several measurements to not exceed the detection limit of the EGM-5, hence a change of 0.0% was recorded. To overcome this, this chapter seeked to measure gaseous flux over long time periods [greater than the 5 minutes initially used in the field experiments]. The measurement period used in the growth-tent expermints ranged from 24 minutes to 3 hours and ANOVA of the results showed that the time of measurement did not have a significant effect on the calculated OR. In measurements made under light conditions, 10% showed no concentration change [i.e. 0.0%] and in dark conditions 26% showed no concentration change.

Hence the longer flux recording period overcame the low O_2 measurement precision in the majority of analyses.

O_2 concentration change ranged from -0.5% to 1.4% under light conditions and -1.0% to 0.2% under dark conditions. CO_2 change ranged from -0.3240% to 0.1699% under light conditions and from 0.03% to 0.3496% under dark conditions. After removal of the 5.21% of the data that failed the Anderson-Darling test, the mean O_2 flux calculated to result from photosynthesis was 6.67μmol m^{-2} s^{-1} with a range of -2.16 to 16.22 μmol m^{-2} s^{-1}. The mean photosynthetic CO_2 flux was -3.78 μmol m^{-2} s^{-1}, ranging from -8.27 to -0.51 μmol m^{-2} s^{-1}. The range and magnitude of measurements of CO_2 concentration change and flux were consistently smaller than that of O_2 resulting in ORs greater than 1.00. An OR value greater than 1 disagrees with previous studies which recommend the use of a photosynthetic stoichiometric ratio or quotient of 1.00 according to the basic photosynthesis Equation 2.2 [see Chapter 2 of this thesis] [e.g., Barker 1935; Rosenberg et al. 1995]. A value of OR higher than the photosynthetic quotient suggests that during photosynthesis the biochemical processes taking place are more complex than the equation would suggest. The increased OR calculated from gaseous flux analysis may relate to variation in the rates of the light and dark reactions which occur during photosynthesis [Bond 1933] or represent a disequilibrium between fluxes of O_2 and CO_2 into the ecosystem [Taddei et al. 2008].

The OR measured by gaseous flux analysis in this study is greater than the value reported by previous studies. Seibt et al. [2004] measured a maximum OR of 1.6 by gaseous flux analysis and interpreted this to represent the formation of high OR compounds such as lignin and fatty acids. The OR of 2.34 returned by this study is too high to be explained by the formation of these compounds as the corresponding OR value is exceeded. This OR value and the range of values measured in this study are also too high to be the result of secondary plant metabolism and diffusion in soils or interplay of reactions involved in assimilation [Halliwell 1984].

The OR value of 0.86±0.70 returned by gaseous flux analysis when dark conditions preceded light conditions is within the range of predicted OR values [Masiello et al. 2008]. This value is in agreement with previous studies [e.g., Ishidoya et al. 2015; van der Laan et al. 2014] which measured OR by atmospheric gaseous fluxes. Hence, this result may suggest that decomposition causes organic matter to become more reduced [i.e. the higher OR measured in the peat organic matter] relative to the O_2:CO_2 flux of formation of the initial biomass in agreement with Baldock et al. [2004]. It is proposed that in future studies measuring OR by this gaseous flux method the dark-chamber measurement should be made first as this study has shown this to be the most accurate method for obtaining an OR value within the accepted range.

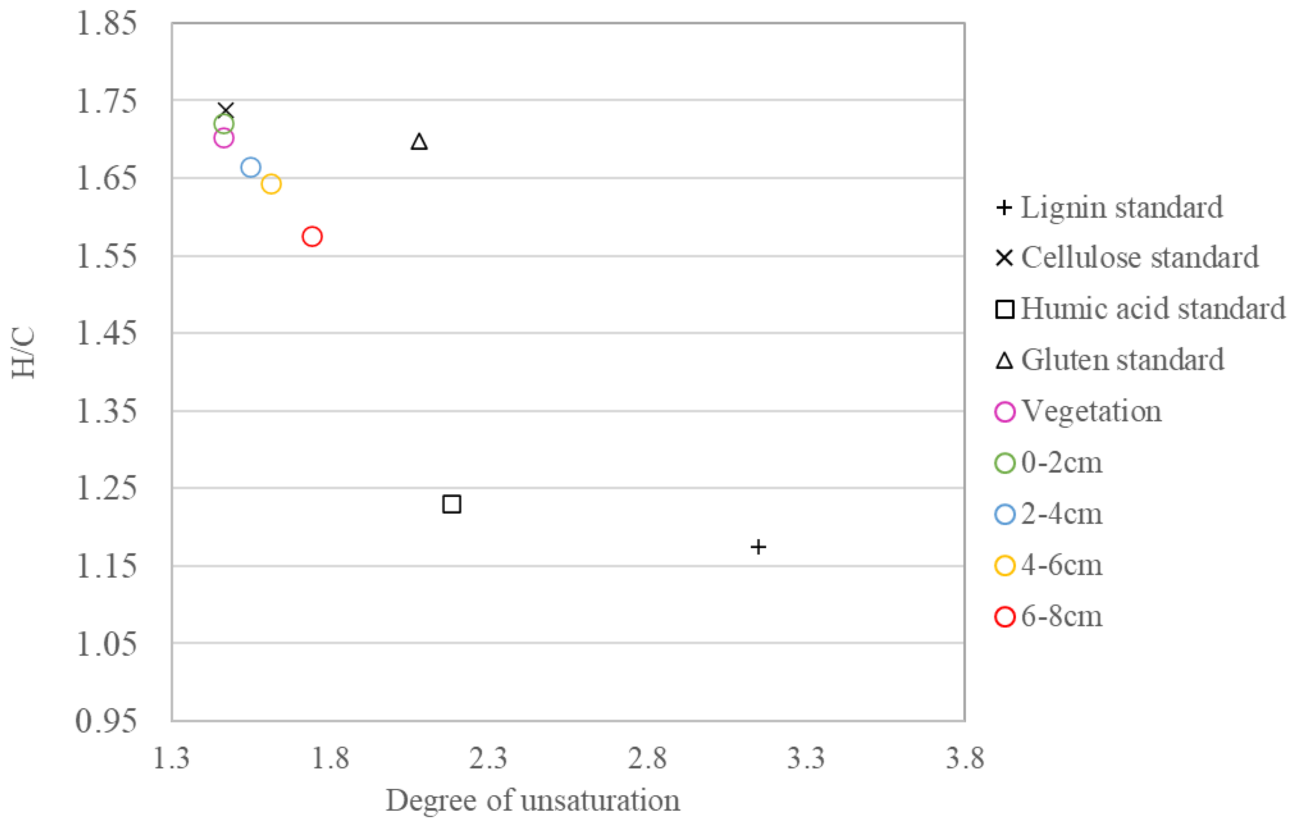
The OR of the all the peat core samples and the vegetation samples measured by elemental analysis [1.02 ± 0.01] was significantly lower than the range allowed by the IPCC's accepted value [1.1 ± 0.05]. Accuracy of the IPCC's value in estimating the C flux of the entire terrestrial biosphere should be questioned as the value does not represent all ecosystems. Results of elemental analysis in this study agree with Worrall et al. [2013] in that 1.1 is not the most appropriate value for OR_{terra} and even suggest that the range is outside the range of natural occurrence of some ecosystems.

Lack of variation in OR and C_{ox} with depth is in agreement with Clay and Worrall [2015a]. It is possible that the depth of cores studied is not great enough to show the variation in these values that would be expected with the change from aerobic to anaerobic conditions in a peat bog [Reddy and D'Angelo 1994]. However, the bottom 4 cm of the cores were permanently below the artificial water table, hence any change in oxidation state relating to water saturation are likely to have been observed.

There was also no significant change in OR or C_{ox} identified between vegetation and soil samples in this study which agrees with Worrall et al. [2013] but disagrees with results of Clay and Worrall [2015a,b]. It is possible that the growth tent cores were insucciciently deep to extend beyond the litter organic matter type. If vegetation and litter are the only organic matter pools sampled, the lack of significant difference in OR may be explained by considering the decay continuum proposed by Fang et al. [2011]. Vegetation and litter have been shown to be closer to each other on this decay continuum than they are to the underlying soil [Worrall et al. 2015b]. Hence, if the samples were of greater depth an increased variation in OR might be observed.

Significant increase in the Ω with depth in the cores agrees with the results of Worrall et al. [2016]. The increase in Ω with depth and significant decrease in H/C with depth [Figure 3.14] can be associated with condensation reactions which form aromatic bonds as the depth in the peat soil increases. A significantly lower Ω and higher H/C in vegetation and samples from a depth of 0-2cm relative to those from 6-8cm [Tables 3.15, 3.16] are strong evidence for an increase in aromaticity with depth in peat soil. Figure 3.15 shows that Core 2 samples follow a compositional array between cellulose and lignin standards with a shift towards lignin composition with increasing depth. A shift away from cellulose composition with depth in peat soils results from the high rates of microbial decomposition of cellulose observed in organic soils [McMahon et al. 1980]. The only parameter found to vary significantly between cores is C/N, this may relate to variation in vegetation species between the cores. However, C/N was found to vary significantly only between Cores 2 and 6, which had similar vegetational distributions at the end of the growth period [Figure 3.4].

Figure 3.15: Variation in H/C with Ω in growth tent core 2 samples at the end of the 3-month growth period.



The OR is defined as the amount of CO_2 sequestered in the terrestrial biosphere for each mole of O_2 produced during photosynthesis [Seibt et al. 2004], it’s value is also used in assessing organic matter synthesis and destruction within the C sinks [Clay and Worrall 2015a]. The ratio of O_2 and CO_2 exchanges depends on the elemental composition and the reduction state of organic material. The value of OR of the same ecosystem measured by gaseous flux analysis and elemental analysis should therefore be the same. Results of this study have measured different values by these two methods. The cause of this difference either results from an error in one or both of the measurement techniques, or, the time period or spatial scale of measurement was insufficient for the O_2:CO_2 exchange ratio to equate to the OR from the average elemental composition [Seibt et al. 2004].

The value of OR measured by gaseous flux analysis falls outside the range of accepted values and is higher than any previously proposed values. Measurement of OR by this method needs substantial development but shows considerable potential. Some development of the measurement technique has been provided by this study. Measurement of gaseous flux over a period exceeding 25 minutes overcame the low measurement precision of O_2 relative to CO_2. Measurement of gaseous flux under dark conditions followed by light conditions resulted in a higher rate of CO_2 fall under light conditions interpreted to result from a higher rate of photosynthesis. Hence, future measurements of OR by gaseous flux analysis should be made by analysing fluxes under dark conditions first to maximise photosynthetic activity.

3.6 Conclusions

Measurement of OR by gaseous flux analysis and elemental analysis returned different values [2.34 and 1.02 respectively]. The value measured by gaseous flux analysis was above the accepted range as a result of a higher magnitude O_2 flux relative to CO_2 flux. The value of OR returned by gaseous flux analysis must be treated carefully, despite this, this study has allowed the development of OR measurement by flux analysis using the EGM-5 and CPY-5 system. Period of recording greater than 25 minutes overcame the low O_2 concentration precision of the equipment and measuring flux under dark conditions prior to light conditions increases the rate of photosynthetic activity under light conditions. When the dark-chamber measurement preceded the light-chamber measurement an OR value [0.86±0.70] within the range defined by previous studies was measured, hence future studies should adopt this method.

The value measured by elemental analysis was significantly lower than the range of values allowed by the IPCCs accepted value. Hence, use of this value may be resulting in underestimation of the total C sink. No significant change in OR with depth was observed, although this may result from the short depth of the peat cores. Increase in Ω and decrease in H/C with depth result from condensation reactions which occur with burial and microbial decomposition of cellulose.

4.0 Oxidative ratio of Austrian peatlands

4.1 Introduction

The value of the oxidative ratio [OR] used by the IPCC [1.1±0.05] is assumed to be representative of the entire terrestrial biosphere. To assess this assumption, it is necessary to measure OR at a range of locations and in a range of ecosystems. This chapter aims to measure the OR of the surface vegetation and sub-surface peat of 10 Austrian peat bogs. By measuring the OR at a range of Austrian locations and depth increments, any changes relating to these factors can be assessed. The data will be added to the global database of OR values as a contribution to the assessment of the use of the value 1.1. Variations in other compositional indicators [Ω, C/N, H/C, O/C] with peatland location and depth are also assessed.

4.2 Aims and objectives

The aim of this chapter was to gain an understanding of how carbon oxidation state [C_{ox}] and OR of a peatland vary with location and depth of sampling. It is hoped that this will develop knowledge of the variation of the oxidative state of the terrestrial biosphere. To meet this aim several objectives are established:

1. Use elemental analysis to measure the C_{ox} and corresponding OR of peat soil cores and dominant vegetation types at a range of Austrian bogs.
2. Assess how the values of OR and other derived variables e.g., Ω, C/N, H/C, O/C vary with location and depth in Austrian peatlands.
3. Assess how OR and other derived variables vary with vegetation type and location of growth in Austrian peatlands.
4. Evaluate whether OR calculated from these cores supports the value of 1.1±0.05 used by the IPCC and studies which calculate the magnitude of the terrestrial carbon [C] sink.

4.3 Materials and methods

4.3.1 Sample collection

Peat cores were taken from 10 Austrian peat bogs: Überlingmoos, Heidenreichstein, Rotmoos, Kojenmoos, The Rhine Delta, Ibm, Sablatnigmoor, Obergurgl, Gstreiklmoos and Purgschachen [Table 4.1, Figure 4.1]. At three of these peatlands [Sablatnigmoor, Gstreiklmoos and Kojenmoos] more than one core was obtained. At each sampling site a representative sample of the dominant vegetation types present was also collected [Table 4.2]. At each site, a location in active deep peat was selected and a core taken to the depth specified in Table 4.1. The depth of core taken at each site ensured the acrotelm and catotelm were represented by the samples [Worrall et al. 2012].

Table 4.1: Locations of Austrian peat samples.

Site	Plot type	Depth of core (cm)	Latitude (°N)	Longitude (°E)
Rotmoos	Hummock	100	47.68308	15.15472
Ibm	Meadow	60	48.06264	12.94694
Sablatnigmoor	Fen	50	46.57608	14.59917
Gstreiklmoos	Pine Bog (pinus mugo)	50	47.16450	13.88472
Überlingmoos	Meadow	50	47.16619	13.89444
Obergurgl	Fen	250	46.84569	11.01944
Kojenmoos	Open Bog	50	47.49164	9.98694
Rhine Delta	Fen	50	47.49572	9.62861
Heidenreichstein	Open Bog	50	48.85481	15.14472
Purgschachen	Pine Bog (pinus mugo)	100	47.58271	14.33069

Figure 4.1: Location map of Austrian peat samples. Map produced in ArcMaps 2019.

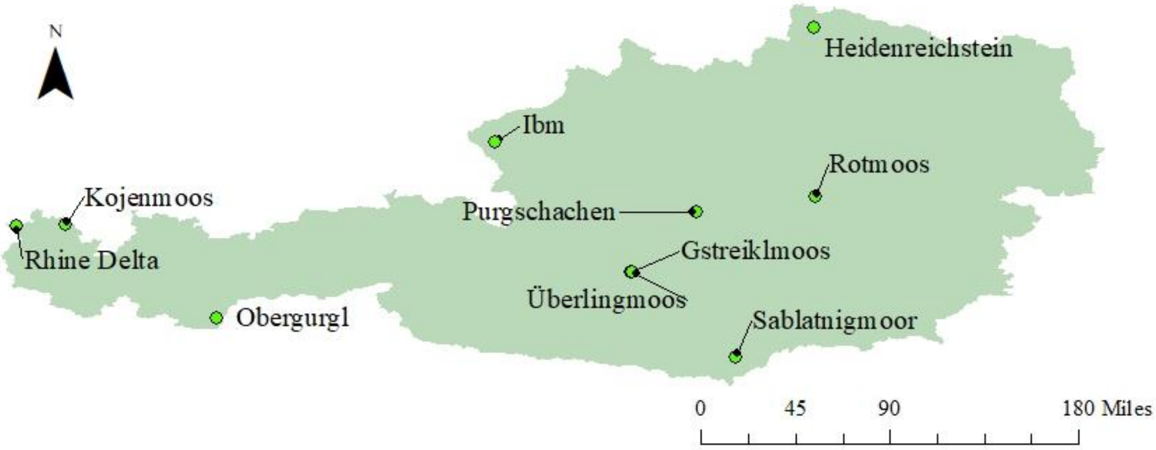


Table 4.2: Dominant vegetation types sampled at each site.

		Vegetation sampled			
Site	Plot type	Moss	Grass	Shrub	Pine
Rotmoos	Hummock			x	x
Ibm	Meadow		x		
Sablatnigmoor	Fen		x		
Sablatnigmoor	Meadow		x		
Gstreiklmoos	Pine Bog (pinus mugo)	x	x	x	
Gstreiklmoos	Fen	x	x		
Gstreiklmoos	Meadow	x	x		
Überlingmoos	Meadow		x		
Obergurgl	Fen		x		
Kojenmoos	Open Bog		x		
Kojenmoos	Open Bog		x		
Kojenmoos	Open Bog		x		
Rhine Delta	Fen		x		
Heidenreichstein	Open Bog		x	x	
Purgschachen	Pine Bog (pinus mugo)		x		x

4.3.2 Sample preparation

All samples were dried at room temperature for 2 weeks. The cores were divided into 10 cm depth intervals for sampling. Peat soil samples were ground using a pestle and mortar.

Following grounding samples were passed through a 1-mm sieve. All samples, both herbaceous vegetation and peat core, were ground to a submillimetre powder using a Retsch MM400 Cryomill.

4.3.3 Elemental analysis

The ground samples were analysed for their carbon, hydrogen, nitrogen [CHN] and separately for their oxygen [O] concentrations by the method described in Section 3.3.4.

4.3.4 Oxidative ratio

Mean C, H, N and O weight % data obtained by elemental analysis were converted to molar concentrations, C_{ox}, OR and degree of unsaturation [Ω] by the method described in Sections 1.2.2, 1.2.3 and 1.5 of this thesis. Elemental ratios O/C, H/C and C/N were also calculated for each sample.

4.3.5 Statistical analysis

The aim of this chapter was to answer three questions. Firstly, is there a change in the value of OR or other derived variables with the location of the peat bog or depth of the peat soil in Austrian peatlands? Secondly is there a change in OR or other derived variables with vegetation type or location of growth of peat sample? Finally, is the value of 1.1±0.05 used by the IPCC representative of the peatland OR measured in this study. To answer these questions, two statistical tests were performed. Response variables considered were OR, C_{ox}, Ω and the elemental ratios C/N, H/C and O/C. The response variables were tested for normality prior to ANOVA using the Anderson-Darling test [Anderson and Darling 1952]. None of the variables measured in this study needed transforming [i.e. Anderson-Darling statistic <5.00].

To answer the first question and assess whether OR or other derived variables varied with the location of the peatland in Austria, a location factor with 10 levels was created. To assess whether OR or other compositional indicators vary with depth in a peatland, at each location there were 6 consistent sampling depths, one of which was the dominant surface vegetation; the dominant vegetation in this test was taken as the average of all vegetation types sampled at a locality. A two-way ANOVA was used to determine the statistical significance of the factors – location of the peat bog or depth of the peat soil – on the response variables. The site-depth interaction factor was also calculated for each response variable.

Second, a two-way ANOVA was designed to test whether OR or the other derived variables varied significantly with vegetation type or the location of growth. In the second ANOVA model the vegetation factor had 5 levels [each vegetation type sampled] and the location factor had 10 levels. In both ANOVA models, the results are expressed as least square means of the response variables for each level of each factor. Significance is judged at the 95% probability of being different from zero unless otherwise stated. All ANOVA were calculated using Minitab 18 software. The Tukey post-hoc analysis test at 95% level was used to determine significant differences between levels of any factor. Where factors were found to cause significant variation in a response variable, the magnitude of the effects of each significant factor and interaction were calculated using the generalised ω^2 [Olejnik and Algina 2003]. As in Section 3.3.4, the samples were compared with standards – lignin cellulose, humic acid and protein.

4.4 Results

In total 18 vegetation samples and 65 peat samples were analysed. None of the data sets needed to be transformed prior to ANOVA. The mean and standard deviation of the oxidative ratio of all the Austrian peat and vegetation samples was 1.07±0.02.

4.4.1 Peat depth profile and site analysis

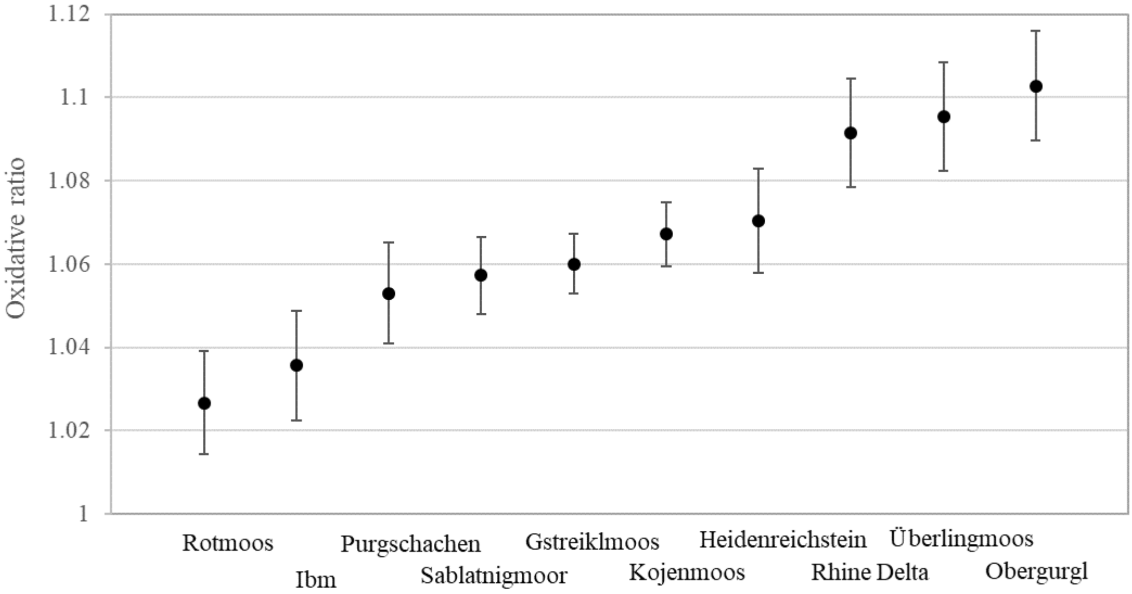
The derived variables OR, C_{ox}, Ω, C/N, H/C and O/C averaged across all organic matter types i.e. vegetation and all core depths, at each of the peat bog locations are shown in Table 4.3.

Table 4.3: Least mean square ± standard error for each derived variable for Austrian peat cores by location.

Location	OR	Cox	Ω
Gstreiklmoos	1.06 ± 0.01	-0.16 ± 0.03	1.84 ± 0.03
Heidenreichstein	1.07 ± 0.01	-0.21 ± 0.05	1.91 ± 0.05
Ibm	1.04 ± 0.01	-0.02 ± 0.05	2.07 ± 0.05
Kojenmoos	1.07 ± 0.01	-0.17 ± 0.03	1.95 ± 0.03
Obergurgl	1.10 ± 0.01	-0.32 ± 0.05	1.69 ± 0.05
Purgschachen	1.05 ± 0.01	-0.15 ± 0.05	2.11 ± 0.05
Rhine Delta	1.09 ± 0.01	-0.22 ± 0.05	1.30 ± 0.05
Rotmoos	1.03 ± 0.01	-0.05 ± 0.05	1.87 ± 0.05
Sablatnigmoor	1.06 ± 0.01	-0.08 ± 0.04	1.80 ± 0.04
Überlingmoos	1.10 ± 0.01	-0.23 ± 0.05	1.85 ± 0.05

Location	C/N	H/C	O/C
Gstreiklmoos	43.03 ± 4.83	1.53 ± 0.01	0.64 ± 0.02
Heidenreichstein	43.81 ± 8.43	1.51 ± 0.02	0.61 ± 0.03
Ibm	25.41 ± 8.80	1.40 ± 0.02	0.63 ± 0.03
Kojenmoos	31.00 ± 5.08	1.47 ± 0.01	0.60 ± 0.02
Obergurgl	25.76 ± 8.80	1.55 ± 0.02	0.57 ± 0.03
Purgschachen	55.75 ± 8.11	1.49 ± 0.02	0.78 ± 0.03
Rhine Delta	25.21 ± 8.80	1.78 ± 0.02	0.71 ± 0.03
Rotmoos	55.58 ± 8.30	1.54 ± 0.02	0.72 ± 0.03
Sablatnigmoor	23.56 ± 6.22	1.52 ± 0.01	0.64 ± 0.02
Überlingmoos	21.60 ± 8.80	1.51 ± 0.02	0.57 ± 0.03

Figure 4.2: The least mean squares of the location factor with respect to OR. Error bars are given as the standard error in the least mean square.



The peat bogs with the highest i.e. most reduced oxidative ratio [1.10±0.01] were Obergurgl and Überlingmoos [Figure 4.2]. These sites also have the lowest C_{ox} values [-0.32±0.05 and -0.23±0.05 respectively] and the lowest O/C ratios [0.57±0.00]. The peatland with the lowest OR [1.03±0.01] was Rotmoos, which also had the highest C_{ox} [-0.05±0.05]. The Tukey post-hoc analysis showed that the OR of organic matter at Rotmoos was significantly different to that of Obergurgl, Überlingmoos and the Rhine Delta [Table 4.4]. The OR of Obergurgl also differed significantly from Ibm.

Table 4.4: Results of the Tukey Pairwise Comparison test at 95% confidence on the OR of organic material sampled at the Austrian peat bogs. Means that do not share a letter are significantly different.

Location	N	Mean	Grouping		
Obergurgl	6	1.10	A		
Überlingmoos	6	1.10	A	B	
Rhine Delta	6	1.09	A	B	
Heidenreichstein	7	1.07	A	B	C
Kojenmoos	18	1.07	A	B	C
Gstreiklmoos	22	1.06	A	B	C
Sablatnigmoor	12	1.06	A	B	C
Purgschachen	16	1.05	A	B	C
Ibm	6	1.04		B	C
Rotmoos	8	1.03			C

Table 4.5 shows the derived variables at each depth increment of the peat soil. Mean OR values for vegetation and each depth interval [Table 4.5] are lower than 1.1 though still within the range of results reported by Worrall et al. [2013]. Vegetation and the top 10 cm of peat soil, which included litter samples, had the lowest OR values [1.05±0.01] [Figure 4.3]. The Tukey Pairwise Comparison test at the 95% confidence interval showed that peat from depth intervals of 0-10cm and 30-40cm were significantly different from each other [Table 4.6]. The oxidative ratio increased with depth, to 1.09±0.01 at 30-40cm depth then decreased to 1.07±0.01 at 40-50cm depth.

Table 4.5: Least mean squares ± standard error for each derived variable for Austrian peat cores by depth.

Depth	OR	Cox	Ω
Vegetation	1.05 ± 0.01	-0.14 ± 0.03	1.79 ± 0.03
0-10cm	1.05 ± 0.01	-0.07 ± 0.04	1.76 ± 0.04
10-20cm	1.06 ± 0.01	-0.14 ± 0.04	1.79 ± 0.04
20-30cm	1.08 ± 0.01	-0.22 ± 0.04	1.88 ± 0.04
30-40cm	1.09 ± 0.01	-0.22 ± 0.04	1.88 ± 0.04
40-50cm	1.07 ± 0.01	-0.18 ± 0.04	1.97 ± 0.04

Depth	C/N	H/C	O/C
Vegetation	50.65 ± 5.24	1.57 ± 0.01	0.68 ± 0.02
0-10cm	35.24 ± 6.16	1.54 ± 0.01	0.69 ± 0.02
10-20cm	32.76 ± 6.16	1.53 ± 0.01	0.64 ± 0.02
20-30cm	29.17 ± 6.16	1.52 ± 0.01	0.61 ± 0.02
30-40cm	29.87 ± 6.16	1.53 ± 0.01	0.63 ± 0.02
40-50cm	33.93 ± 6.16	1.48 ± 0.01	0.62 ± 0.02

Table 4.6: Results of the Tukey Pairwise Comparison test at 95% confidence on OR of the dominant vegetation and depth intervals in Austrian peat bogs. Means that do not share a letter are significantly different.

Depth	N	Mean	Grouping	
30-40cm	15	1.09	A	
20-30cm	15	1.08	A	B
40-50cm	15	1.07	A	B
10-20cm	15	1.06	A	B
vegetation	32	1.05	A	B
0-10cm	15	1.05		B

Figure 4.3: Least mean squares peat profile for the OR.

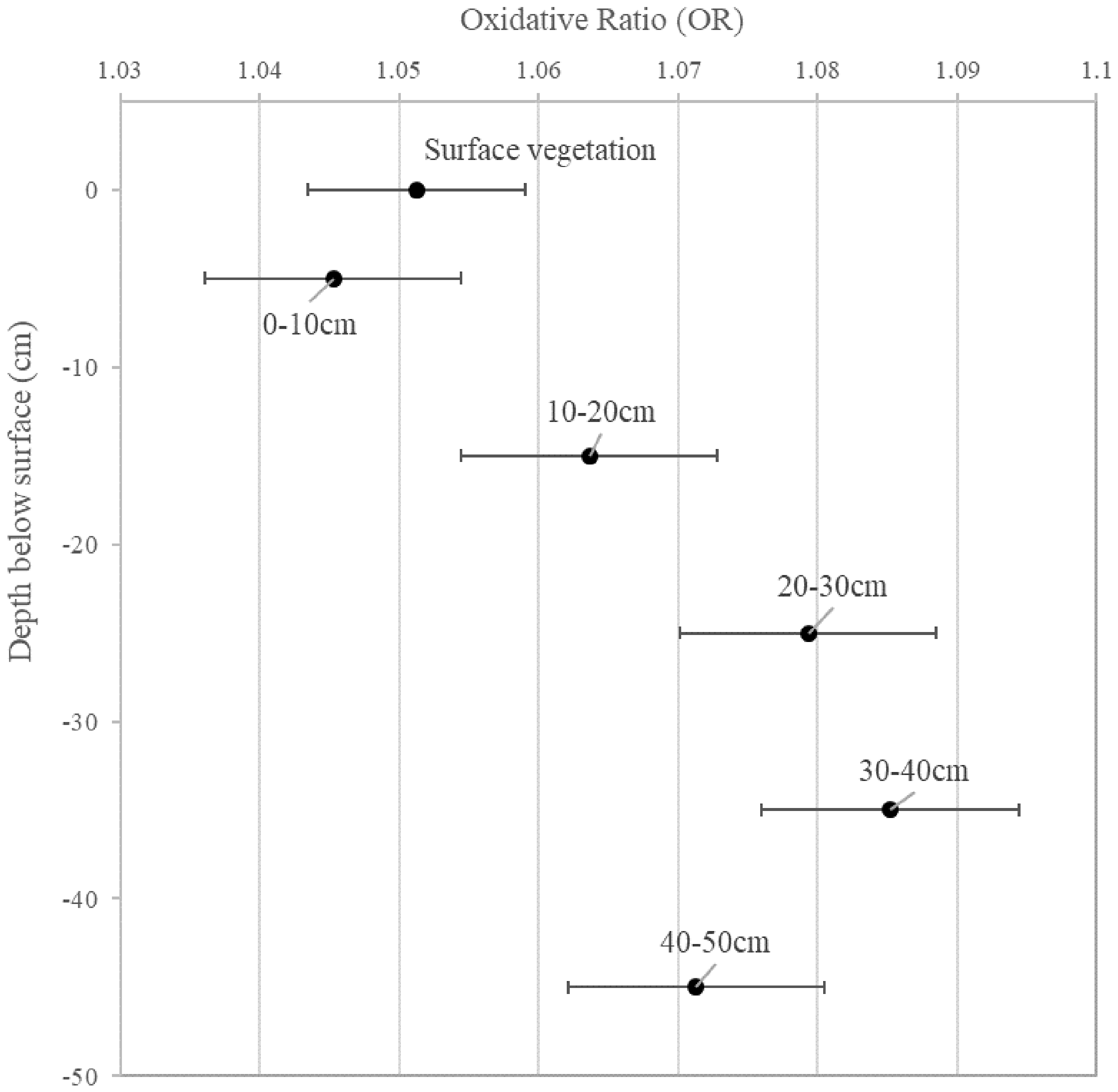
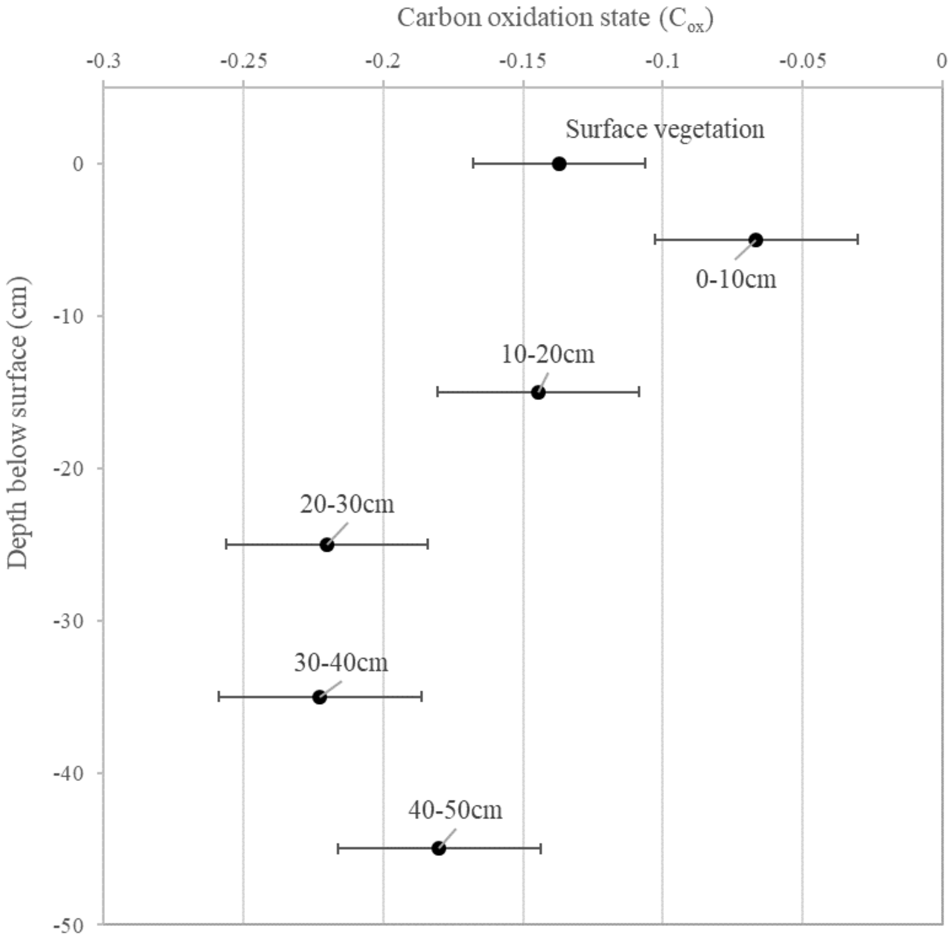


Figure 4.4: Interval Plot of C_{ox} with standard error of the mean plotted.



All vegetation and depth increments in the peat have negative C_{ox} values [Figure 4.4]. Vegetation had a more negative, i.e. more reduced, C_{ox} [-0.14±0.03] than the top 0-10cm [-0.07±0.04] [Table 4.5]. C_{ox} decreased [became more negative] with depth in the peat profile to 30-40cm, then increased in the 40-50cm sample. *Post-hoc* analysis showed that C_{ox} of soil at 0-10cm depth [assumed to represent litter] was significantly different to that at 20-30cm and 30-40cm depth [Table 4.7].

Table 4.7: Results of the Tukey Pairwise Comparison test at 95% confidence on C_{ox} *of the dominant vegetation and depth intervals in Austrian peat bogs. Means that do not share a letter are significantly different.*

Depth	N	Mean	Grouping	
0-10cm	15	-0.05	A	
10-20cm	15	-0.14	A	B
vegetation	32	-0.16	A	B
40-50cm	15	-0.18	A	B
20-30cm	15	-0.22		B
30-40cm	15	-0.23		B

Vegetation had a higher Ω [1.79±0.03] than the top 0-10cm of the peat soils [1.76±0.04] [Figure 4.5]. The Ω increased with depth in the peat soil to 1.97±0.04 at 40-50cm depth. *Post-hoc* anaylsis showed that the Ω at 40-50cm depth was significantly different to that of vegetation and soils from 0-10cm and 10-20cm depth. The site-depth interaction term caused significant variation in Ω, explaining 24% of the variation observed [Table 4.9].

Figure 4.5: Interval Plot of Ω with standard error of the mean plotted.

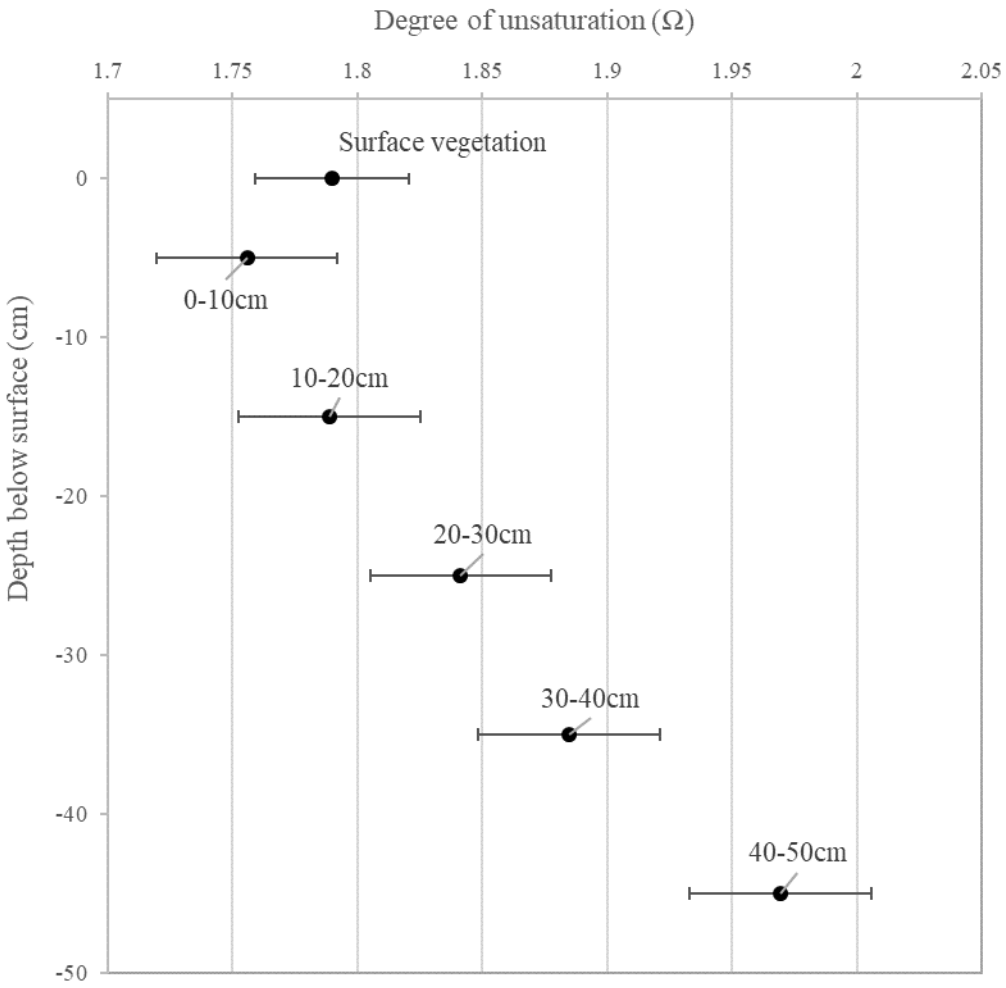
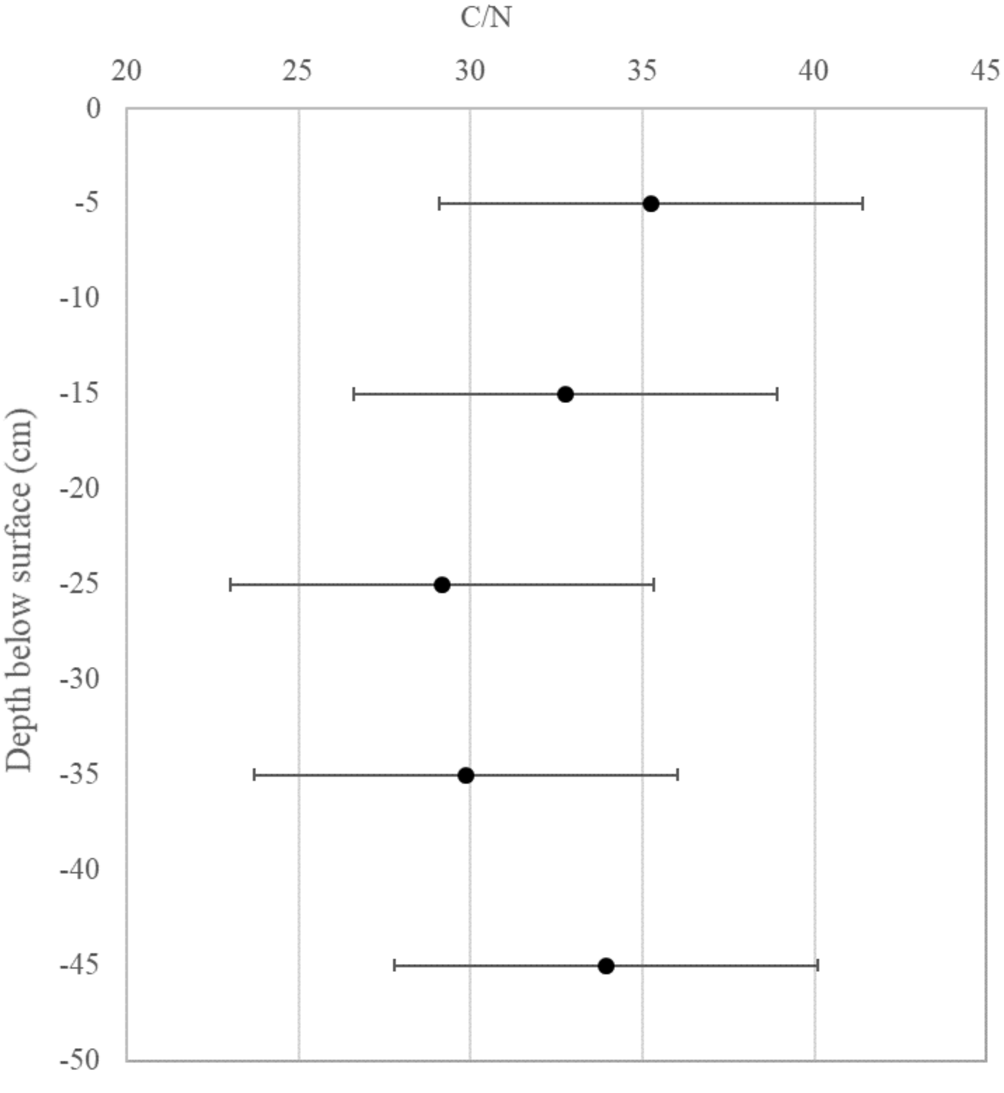


Table 4.8: Results of the Tukey Pairwise Comparison test at 95% confidence on Ω of the dominant vegetation and depth intervals in Austrian peat bogs. Means that do not share a letter are significantly different.

Depth	N	Mean	Grouping	
40-50cm	15	1.97	A	
30-40cm	15	1.88	A	B
20-30cm	15	1.84	A	B
vegetation	32	1.79		B
10-20cm	15	1.79		B
0-10cm	15	1.76		B

The C/N ratio decreased from 50.65±5.24 in vegetation to 35.24±6.16 in samples from 0-10cm depth. The C/N ratio decreased to 29.17 in 20-30cm and 29.87 in 30-40cm samples. An increase to 33.93 in samples from 40-50cm was observed in the Austrian peat bogs analysed [Figure 4.6].

Figure 4.6: Interval Plot of C/N with standard error of the mean plotted.



The results of the two-way ANOVA performed on the derived variables are shown in Table 4.9. All of the derived variables varied significantly with site and depth except C/N which only varied significantly with site. There were significant interactions between site and peat depth for Ω, H/C and O/C explaining 24%, 37% and 25% of the variation in the datasets respectively.

Results of ANOVA showed that the depth factor did not cause a significant change in the C/N ratio of organic matter [Table 4.9]. H/C and O/C changed significantly with depth. H/C decreased with depth from 1.57±0.01 in the dominant vegetation to 1.48±0.01 in peat soil at a depth of 40-50cm. The O/C ratio was highest in surface vegetation [0.68±0.02] and peat soil at a depth of 0-10cm [0.69±0.02] and lowest in the soil at 20-30cm depth [0.61±0.02] and 40-50cm depth [0.62±0.02]. Hence, a decrease in O/C with depth occurred in the Austrian peatlands sampled [see Table 4.5].

Table 4.9: ANOVA for site and peat depth increments for OR, C_{ox}, Ω and elemental ratios. df = degrees of freedom, p=probability of factor being zero, ω^2=generalised proportion of variance explained. Factors and interactions found to be significant [i.e. $p<0.05$] are highlighted in bold.

	OR			Cox			Ω		
	df	p	ω^2	df	p	ω^2	df	p	ω^2
Site	9	**0.001**	0.267	9	**0.002**	0.244	9	**0.000**	0.523
Depth	5	**0.017**	0.109	5	**0.031**	0.094	5	**0.001**	0.057
Site*Depth	45	0.879	0.000	45	0.926	0.000	45	**0.000**	0.240
Error	47			47			47		
Total ω^2			0.375			0.338			0.820

	C/N			H/C			O/C		
	df	p	ω^2	df	p	ω^2	df	p	ω^2
Site	9	**0.006**	0.221	9	**0.000**	0.471	9	**0.000**	0.323
Depth	5	0.083	0.065	5	**0.000**	0.055	5	**0.016**	0.064
Site*Depth	45	1.000	0.000	45	**0.000**	0.374	45	**0.013**	0.253
Error	47			47			47		
Total ω^2			0.286			0.901			0.640

4.4.2 Vegetation type and site analysis

Oxidative ratios measured in dominant vegetation types ranged from 1.09±0.03 to 1.03±0.02. The peatland with vegetation of the highest OR was Obergurgl [1.09±0.03] [Table 4.10]. Vegetation at this peat bog also had the lowest C_{ox} value [-0.29±0.12] and the lowest O/C ratio [0.61±0.06]. The peatland with the lowest OR [1.03±0.02] was Rotmoos, which also had the highest C_{ox} [-0.08±0.05].

Table 4.10: Least mean squares ± standard error for each derived variable for the dominant vegetation types at Austrian peat bogs by location.

Location	OR	Cox	Ω
Gstreiklmoos	1.07 ± 0.01	-0.22 ± 0.06	1.83 ± 0.06
Heidenreichstein	1.06 ± 0.02	-0.20 ± 0.08	1.81 ± 0.09
Ibm	1.05 ± 0.03	-0.13 ± 0.12	1.75 ± 0.12
Kojenmoos	1.08 ± 0.02	-0.25 ± 0.08	1.83 ± 0.09
Obergurgl	1.09 ± 0.03	-0.29 ± 0.12	1.84 ± 0.12
Purgschachen	1.05 ± 0.02	-0.18 ± 0.08	1.90 ± 0.09
Rhine Delta	1.05 ± 0.03	-0.17 ± 0.12	1.83 ± 0.12
Rotmoos	1.03 ± 0.02	-0.08 ± 0.07	1.82 ± 0.07
Sablatnigmoor	1.06 ± 0.02	-0.18 ± 0.09	1.83 ± 0.10
Überlingmoos	1.07 ± 0.03	-0.23 ± 0.12	1.80 ± 0.12

Location	C/N	H/C	O/C
Gstreiklmoos	71.44 ± 7.11	1.56 ± 0.03	0.64 ± 0.03
Heidenreichstein	66.75 ± 9.66	1.56 ± 0.03	0.65 ± 0.04
Ibm	62.20 ± 13.60	1.59 ± 0.05	0.69 ± 0.06
Kojenmoos	58.58 ± 9.66	1.57 ± 0.03	0.62 ± 0.04
Obergurgl	72.40 ± 13.60	1.55 ± 0.05	0.61 ± 0.06
Purgschachen	94.24 ± 9.60	1.57 ± 0.03	0.68 ± 0.04
Rhine Delta	85.80 ± 13.60	1.56 ± 0.05	0.68 ± 0.06
Rotmoos	54.08 ± 8.03	1.56 ± 0.03	0.71 ± 0.03
Sablatnigmoor	79.20 ± 10.80	1.56 ± 0.04	0.67 ± 0.05
Überlingmoos	66.50 ± 13.60	1.57 ± 0.05	0.64 ± 0.06

Table 4.11: Least mean squares ± standard error for each derived variable for the dominant vegetation types in Austrian peat bogs.

Depth	OR	C_{ox}	Ω
Eriophorum	1.06 ± 0.03	-0.16 ± 0.14	1.83 ± 0.14
Grass	1.04 ± 0.01	-0.09 ± 0.03	1.75 ± 0.03
Moss	1.00 ± 0.02	0.05 ± 0.08	1.66 ± 0.08
Pine Bog	1.11 ± 0.02	-0.41 ± 0.10	1.93 ± 0.10
Shrub	1.10 ± 0.02	-0.36 ± 0.07	1.94 ± 0.08

Depth	C/N	H/C	O/C
Eriophorum	56.20 ± 16	1.54 ± 0.06	0.65 ± 0.07
Grass	40.00 ± 3.65	1.58 ± 0.01	0.71 ± 0.02
Moss	61.49 ± 9.21	1.61 ± 0.03	0.81 ± 0.04
Pine Bog	122.70 ± 11.4	1.55 ± 0.04	0.55 ± 0.05
Shrub	75.24 ± 8.57	1.54 ± 0.03	0.57 ± 0.04

In this study, pine was the most reduced vegetation type [OR=1.11±0.02]. Pine also had the lowest C_{ox} and highest O/C and C/N ratios [Table 4.11]. Shrub, which represents Calluna [heather] had the second highest OR and second lowest C_{ox}. Shrub had the highest degree of unsaturation. Moss had the lowest OR [1.00±0.02] and highest C_{ox} [0.05±0.08] and O/C [0.81±0.04]. Moss was the only vegetation type with a positive carbon oxidation state [$C_{ox} > 0.00$]. Two-way ANOVA performed on the results of elemental analysis showed that the sampling site of the dominant vegetation types did not cause significant difference to the value of the derived variables [OR, C_{ox}, Ω, C/N, H/C and O/C.]. The vegetation type was found to cause significant difference to OR, C_{ox}, C/N and O/C [Table 4.12]. The Tukey post-hoc analysis test showed that the OR of moss was significantly different to pine and shrub [Table 4.13]. Both H/C and Ω were not found to vary significantly with either site or vegetation type.

Table 4.12: ANOVA for site and vegetation type for OR, C_{ox}, Ω and elemental ratios. df = degrees of freedom, p=probability of factor being zero. Factors found to be significant [i.e. $p<0.05$] are highlighted in bold.

	OR		Cox		Ω	
	df	p	df	p	df	p
Site	9	0.836	9	0.898	9	0.993
Vegetation type	4	**0.012**	4	**0.01**	4	0.131
Error	9		9		9	

	C/N		H/C		O/C	
	df	p	df	p	df	p
Site	9	0.165	9	1.000	9	0.834
Vegetation type	4	**0.001**	4	0.544	4	**0.006**
Error	9		9		9	

Table 4.13: Results of the Tukey Pairwise Comparison test at 95% confidence on the OR of dominant vegetation types at Austrian peat bogs. Means that do not share a letter are significantly different.

Vegetation	N	Mean	Grouping	
Pine Bog	2	1.11	A	
Shrub	3	1.10	A	
Eriophorum	1	1.06	A	B
Grass	14	1.04	A	B
Moss	3	1.00		B

4.5. Discussion

This study has measured the oxidative ratio [OR] of dominant vegetation types and peat soils from 10 Austrian peat bogs to assess whether the accepted OR value represents peatland ecosystems. Variation in OR and the other derived variables with location and depth of peat soils was also assessed to identify if these factors control composition. Change in OR and other derived variables with vegetation type and location of growth has also been measured. The OR [1.07±0.02 n=83] measured was lower than but not outside the range of values allowed by the IPCCs assumed value of 1.1±0.05. Significant differences were found between the ORs of different sites and depths of peatlands and between the different vegetation functional groups growing there. These differences can be explained by considering the different processes occurring and material types present in each organic matter type.

The OR of combined above ground biomass [1.05±0.01] is between that of the individual functional vegetation types measured [Figure 4.7]. This suggests that aboveground biomass is a mixture of the vegetation types present. Pine and shrub were found to be the most reduced vegetation functional types. These are also the vegetation types with the highest degrees of unsaturation and C/N ratios. These results largely agree with studies of Moor House peatland, UK [Worrall et al. 2015] and Fennoscandian ecosystems [Clay et al. 2018]. These previous studies also found "little difference between the mosses and the grass/sedges", which was also found this study. The moss and grass vegetation types were the most oxidised [highest C_{ox}, lowest OR] and had the lowest degree of unsaturation [Ω] and C/N. Post-hoc analysis of the results also suggest that moss was significantly different from pine and shrub vegetation at the 95 % confidence level. The OR, C_{ox}, C/N and O/C varied significantly between vegetation functional groups. Differences in these values may be due to varying proportions of biochemical compounds making up the different vegetation types, eg. more lignin in pine than in moss and more carbohydrate in moss than in pine. Results of this study suggest that the location of the peat bog does not cause significant variation in the oxidation state of vegetation.

The mean OR-, Ω- and C/N ratio defined composition of Austrian moss, grass and shrub is within the ranges defined by corresponding UK samples analysed in Clay and Worrall [2015a]. Comparison of the results of this study with those of Clay and Worrall [2015a] shows that the high Ω and high OR measured in Austrian shrub vegetation is also observed in UK bogs [Figure 4.8a]. Mosses and grasses have overlapping *Ω* and C/N ratios in peat bogs from both countries and are found to have degrees of unsaturation which extend to values lower than that measured in shrub vegetation [Figure 4.8b]. Differing compositions of the vegetation groups at the different locations may relate to different species analysed; however similarities in the *Ω* may relate to contribution from similar organic components in each vegetation type i.e. lignin is in higher proportion in shrub and cellulose is in higher proportion in moss. Shrub is the most reduced vegetation type in UK and Austrian bogs, however significant overlap with the oxidation state of grass is observed in UK localities. The results of this study and others therefore suggest that the oxidation state and OR of vegetation is controlled by the type of vegetation and not the location where it grows.

Figure 4.7: Plot of least mean squares OR-Ω for the vegetation types and peat soil depth intervals including individual and dominant vegetation types. Standard materials [cellulose, lignin, humic acid and gluten] are included for comparative purposes.

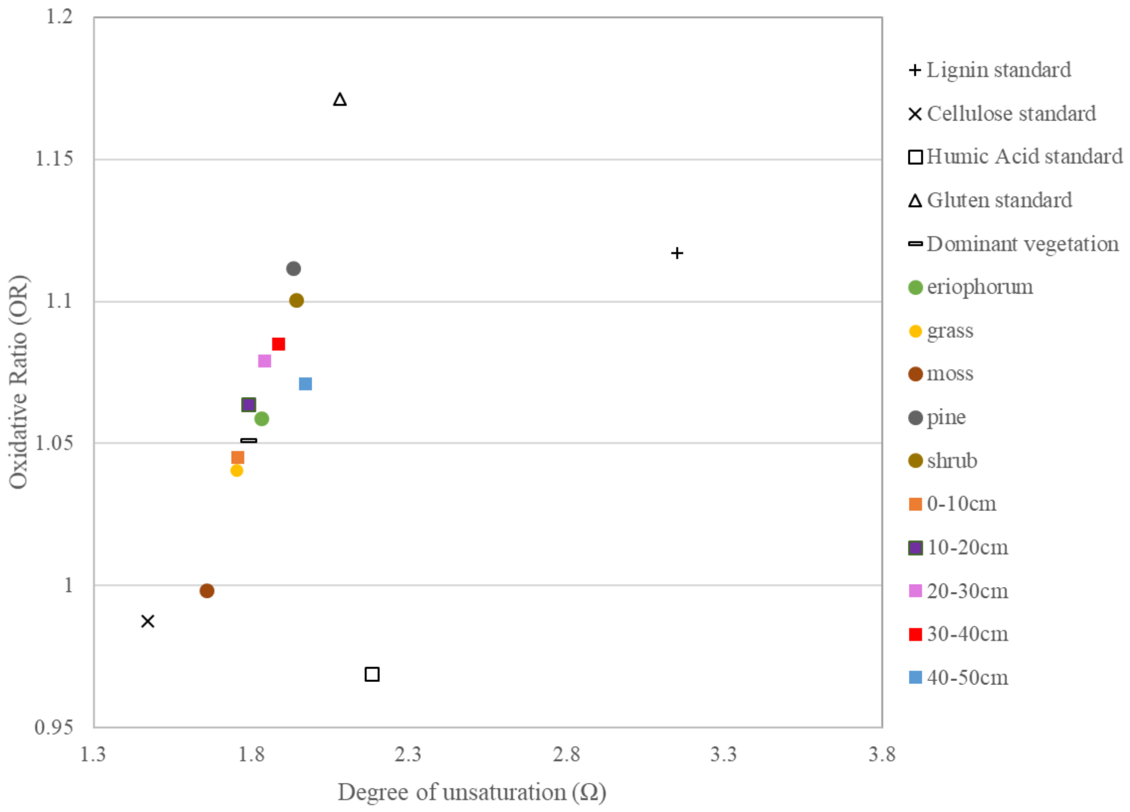
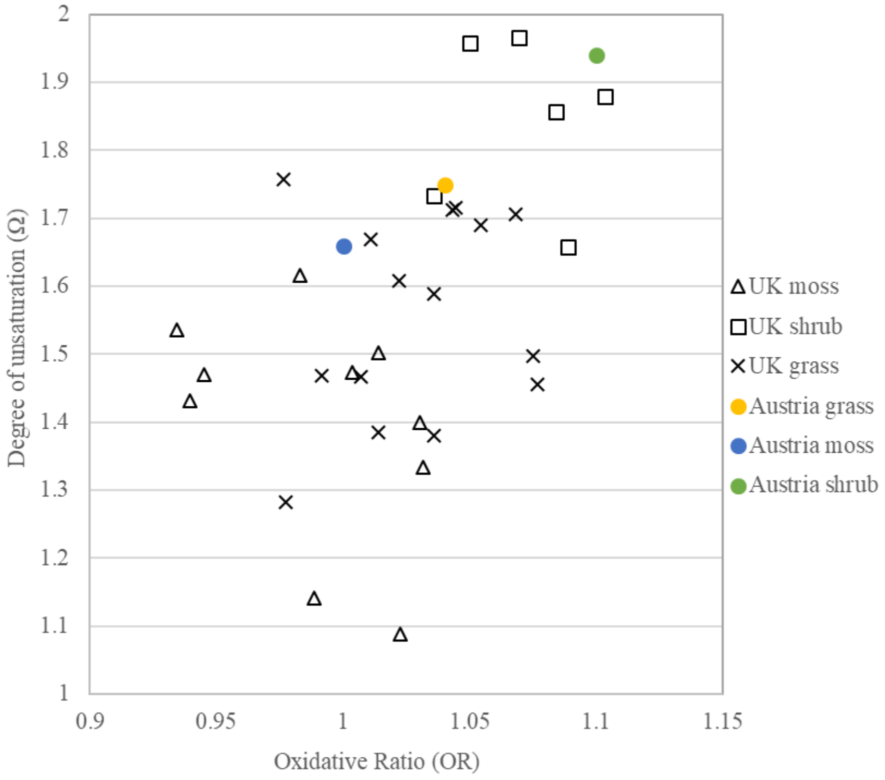


Figure 4.8: Ω plotted with [a] OR and [b] C/N for moss, shrub and grass samples averaged across the Austrian bogs analysed in this study and all samples analysed from the UK bogs analysed in Clay and Worrall [2015a].

a]



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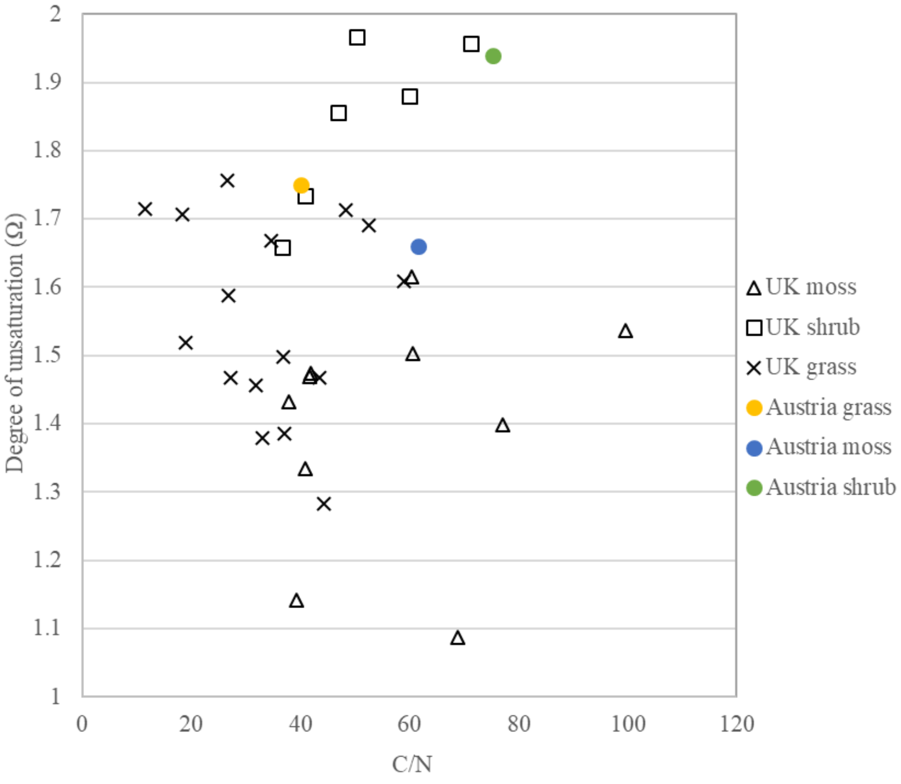


In the Austrian bogs analysed, the depth factor was found to cause significant differences in OR, C_{ox}, Ω, H/C and O/C. OR decreased between vegetation and the top 10 cm of the peat soil, then increased to 50 cm depth; this is the opposite pattern in OR to that observed in Hockaday et al. [2009] which found an increase in OR from vegetation to 5 cm depth, followed by a decrease to 20 cm. The significant change in OR with peat depth observed in the Austrian cores of this study disagrees with the results of Worrall et al. [2013] which assessed cores from the Moor House peatland [discussed in Chapter 2 of this thesis]. The results of the present study also disagree with those of Clay and Worrall [2015a] which found that depth was not a significant factor for C_{ox} or OR variation in UK peatlands [see Figure 4.10]. The significant increase in OR and decrease in C_{ox} between 0-10 cm and 30-40 cm depth observed in this study may be explained by considering the classical explanation of peat formation. Persistent water logged conditions in the peatland result in slow ingress of air leading to successive use and exhaustion of redox couples [Reddy and D'Angelo 1994]. As the peat profile becomes more anaerobic with depth, a shift to more reduced values of OR is observed.

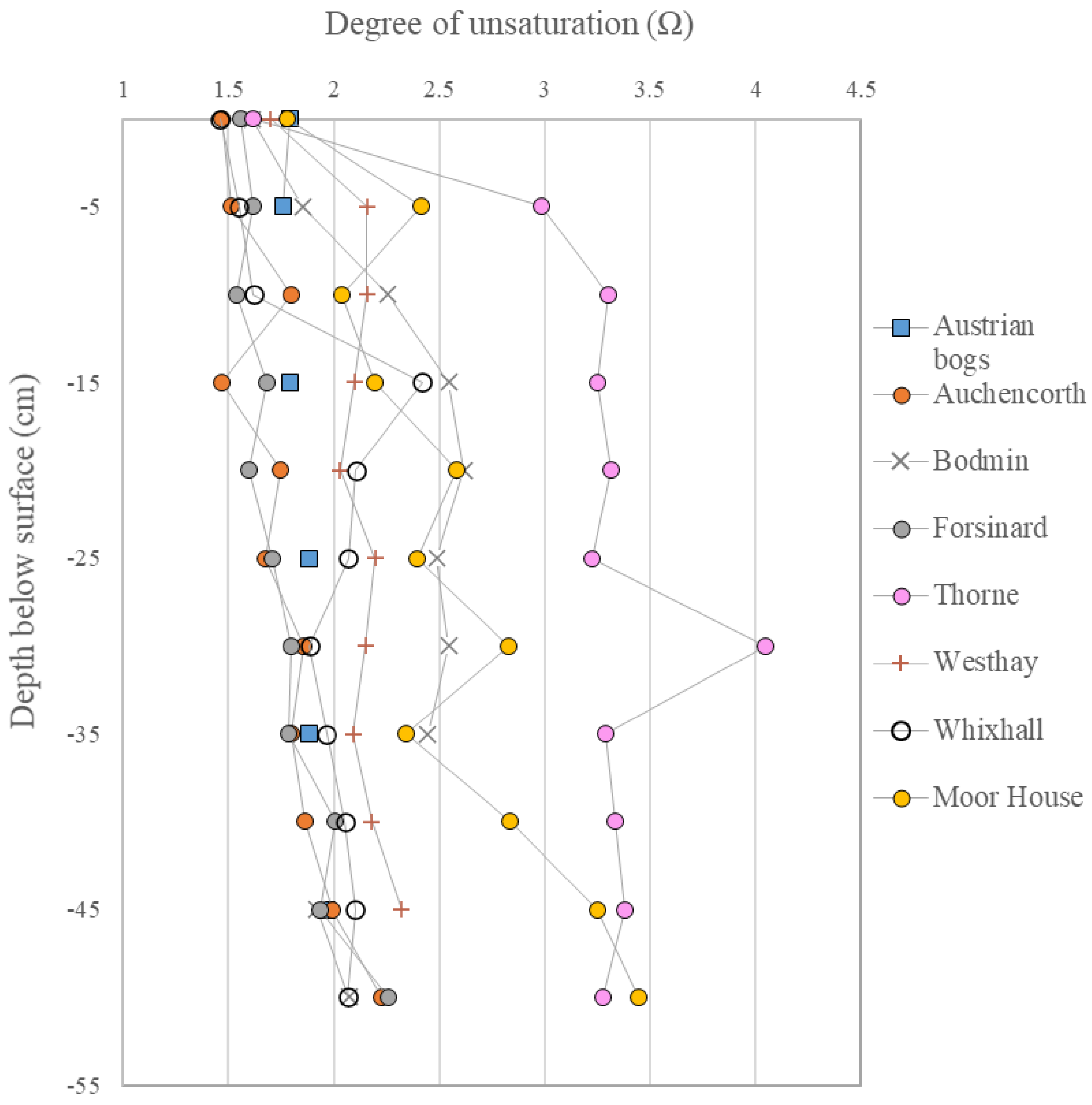
In the present study, vegetation and the top 10cm of peat soil, which included litter samples, had the lowest OR values. This observation is in agreement with the results of Worrall et al. [2013] and Clay and Worrall [2015a], however disagrees with the results of Clay and Worrall [2015b] who found that soils had the lowest OR values compared to vegetation and litter. The results of Clay and Worrall [2015b], which showed the reverse of the results found in this study, may be due to the inclusion of oxisols and ultisols in their study. Oxisols and ultisols are old and oxidised soils typified by highly oxidised organic content.

The OR of vegetation and litter [taken to be represented by the top 0-10cm of soil] samples measured by this study are not significantly different from each other. The similarity between vegetation and litter results from a decay continuum between vegetation and peat soils, on which the litter samples lie [Fang et al. 2011]. It is proposed that the vegetation and litter samples are closer to each other on this continuum than they are to the underlying peat, which supports the conclusions of Clay and Worrall [2015b]. The lower OR and lower C/N ratio of litter relative to vegetation implies that litter is either formed from only a component of the vegetation or represents a sink of N. The change in C/N with depth in the soil is much less than between vegetation and litter/soil suggesting that vegetation absorbs N in the transition to litter, but thereafter change in N content was lower between surface soil layers. The increase in C/N observed from 30-40cm samples to 40-50cm samples may support results of Worrall et al. [2012] which suggested that the acrotelm-catotelm boundary occurred at 42cm depth.

Clay and Worrall [2015a] found that material type [eg. soil vs vegetation] was significant in causing variation in C_{ox} and OR. The results of this study agree with this finding but suggest that variation within the organic matter pools i.e. vegetation type and depth in the peat profile, is also significant in determining oxidation state. Tukey *post-hoc* analysis on the derived oxidative ratios on soils in this study showed that soils at 0-10cm depth differed with more than 95% confidence from soils at 30-40cm. Since OR varies significantly with depth in a peat soil, it may not be appropriate to just sample the surface peat rather than coring as concluded by Clay and Worrall [2015a].

Significant increase in degree of unsaturation with depth was observed in the soils sampled. On a OR-Ω plot, litter, herbaceous vegetation and tree samples plot on a line between the cellulose and gluten/lignin standards, with moss at the most oxidised end and pine at the most reduced [Figure 4.6]. The position of the dominant vegetation, litter [0-10cm peat soil] and peat soils between the individual vegetation types on Figure 4.6 suggests each individual vegetation composition contributes to the composition of the peat soil. An array of litter, tree and herbaceous vegetation compositions between lignin and cellulose standards has previously been identified by Clay et al. [2018] and Clay and Worrall [2015a]. The Ω is seen to increase with depth in the peat soil to above that of pine and shrub vegetation at 40-50cm. Increase in Ω combined with the fall in H/C with depth in the peat profile may result from condensation reactions which occur as organic matter is buried. Figure 4.6 shows that as the soils increase in depth from 0-10 cm to 40-50 cm there is a shift towards lignin composition from cellulose. The soil samples are also closer than the moss and grass samples to the lignin standard on the compositional array, in agreement with McMahon et al. [1980], which states that cellulose is susceptible to microbial decomposition and its composition in organic soils is lower than that of the original plants. The increase in degree of unsaturation with depth observed in Austrian peatlands of this study has also been observed in studies of UK peatlands [Figure 4.8].

Figure 4.9: Mean Ω with depth in Austrian peat bogs of this study plotted with Ω of UK peatlands. Data is shown for average surface vegetation and depth intervals to 50cm. UK peat bog data taken from Clay and Worrall [2015a] and Worrall et al. [2016], details of the peat bog locations and data analysis methods can be found in the aforementioned studies.

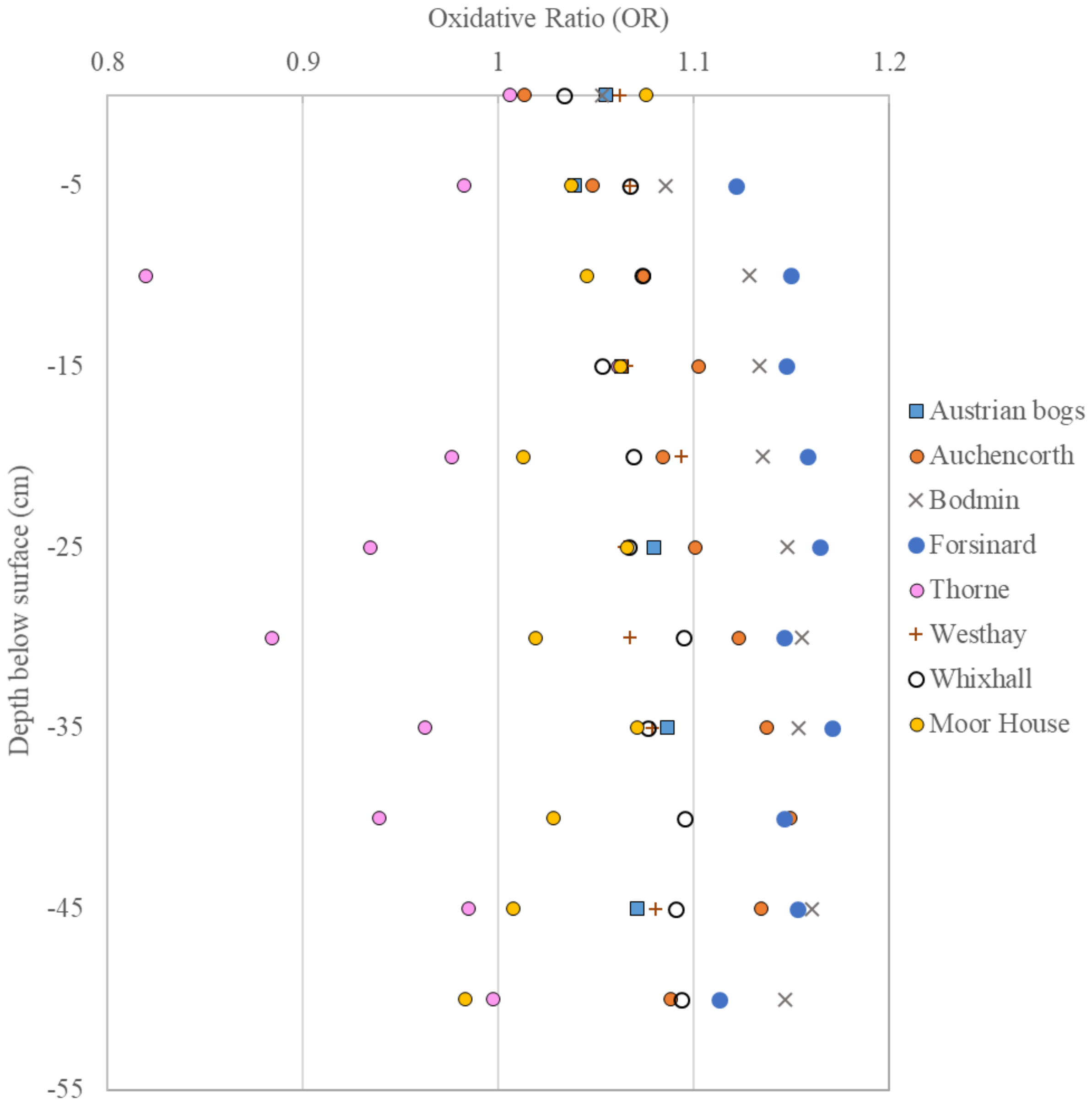


In the ANOVA model considering site and depth in the Austrian peat profile, for all the measured parameters, the site factor was found to be significant [$p<0.05$]. Significant differences between peatland sites explained 27% and 25% of the OR and C_{ox} data respectively. These results disagree with those of Clay and Worrall [2015b], which found that the site factor caused no significant difference to the OR of Southern African soils. The results of the present study do however agree with Clay and Worrall [2015b] in that the site factor does not appear to cause any variation to the oxidation state of vegetation. The significant differences observed between vegetation functional groups with respect to elemental composition and OR, but not with site combined with the significant variation in peat soil OR between sites suggests the control on OR of peat soils may relate to varying proportions of biochemical compounds between vegetation types or and varying proportions of vegetation at the different sites. Differing proportions of vegetation types of significantly different ORs determine the composition of soils that form; which may explain the significant variation in OR with site.

The site-depth interaction factor was not found to be significant in the OR or C_{ox} results of this study which suggests that the difference in the OR between vegetation and the different depth increments does not vary with the position of the peatland in Austria. Hence, there is a fixed relationship between OR and C_{ox} of vegetation and peat depth or organic matter type. Since the interaction term was not significant in OR assessments, differences in the oxidation state of organic matter is likely to be independent of the change between sites. The site-depth interaction factor was, however, significant in the degree of unsaturation, H/C and O/C terms. Hence, the elemental composition may be site-dependant.

Comparison of Austrian peat bogs of this study with UK peatlands analysed in Clay and Worrall [2015a] and Worrall et al. [2016] reveals differences in the patterns of OR measured with depth [Figure 4.10]. On average, the OR of samples from 0-10cm depth intervals in Austrian bogs showed a lower OR than surface vegetation. This decrease in OR from vegetation to litter was observed in two UK peatlands – Thorne and Moor House. All other UK peatlands showed an increase in OR from vegetation to litter. The increase in peat soil OR observed with depth to 40 cm in the Austrian bogs was observed at UK peatlands [Auchencorth, Bodmin and Forsinard]. This increase in OR with depth may relate to anaerobic conditions further down in the peat soil, however Clay and Worrall [2015a] did not find a significant change in OR with depth. Thorne shows a different pattern of OR with depth to the other UK and Austrian soils and values measured at Thorne were significantly lower and showed greater variation. In Clay and Worrall [2015a], Thorne peat bog was found to be the only site which was significantly different to all other sites. The variation in OR with depth in peatlands varies between sites. The large variation in trend in OR with depth in peat soils analysed in this study and others suggests that the oxidation state of a soil might relate to its genetic origin as well as biogeochemical processes which occur with burial. The Ω shows an increase in value with depth in peat soils; the increase observed has been suggested to result from condensation reactions and loss of cellulose which occur with burial. Hence, Ω may be more reliable than OR as a compositional or depth indicator than OR.

Figure 4.10: Mean OR in Austrian peat bogs of this study plotted with OR of UK peatlands. Data is shown for average surface vegetation and depth intervals to 50cm. UK peat bog data taken from Clay and Worrall [2015a] and Worrall et al. [2016], details of the peat bog locations and data analysis methods can be found in the aforementioned studies.



4.6. Conclusions

Measurement of the oxidative ratio of Austrian peat bogs has returned a value [1.07±0.02] lower than, but within the range allowed by, the IPCCs accepted value. This study has contributed to the growing expanse of data of ecosystem OR and developed the understanding of oxidation state variation within one particular soil group: the Histosols. This chapter has shown that there is a significant change in the value of the OR with location of the peat bog and depth of the peat soil in Austrian peatlands. OR of vegetation has been found to vary significantly with type but not with location of growth. Hence, variation in peat soil OR with site may relate to varying proportions of vegetation types at each site.

Analysis suggests that the OR varies not only with organic matter types but also within the individual organic matter types i.e. with depth in the peat soil. Hence, accurate measurement of OR of an ecosystem requires sampling all depth increments. The elemental composition of a peat soil at different depths has been shown to vary significantly with the site of formation, though results suggest this does not affect oxidative state at different depths in a peat bog. The increase in Ω combined with the fall in H/C with depth in the peat profile results from condensation reactions which occur as organic matter is buried and provide insight into the processes involved in peat formation. Comparison of results from this study with OR and compositional indicators from other studies suggests that the Ω may provide a more consistent means of assessing peatland composition.

5.0 The effect of burning on the oxidative ratio of Swineshaw peatland, UK

5.1 Introduction

Peat bogs are subject to fires as a result of managed and wildland fires [Turetsky et al. 2004]. Previous studies have investigated the effect of wildfires on soil C [Turetsky et al. 2014] and nutrient reservoirs [Allen 1964]. Effects of fires on chemical and physical properties of soils are widely reported [e.g., González-Pérez et al. 2004]. Extensive research into the emissions products of wildfires has also been performed [e.g., McMahon et al. 1980]. Despite extensive research into the effects of burning on soil C, little is known about the effects on carbon oxidation state [C_{ox}]. The effect of burning on the oxidative ratio [OR] of soils is not widely discussed in the literature. Hockaday et al. [2009] is the only study identified which has looked at the effects of burning on soil oxidation state; burnt soil residues were found to be substantially oxidised in comparison to unburnt horizons. The effect of burning on oxidative state and soil chemistry should be better understood as any changes in the soil C storage potential may alter the global C cycle [Almendros et al. 2003]. This chapter seeks to contribute to overcoming this gap in the literature by comparing the ORs, C_{ox} and other composition indicators of burnt and unburnt peatland cores, vegetation and char samples from the same site to gain an understanding of the effects of burning on soil oxidation state. It is hoped that the biogeochemical processes which occur in peat soils as a result of burning will be better understood by combining the results of these compositional indicators which act as tracers of organic matter.

5.2 Aims and objectives

The aim of the chapter was to understand change in oxidation and compositional state of peat ecosystems affected by wildfire. Several objectives were identified:

1. Measure the OR, C_{ox}, Ω, and elemental ratios of peat cores sampled at times of burnt and unburnt status of the same bog by elemental analysis [EA].
2. Measure OR, C_{ox}, Ω, and elemental ratios of unburnt vegetation and char by EA.
3. Identify any changes in oxidation or saturation state or elemental composition between the burnt and unburnt cores or with depth in the cores.
4. Suggest how burning effects peat soils and surface organic matter in terms of chemical changes.

5.3 Methodology

5.3.1 Sample collection

Samples were collected from Swineshaw peatland [latitude and longitude of 53.45859°N and -1.93673°E, respectively – Figure 5.1, Table 5.1] in the UK on two separate occasions in the aftermath of a wildifre. Swineshaw peatland was subject to two wildfires in Summer 2018; these initiated on June 24th and June 28th and each burnt for ~4 days before emergency services were able to extinguish them. It is not possible to know beforehand where a wildfire will occur and so no pre-wildfire control was possible and so peat soils within the burnt area were compared to peat from unburnt heather moorland adjacent to the fire front at the point where it was halted by fire crews. The first sampling visit [10/07/18] was as soon after the fire started that emergency services deemed it safe to go in to the burnt area, at this time it was not deemed safe to visit the unburnt moorland near the fire front and so that necessitated a second, later sampling visit. On the first sampling visit, 56 quadrats were surveyed within the burnt area [data not reported here] and from within these quadrats samples of peat, vegetation and char were taken. Two cores of peat were taken within the burnt area along with charred vegetation on the surface of these cores. The second sampling visit was on 11th January 2019, when it was possible to visit the heather moorland immediately outside the burnt area and adjacent to the former fire front. On this occasion one peat core and 12 surface samples were taken from the Swineshaw peatland [Table 5.2]. All three cores were 100 cm in depth. The 12 unburnt surface samples taken in January 2019 include 3 different vegetation types: moss litter, heather and cotton grass as well as a bulk dominant vegetation sample and 2 surficial peat samples. In total 75 samples were collected for analysis.

Figure 5.1: Location of Swineshaw peatland in the UK.

Table 5.1: Summary of burn status and depth of the Swineshaw cores. The cores are referred to by these terms throughout the study.

Core	Date of Sampling	Burn status	Depth of core
Burnt core 1	Jul-18	Burnt	100cm
Burnt core 1	Jul-18	Burnt	100cm
Unburnt core	Jan-19	Unburnt	100cm

Table 5.2: Unburnt surface samples taken in January 2019, with number of samples and location of sampling.

Sample type	N	Quadrat of sampling
Moss litter	4	4, 5, Unburnt core, Unknown
Heather	4	3, 4, 5, 11
Dominant Vegetation	1	1
Surface peat	2	11, 17
Cotton grass	1	15

5.3.2 Sample preparation

The cores were divided into depth groups for sampling; for unburnt Core 1 the depth intervals were 0-2cm, 2-5cm, 5cm depth intervals to 50 cm and 10 cm intervals to 100 cm; for the burnt cores the intervals were 2 cm depth intervals to 20 cm, 5 cm intervals to 50 cm then 10 cm divisions to 100cm. All samples were dried at 60°C for 72 hours. Peat soil samples were ground using a pestle and mortar. Following grounding samples were passed through a 1-mm sieve tray. All samples, both vegetation, litter and peat core, were ground to a submillimetre powder using a Spex 6770 Freezer Cryomill.

5.3.3 Elemental analysis

The ground samples were analysed for their carbon, hydrogen, nitrogen [CHN] and separately for their oxygen [O] concentrations on a Costech ECS 4010 Elemental combustion system with pneumatic autosampler, as described in Section 3.3.4 of this thesis.

5.3.4 Oxidative ratio and compositional analysis

Mean C, H, N and O data obtained by elemental analysis were converted to molar concentrations, carbon oxidation state [C_{ox}], OR, degree of unsaturation [Ω], C/N, H/C and O/C by the methods described in Sections 1.2.2, 1.2.3 and 3.3.4 of this thesis. For comparison purposes, samples were compared with lignin, cellulose, humic acid and gluten standards as described in Section 3.3.4.

5.3.5 Statistical analysis

To assess the effect of burning on the OR of the peatland ecosystem, a two-way ANOVA was performed on the results of elemental analysis. The effect of site and depth on the composition of the peat cores was tested. The site factor had 3 levels – one for each core taken. The depth factor had 21 levels – the depth intervals of the cores. Significant differences between factors was assessed at the 95% probability of being different from zero unless otherwise stated. Response variables used in the analysis were C_{ox}, OR, Ω, C/N, H/C and O/C. Prior to ANOVA the data sets were tested for normality using the Anderson-Darling test [Anderson and Darling 1952]. None of the datasets needed transforming prior to analysis. *Post-hoc* testing of the results was performed using the Tukey test at 95% level to determine significant differences between levels of any factor. Results are expressed as least squares means.

5.4 Results

The mean and standard deviation of OR of all samples was 1.04±0.04 [n = 70] [Table 5.3]. The highest OR [1.10] was measured in cotton grass and one of the surface peat samples. The lowest OR was measured in the moss litter of Core 1 [0.96]. The char sample had the second lowest OR [1.01]. The highest Ω was measured in the char sample [3.56] and the lowest Ω in Cotton grass [1.55].

Table 5.3: The arithmetic mean values of OR, C_{ox}, Ω, C/N, H/C and O/C in the surface samples and peat cores used in this study, with number of samples analysed (N). All the samples shown in the table were taken in January 2019 except the char sample and burnt cores 1 and 2 which were taken in July 2018.

Sample type	N	OR	C_{ox}	DOU	C/N	H/C	O/C
Char	1	1.01	0.06	3.56	29.96	0.85	0.40
Cotton grass	1	1.10	-0.23	1.55	19.60	1.65	0.63
Heather	4	1.09	-0.31	2.06	61.87	1.49	0.57
Surface peat	2	1.07	-0.17	2.26	31.60	1.25	0.49
Dominant vegetation	1	1.05	-0.15	2.19	50.86	1.42	0.60
Moss litter	4	1.03	-0.05	1.88	42.11	1.53	0.70
Unburnt core	16	0.98	0.16	2.37	46.55	1.27	0.68
Burnt core 1	20	1.07	-0.20	2.58	44.18	1.25	0.49
Burnt core 2	21	1.05	-0.12	2.60	54.46	1.25	0.54

Two-way ANOVA performed on the results identified significant differences in compositional indicators between the sites and depths analysed in the study [Tables 5.4 and 5.5]. The site of core sampling was shown to be significant in all of the elemental molar concentrations and derived variables except H/C. N concentration and C/N were the only factors which varied significantly with depth in the peat soil. The OR and C_{ox} of all three cores were significantly different from each other.

Table 5.4: ANOVA for site and peat depth increments for CHNO molar concentrations. df = degrees of freedom, p = probability of factor being zero. Factors and interactions found to be significant [i.e. p<0.05] are highlighted in bold.

	C		H		N		O	
	df	p	df	p	df	p	df	p
Site	2	**0.000**	2	**0.000**	2	**0.000**	2	**0.000**
Depth	21	0.269	21	0.066	21	**0.008**	21	0.090
Error	36		36		36		36	

Table 5.5: ANOVA for site and peat depth increments for OR, C_{ox}, Ω and elemental ratios. df = degrees of freedom, p = probability of factor being zero, ω^2 = generalised proportion of variance explained. Factors and interactions found to be significant [i.e. p<0.05] are highlighted in bold.

	OR		Cox		Ω	
	df	p	df	p	df	p
Site	2	**0.000**	2	**0.000**	2	**0.001**
Depth	20	0.189	20	0.112	20	0.237
Error	34		34		34	

	C/N		H/C		O/C	
	df	p	df	p	df	p
Site	2	**0.000**	2	0.736	2	**0.000**
Depth	20	**0.000**	20	0.385	20	0.412
Error	34		34		34	

5.4.1 Variation with site

Significant variation in the derived variables between peat cores was identified. The unburnt core had a lower OR [0.98±0.00] i.e. was more oxidised than the burnt core 1 [1.07±0.00] and burnt core 2 [1.05±0.00] [Table 5.8, 5.9]. The C_{ox} of the unburnt core was significantly higher than burnt core 1 and burnt core 2. Burnt core 2 had a lower OR and higher C_{ox} than burnt core 1. The Ω was significantly lower in the unburnt core than burnt cores 1 or

2 [Table 5.10]. The ratio O/C was significantly different between all three cores; the highest value [0.68±0.01] was measured in the unburnt core and the lowest was in burnt core 1 [0.49±0.01] [Table 5.11]. The C/N ratio was highest in burnt core 2 [54.46±1.07] and lowest in burnt core 1 [44.18±1.04].

Table 5.6: Least squares mean ± standard error of elemental molar contents in soils at each site.

Location	C	H	N	O
Unmburnt core	3.85 ± 0.08	4.86 ± 0.10	0.08 ± 0.00	2.61 ± 0.07
Burnt core 1	4.37 ± 0.06	5.48 ± 0.08	0.10 ± 0.00	2.14 ± 0.05
Burnt core 2	4.41 ± 0.07	5.53 ± 0.08	0.08 ± 0.00	2.37 ± 0.06

Table 5.7: Least squares means ± standard error of the derived variables in soils at each site.

Depth	OR	C_{ox}	Ω
Unburnt core	0.98 ± 0.00	0.16 ± 0.01	2.37 ± 0.04
Burnt core 1	1.07 ± 0.00	-0.20 ± 0.01	2.58 ± 0.04
Burnt core 2	1.05 ± 0.00	-0.12 ± 0.01	2.60 ± 0.04

Depth	C/N	H/C	O/C
Unburnt core	46.55 ± 1.26	1.27 ± 0.01	0.68 ± 0.01
Burnt core 1	44.18 ± 1.04	1.25 ± 0.01	0.49 ± 0.01
Burnt core 2	54.46 ± 1.07	1.25 ± 0.01	0.54 ± 0.01

Table 5.8: Results of the Tukey Pairwise Comparison Post-hoc analysis at 95% confidence on site soil OR.

Site	N	Mean	Grouping		
Burnt core 1	21	1.07	A		
Burnt core 2	20	1.05		B	
Unburnt core	16	0.98			C

Table 5.9: Results of the Tukey Pairwise Comparison Post-hoc analysis at 95% confidence on site soil C_{ox}.

Site	N	Mean	Grouping		
Burnt core 1	16	0.16	A		
Burnt core 2	20	-0.12		B	
Unburnt core	21	-0.20			C

Table 5.10: Results of the Tukey Pairwise Comparison Post-hoc analysis at 95% confidence on site soil Ω.

Site	N	Mean	Grouping	
Burnt core 1	21	2.60	A	
Burnt core 2	20	2.58	A	
Unburnt core	16	2.37		B

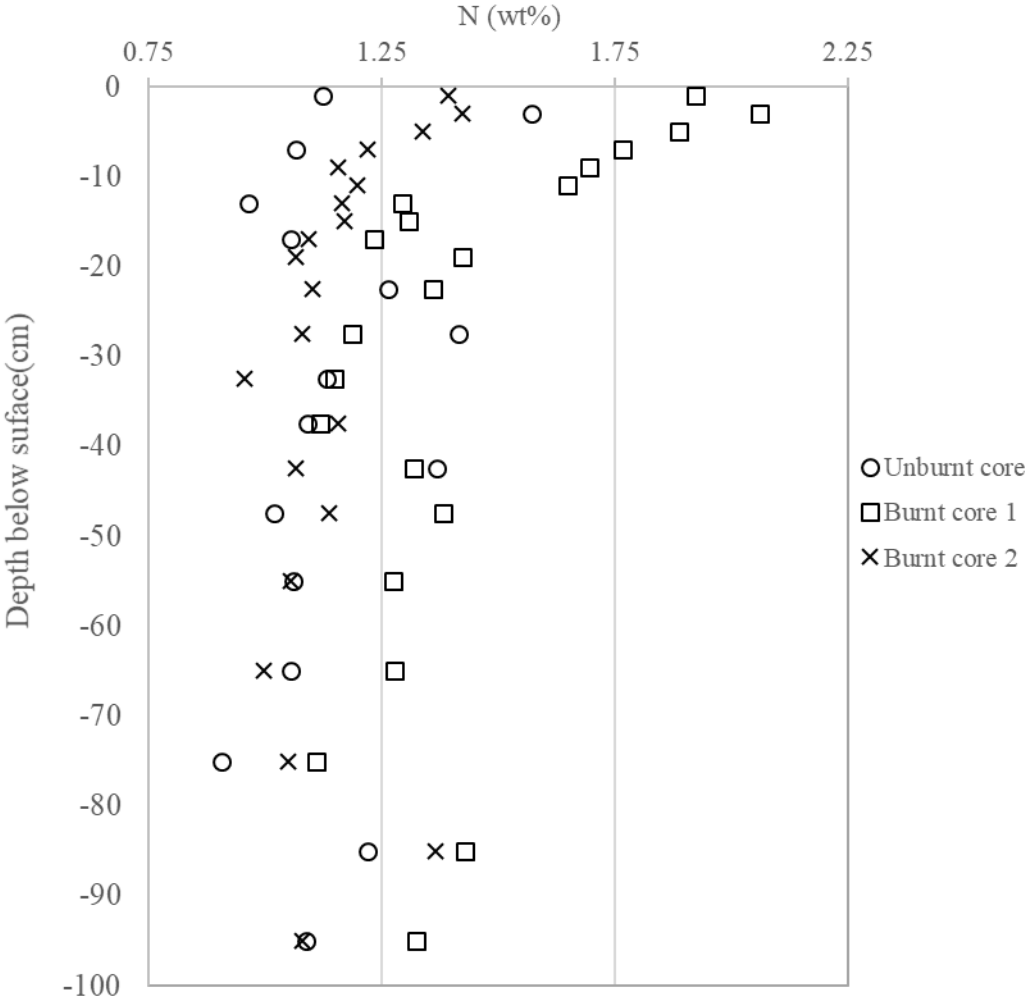
Table 5.11: Results of the Tukey Pairwise Comparison Post-hoc analysis at 95% confidence on site soil O/C.

Site	N	Mean	Grouping		
Unburnt core	16	0.68	A		
Burnt core 2	20	0.54		B	
Burnt core 1	21	0.49			C

5.4.2 Variation with depth

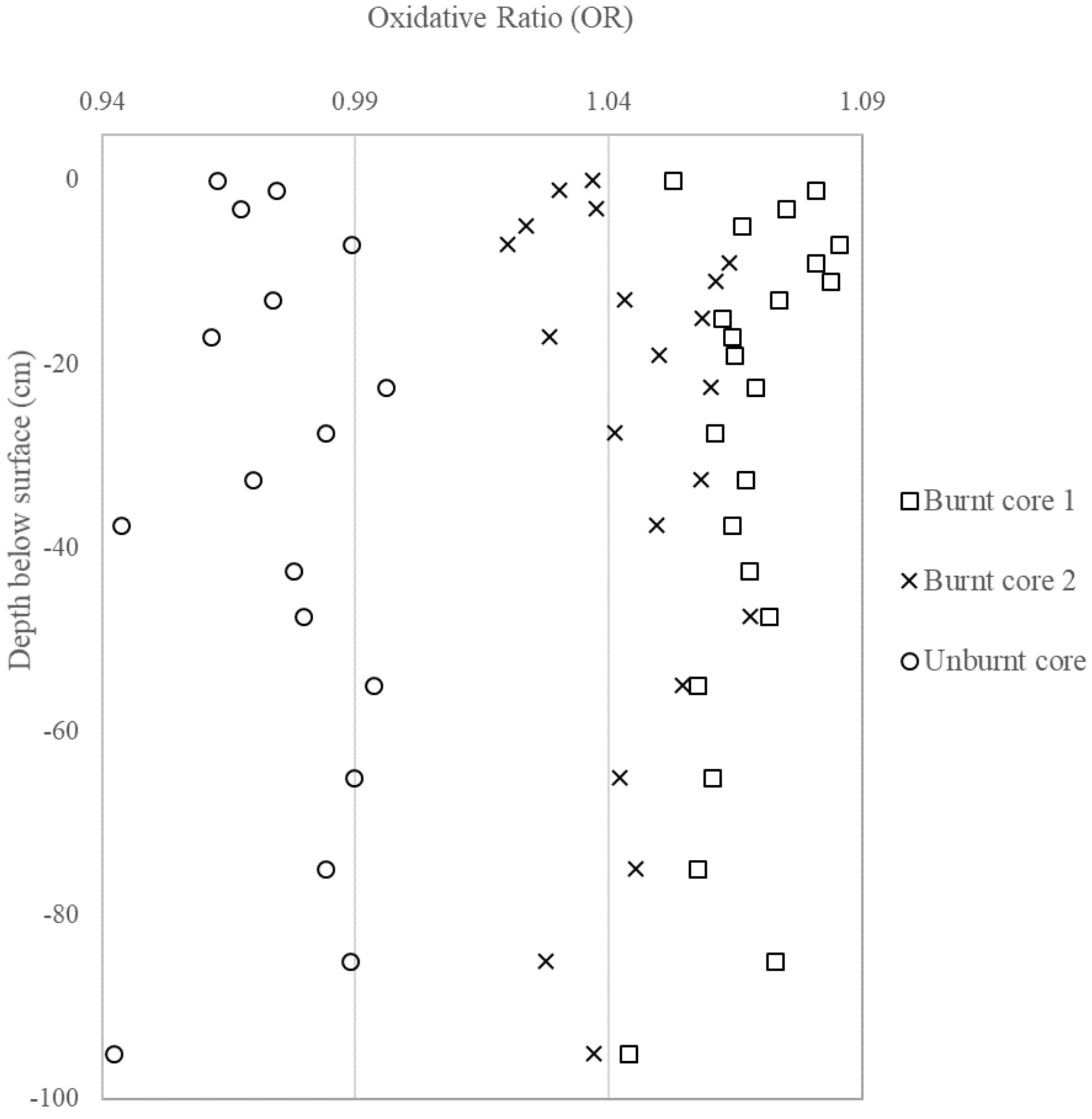
Change in elemental concentrations and derived variables with depth in the peat cores was observed; though was not found to be significant in all cases. Nitrogen was the only elemental concentration which varied significantly with depth in the peat soils. In the burnt cores, the concentration of N decreased in the top 20 cm of the soil [Figure 5.2]. The unburnt core did not appear to show any particular trend in N concentration with depth, but showed a wide range of values ranging from 0.91 wt.% at 70-80cm to 1.57 wt.% at 2-4cm.

Figure 5.2: Variation of Nitrogen concentration [weight %] with depth in each peat core.



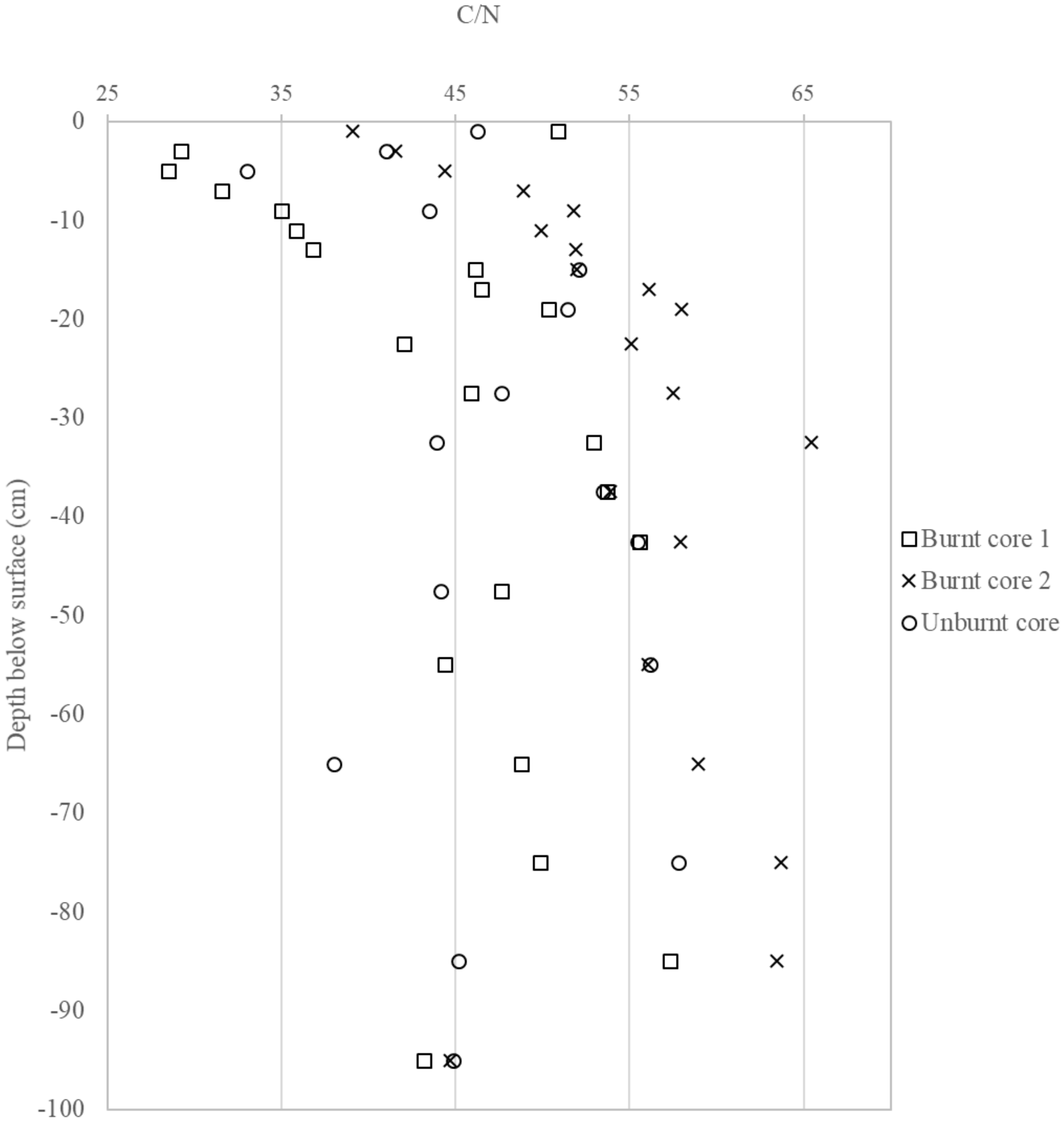
There was no significant difference with depth for either OR or C_{ox} identified in the peat cores of this study [Figure 5.3]. Whilst OR of the unburnt core was significantly lower than that of the burnt cores 1 and 2, the depth factor was not found to cause significant variation in OR in the cores.

Figure 5.3: Oxidative ratio of the three peat cores plotted against depth.



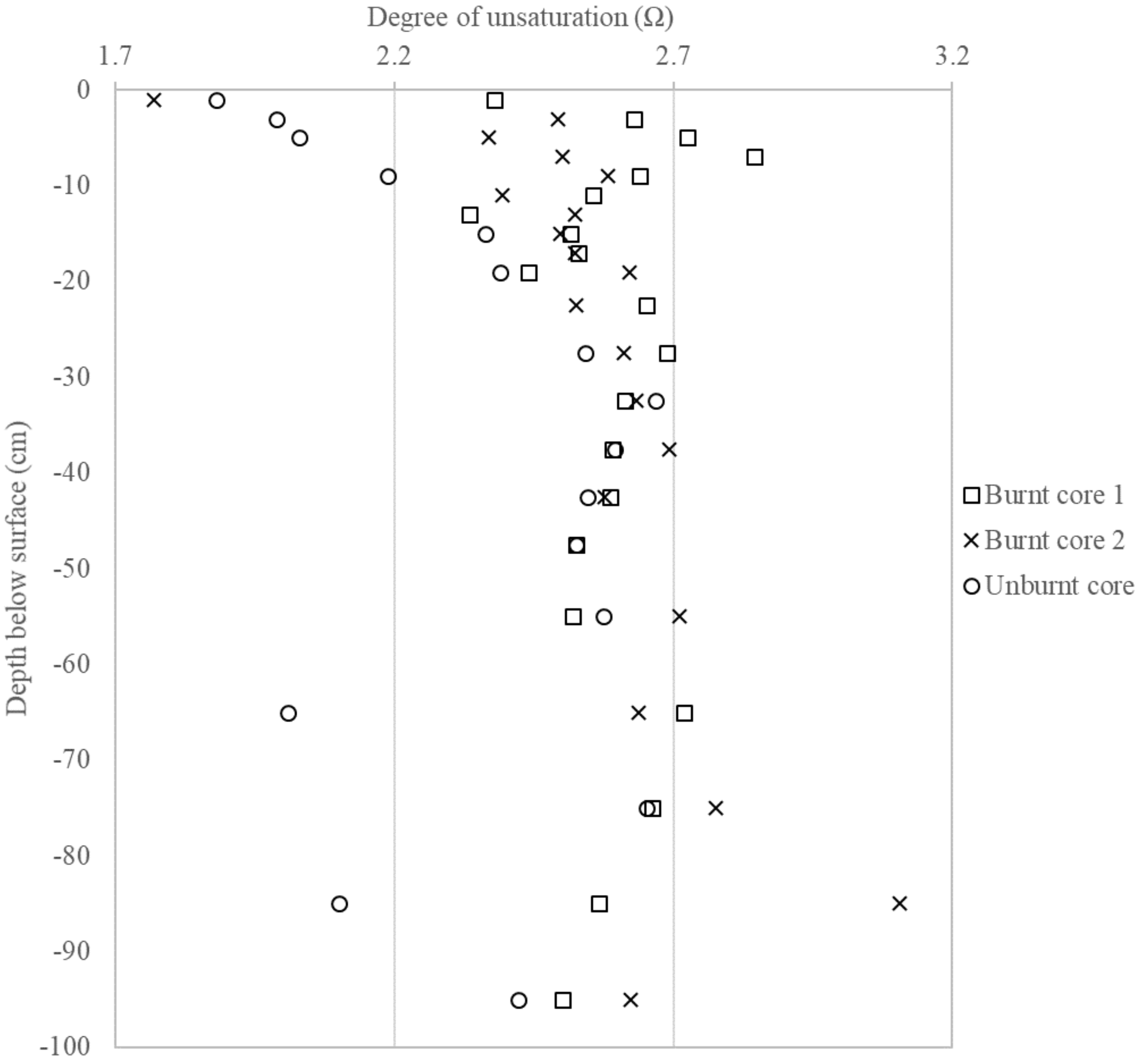
The only derived variable found to vary significantly with depth in the peat soils at Swineshaw was the C/N ratio [Table 5.5]. The C/N ratio increased with depth in both burnt cores [Figure 5.4]. The increase is not observed in the unburnt core. Change in C/N with depth is most pronounced in burnt cores 1 and 2 at depths less than 20cm.

Figure 5.4: C/N of the three peat cores plotted against depth.



The degree of unsaturation varied significantly with site between the three peat cores analysed; the unburnt core had a significantly lower Ω than the two burnt cores. The Ω was not found to vary significantly with depth in the peat cores [Figure 5.5]. In surficial samples the Ω was lowest in the unburnt core, this increased with depth to ~30cm to a value more similar to that measured in burnt cores 1 and 2.

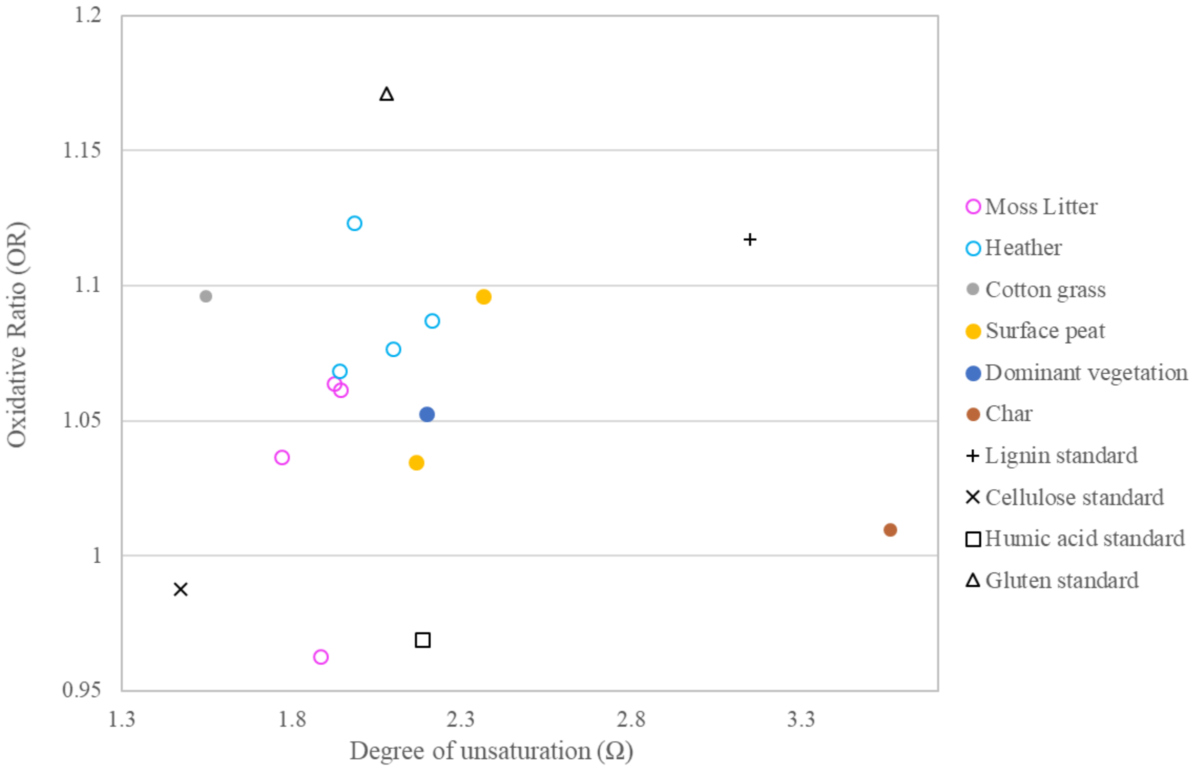
Figure 5.5: Ω of the three peat cores plotted against depth.



5.4.3 Vegetation

All surface peat, heather and dominant vegetation samples plot within the compositional array defined by the lignin, cellulose, humic acid and gluten standards [Figure 5.6]. Compositional array is defined here as the range of values of the chemical parameters i.e. OR and Ω within which the composition of the majority of samples lie. Cotton grass has a low Ω for its OR value, and plots outside the compositional array. For the moss litter samples, 75% of samples plotted along the array defined by the cellulose and lignin standards; one of the four lies above this line, closer to the gluten standard. The dominant vegetation sample lies centrally between the four standard compositions. The char sample plotted outside the range defined by the standard composition array due to its low OR and high Ω.

Figure 5.6: OR- Ω plot of all vegetation, none-core surficial peat and char samples. Lignin, cellulose, humic acid and gluten standards are also plotted.



5.5 Discussion

This study has returned an OR value [1.04±0.04 n = 70] below the IPCC's accepted value, though the ranges overlap. Post-hoc analysis on the OR results showed that OR of the burnt cores was significantly higher than the unburnt core, with a maximum difference of 0.09 between the unburnt core [mean and standard error of OR = 0.98 ± 0.00, n=16] and burnt core 1 [OR = 1.07 ± 0.00, n=21]. Complete combustion converts organic matter to CO_2 and H_2O, e.g., by Equation 5.1, which shows the complete combustion of cellulose.

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O \qquad \text{[Equation 5.1]}$$

Peat soil affected by wildfire is often assumed to have undergone the reaction shown in Equation 5.1 and other similar combustion reactions [Rein et al. 2008]. In this study, peat soils affected by burning were observed to be more reduced [i.e. higher OR]. The higher OR of the burnt soils may result from O being lost or driven off from organic compounds in the soil. The loss of O-containing functional groups as a result of dehydration reactions that occur during combustion have previously been reported by studies into soil fires [e.g., Almendros et al. 1990]. The increased OR in burnt relative to unburnt cores could imply an effect of burning over the full depth of the peat profile since no significant change in OR with depth was observed in the cores [Figure 5.3]. The oxidation state of the two burnt cores was found to be significantly different [Figure 5.7], suggesting that some of the compositional variation in burnt soils relates to spatial heterogeneity of the soils.

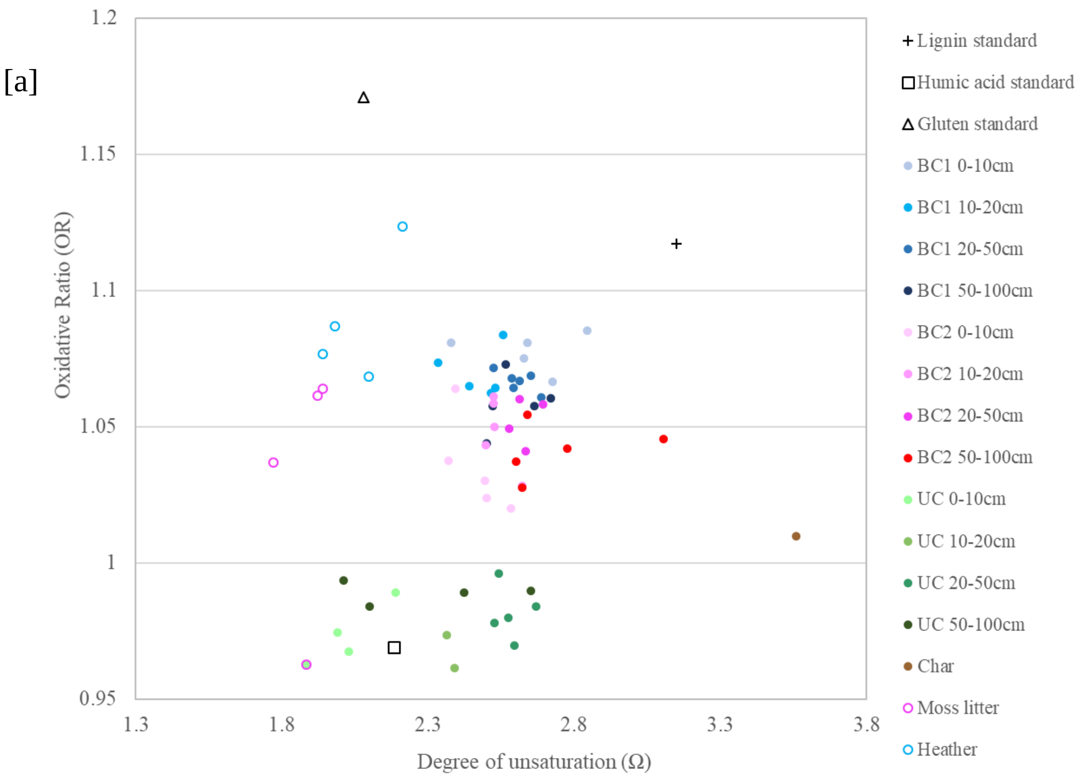
OR of the char was lower than the unburnt vegetation samples, which disagrees with the measured OR of burnt peat cores. The char sample also had a low OR relative to the burnt surficial peat from burnt cores 1 and 2. Lower OR of char samples suggests that burning does not cause reduction of all organic matter. The lower OR of char is in agreement with Masiello et al. [2008]. Hockaday et al. [2009] measured burnt soil residues to be “substantially oxidised relative to the unburnt soil horizons”; this is in agreement with the OR of the char residue taken from Swineshaw but disagrees with the OR of burnt soils. However, the O/C ratio was lowest in the char sample and burnt cores relative to the vegetation samples and unburnt peat soil respectively, which suggests burning of organic matter may consistently cause a substantial loss of O-containing functional groups. The results of this study are in partial agreement with those of Almendros et al. [2003] which found a loss of H and O in burnt soils as the present study measured a loss of O but increase in H in burnt samples [Table 5.6]. Hockaday et al. [2009] measured burnt residues to have lower [i.e. more oxidised] OR values relative to unburnt soils which agrees with results of the char sample in this study. The higher OR measured in post-burn soils relative to unburnt soils in this study disagrees with Clay et al. [2018] which suggested that increased disturbance to the terrestrial biosphere would cause a decrease in OR_{terra}; Clay et al. [2018] were investigating the effects of climate and land use changes on OR and did not consider wildfire, hence different types of disturbance appear to have different effects on OR.

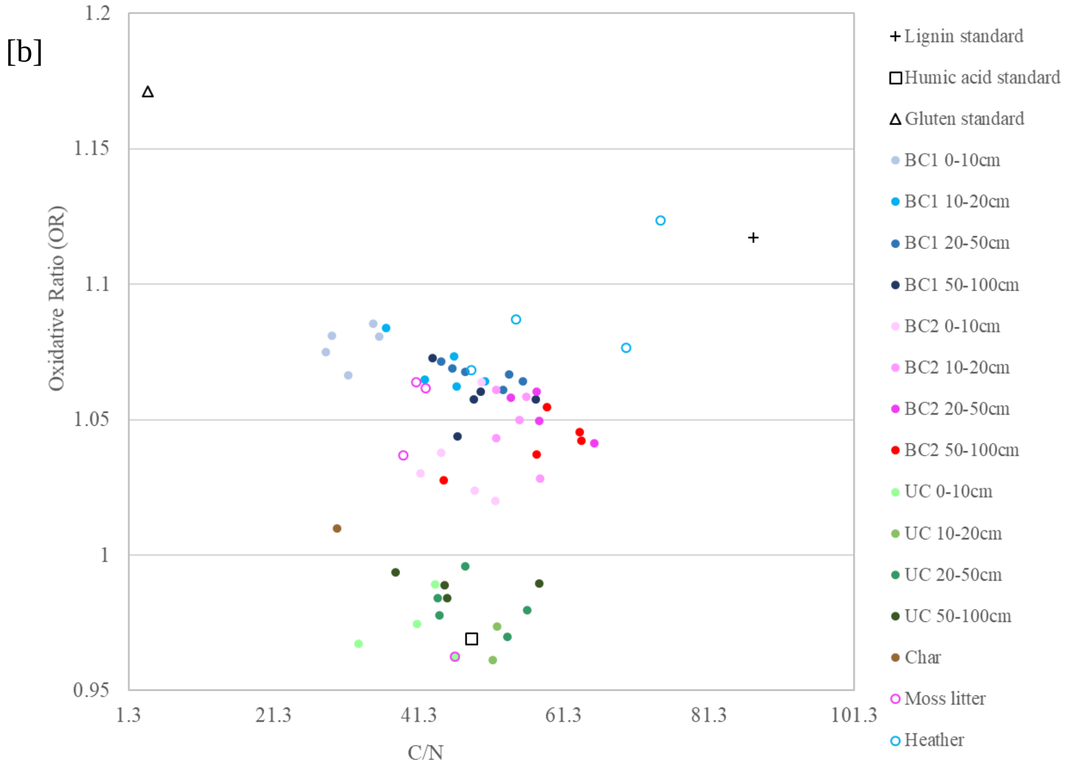
A lower H/C ratio measured in the char sample [0.85] relative to the unburnt surface samples [Table 5.3] suggests an increase in aromaticity results from burning of organic material. An increased Ω measured in the burnt cores and the char sample relative to the unburnt core and vegetation samples, respectively, also implies an increase in aromaticity [Figure 5.7a]. The measured C concentration in the peat cores was significantly higher in burnt core 1 [4.37±0.06] and burnt core 2 [4.41±0.07] relative to the unburnt core [3.85±0.08]. Higher Ω and C concentration in soils affected by wildfire has previously been attributed to accumulation of charcoal and hydrophobic organic matter [Johnson and Curtis 2001]. The high Ω and C concentration of burnt material in this study is in agreement with previous studies which show that an increase in aromaticity is observed in charring of peat soils [Freitas et al. 1999].

Black carbon [BC] has been defined by Novakov [1984] as “combustion produced black particulate C having a graphitic microstructure”. It has been shown that BC forms by condensation reactions of carbohydrates, lipids and peptides [Knicker et al. 1996]. However, BC does show a compositional continuum from partly charred plant material through char to graphite. Compositional analysis has previously shown BC to be highly aromatic [Schmidt and Noack 2000] with a substantial alkyl domain and considerable O content [Almendros et al. 2003]. The significantly higher Ω of the burnt soils of this study agrees with a contribution to burnt soils from BC. The char sample has the highest Ω and its OR is lower [i.e. more oxidised] than expected, suggesting it may lay on the BC continuum.

The increased Ω of the peat cores affected by wildfire may also result from Maillard reactions where condensation of amino acids and peptides form macromolecular structures during burning [Maillard 1916]. The Maillard reactions represent charring of carbohydrates and produce a range of highly unsaturated compounds [Ikan et al. 1986]. Peatlands have previously been suggested to be the most probable environment where these humification processes could occur [Kumada 1983; Shindo et al. 1986a; González-Pérez et al. 2004]. An increase in the Ω with depth in the unburnt core from Swineshaw [Figure 5.5 and 5.7a] is in agreement with previous studies [e.g., Worrall et al. 2015]. Section 4.5 showed an increase in Ω with depth in unburnt Austrian and UK peat cores. This study has identified an increase in degree of unsaturation of burned samples relative to unburned samples [Table 5.3]. Increased Ω in topsoils affected by burning may override the usually-observed increase with depth observed in unburnt organic soils i.e. the unburnt core of this study [Figures 5.5 and 5.7a].

Figure 5.7: Plot of OR with [a] Ω and [b] C/N for the three peat cores, vegetation, char and moss litter samples. BC1 = burnt core 1, BC2 = burnt core 2, UC = unburnt core. Lignin, cellulose, humic acid and gluten standards are also plotted.





The increased OR of burnt soils relative to unburnt soils is observed in Figure 5.7. The increased OR, C/N and Ω of unburnt heather samples compared with moss litter is in agreement with section 4.5 of this study and the results of Clay and Worrall [2015a] referred to therein. Increase in Ω with depth in the unburnt core supports the proposed condensation reactions which occur with burial in a peat soil and a shift towards a more lignin-rich composition.

The only derived variable found to vary significantly with depth in the Swineshaw peat soils was C/N [Figure 5.4]. In the burnt cores of this study C/N was observed to increase with depth, which agrees with results of several previous studies into post-fire soils [e.g., Almendros et al. 1984, a, b; Viro 1974; Vega 1986]. Hockaday et al. [2009] also found a lower C/N ratio in burnt soil residues. The only elemental concentration which varies significantly with depth in the Swineshaw peat soil cores is that of N. The N concentration in the burnt cores decreased with depth in the top 20cm of the soil. Hence, decrease in N concentration in the soils is thought to be the contributing factor to the increase in the C/N ratio observed with depth. The unburnt core had a C/N ratio intermediate between that of the two cores affected by burning; the value of C/N is therefore proposed to be controlled by the original composition of the soils. The pattern of increase of the C/N ratio with depth in surface soils is, however, proposed to be a result of burning. Clay and Worrall [2015a] observed an increase in C/N with depth in unburnt UK peat soils, however this increase occurred over a greater depth and was not as pronounced as seen in the top 20cm of burnt soils at Swineshaw [Figure 5.8].

Matson et al. [1987] found that amounts of ammonium [NH_4^+] and nitrate [NO_3^-] increased substantially in tropical surface soils in the first 6 months after burning. It may be the case that an increase in these nitrogen species was seen in the burnt surface of peatland cores at Swineshaw. Results of this study suggest that after a fire the nitrogen-containing nutrient availability in the most surficial soil increases, which may be a result of ash deposits that fall and contribute high quantities of water-soluble components. The results of Allen [1964], however, disagree with the results of this study and suggest that “there is little indication that the N ions had moved downwards in the profile”. However, Allen [1964] did acknowledge that increased N content might be present under field conditions, as observed in the present study. Johnson [1992] found an increased presence of N-fixing bacteria after wildfires which may contribute to the higher N abundances in burnt surface soils observed at Swineshaw.

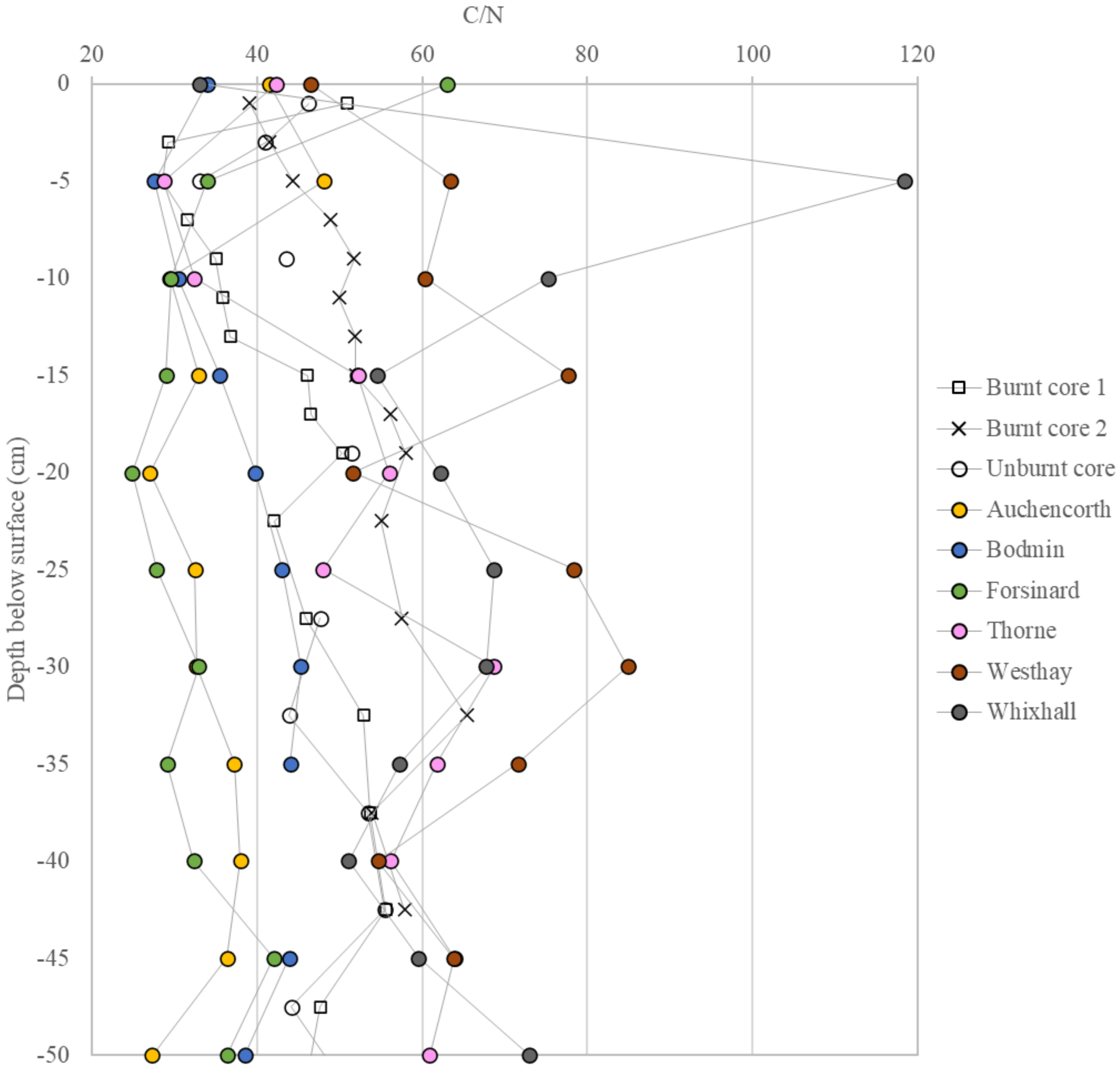
Nitrogen oxide [NO_x] emissions from organic soil fires have previously been found to be low as a result of the low combustion temperature at which the fires occur [McMahon et al. 1980]. Little loss of N relative to C in the fires at Swineshaw may also contribute to the lower C/N ratios observed in surface soils affected by burning [Figure 5.4]. This explanation of the increased N content of the burnt soils in this study again disagrees with the results of Allen [1964] which found N losses to be high. Increased activity of N-fixing microorganisms after burning could potentially outweigh the N lost during burning in this case, as proposed by Fowells and Stephenson [1934] and Tamm [1950]. The recovery of soil microbial biomass C and N to pre-fire levels has been found to take more than 10 years in some cases [Fritze et al. 1993]; hence the effects of fire on the post-burn soils of this study are likely to be considerable. Allen [1964] also suggest that temporary, short-term increase in nutrient input from heather ash after burning may prevent losses in soil N, which may explain the low C/N ratio observed in burnt topsoils in this study.

An alternative explanation to the high concentration of N in the shallow burnt soils is the accumulation of heterocyclic nitrogen forms as proposed by Baldock and Smernick [2002] and Knicker et al. [2003]. These compounds form only by pyrogenic processes as a result of heat-induced dehydration and cyclization reactions. Build-up of heterocyclic N forms in soils affected by wildfire at Swineshaw would contribute to the low C/N, high Ω and low O/C observed in the burnt cores and the char sample. Maillard reactions discussed above have previously been proposed to form amide compounds amongst others with high N content and high Ω [Ellis 1959; Nguyen and Harvey 1998; Almendros et al. 2003]. The burnt peat cores taken from Swineshaw were sampled a few days after the fires had been put out, hence, some of the effects of wild fire such as an increased presence of N-fixing bacteria may not have occurred by this stage. In the case of the samples analysed here, it is suggested that direct effects of burning such as Maillard and pyrogenic chemical reactions and minimal loss of nitrous oxides during burning are the most likely causes of the increase in C/N with depth in burnt soils. Trends observed in the C/N ratio with depth in the top 20cm of burnt soils were not observed in the unburnt soils of this study or the unburnt peat cores analysed by Clay and Worrall [2015a] [Figure 5.8]. This provides further evidence that the cause of an increase in C/N with depth in the top 20cm of the burnt cores was a result of burning and not a compositional effect of the peat.

At depths greater than 20 cm in the burnt peat soils the C/N ratio showed less change in value than it had in the surface soils [Figure 5.8]. The lack of change of C/N in burnt cores at depth is thought to result from a lack of effects of burning in soils deeper than ~20cm. It is proposed, therefore, that the soils at Swineshaw peatland were only affected by burning up to a depth of 20 cm by the wildfires of June 2018. The maximum burn depth of ~20cm observed in this study is in agreement with the results of experiments performed on organic soils by Benscoter et al. [2011]. Dryer surface soils are more easily combustible and hence the effects of burning were only seen in the surface 20cm in agreement with McMahon et al. [1980]. Fires which only propagate to the top 20cm of a peat soil have previously been defined as ‘surface peat fires’ by Usup et al. [2004]. Low moisture content, high C content and low decomposition level in the surface peats make them more easily combustible than deep soils [Yonebashi et al. 1992]. Wildfires have been found to affect soils up to depths of 100cm in previous studies [e.g., Boemh et al. 2001], hence effects of burning on soil composition should be investigated in locations where the burn depth exceeds 20cm.

The simultaneous increase in Ω in burned soils and decrease in N in topsoils observed in Figure 5.7 may support Parker et al. [2001] which suggested that vegetation fires play a substantial role in the long-term sequestration of C and N in soils. These elements [C and N] which became enriched in post-burn soils have previously been suggested to do so because of their presence in the most-resistant or newly-formed structures [Almendros et al. 2003]. The significantly higher OR observed in burnt cores 1 and 2 relative to the unburnt core combined with the lower C/N of these soils is in agreement with Severinghaus [1995] which postulated that the only way for an ecosystem to have a high OR during net oxidation of biomass would be if a growing pool of NO_3^- existed in the ecosystem or if denitrification was occurring with a growing pool of N_2.

Figure 5.8: Variation in C/N ratio with depth in the burnt and unburnt peat cores of this study plotted with that of the unburnt UK peat cores analysed by Clay and Worrall [2015a].



In this study, samples affected by wildfire have been observed to have a higher Ω and a lower C/N ratio. Burnt peat cores have higher OR than unburnt cores, however char left behind by burning has a lower OR than vegetation samples. It is hence suggested that a combination of C/N and Ω could be used to trace the effects of burning in peat cores as the OR does not appear to show a predictable trend with burning.

Whilst the results of this chapter have contributed to the understanding of the effects of wildfire on the chemical characteristics of peat soil, understanding of post-burn OR is still lacking. A significant limitation of this study was the inclusion of only one char sample which future research should overcome. It would also be beneficial to carry out soil sampling at a range of time intervals both pre- and post-burn to assess how OR and other derived variables vary throughout the recovery process and estimate the duration of the recovery period.

5.6 Conclusions

This study measured the OR, C_{ox}, Ω, and elemental ratios of peat cores sampled at times of burnt and unburnt status of the same bog and returned an OR value below the range used by the IPCC in estimates of the global C sink. OR of char was lower than unburnt vegetation whereas burnt soil had a higher OR than unburnt soils, hence, the effects of burning on the OR of organic matter did not show a predictable trend. The differences in oxidation state between burnt and unburnt soils shows that disturbance to ecosystems as a result of burning affects the state of the organic C sink. Further investigation of how wildfire affects the OR of peatlands may aid in understanding how the increased disturbance predicted to occur with climate change will impact global OR and the terrestrial C sink.

Burning results in a shift to higher values of Ω, which result from condensation and dehydration reactions as well as Maillard reactions which occur during burning. Accumulation of black carbon in burnt soils contributes to the increased Ω. The C/N ratio of a burnt soil is controlled by the soil's original composition, however an increase in this ratio with depth in burnt soils is consistent with a preferential loss of C relative to N from surface soils. The cause of the increase in C/N with depth in the top 20cm of the soil may relate to nitrogen-containing ash fall deposits or build-up of heterocyclic nitrogen. Further research should look in more detail at the cause of the N build-up in post-burn topsoil. Use of thermogravimetric analysis on the samples in this study and other post-burn soils may aid in understanding of the chemical reactions which occur in soils as a result of burning.

6.0 Discussion and Conclusions

6.1 Introduction

The oxidative ratio [OR], defined as the number of moles of O_2 released relative to CO_2 sequestered, is a value used to calculate the amount of C stored in the terrestrial biosphere. C storage plays a crucial role in the control of global atmospheric greenhouse gas concentrations and hence understanding of the OR is necessary for predicting future changes in the global C budget. The OR value relates numerically to the carbon oxidation state [C_{ox}] of material present in an ecosystem. In recent years, the accepted value of the OR [1.1±0.05] has been questioned [Clay et al. 2018]. Several studies have found OR values lower than this [e.g., Worrall et al. 2013]. If the accepted value is in fact higher than the mean OR of the terrestrial biosphere, then the C stored may be being underestimated by use of this value. This thesis aimed to assess whether this accepted OR value is representative of peatlands. Variation in OR and C_{ox} with site location and depth in the peat soil has previously been identified [e.g., Worrall et al. 2016].

Measurement of OR can be achieved by compositional or gaseous flux analysis. Gaseous flux analysis has not previously been widely used in OR measurement because of the high cost and difficult logistics of measurement, however recent advances have made it more feasible. Consequently, a key purpose of this thesis was to investigate whether OR can be measured from direct gaseous flux measurement as an alternative method to elemental analysis. Results of the study showed that for the most efficient measurement of OR by gaseous flux analysis measurements should be made on highly photosynthetic systems over long (greater than 30 minute) time periods. Measurement of peatland OR by the well-established compositional analysis method was adopted across a range of locations to assess whether depth or site is a significant control on oxidation state or composition of a peat soil. Effect of burning on peat soil composition was also investigated.

6.2 Thesis aims and objectives

Several objectives of this thesis were identified, both for the broad scope of the thesis as a whole, and individual chapters. The broad aim of the thesis was to measure the OR of peatland ecosystems and assess whether the accepted value of the OR of the terrestrial biosphere is representative of peatlands. The objectives of the individual chapters were:

- Chapter 2 measured the OR of the Moor House peatland by gaseous flux analysis. Photosynthetic O_2 and CO_2 fluxes were measured by a CPY-5 and EGM-5 gaseous flux system and the OR was calculated from these on 4 occasions over a 12-month period.
- Chapter 3 measured the OR of laboratory grown peat cores by gaseous flux and elemental analysis. The method of OR measurement by gaseous flux analysis was investigated and developed in this chapter. Elemental analysis allowed changes in composition of the peat cores with depth in the soil and between individual cores to be assessed.
- Chapter 4 measured the OR of 10 Austrian peat bogs by elemental analysis. Variation in oxidation state and composition with location of the peat bog and with depth in the peat soil were assessed.
- Chapter 5 assessed the effects of wildfire on the oxidation state and composition of peat soils from the Swineshaw moorland, UK. As a predicted impact of climate change is an increase in wildfire occurrence, understanding the effects of these events on the global terrestrial C balance is needed.

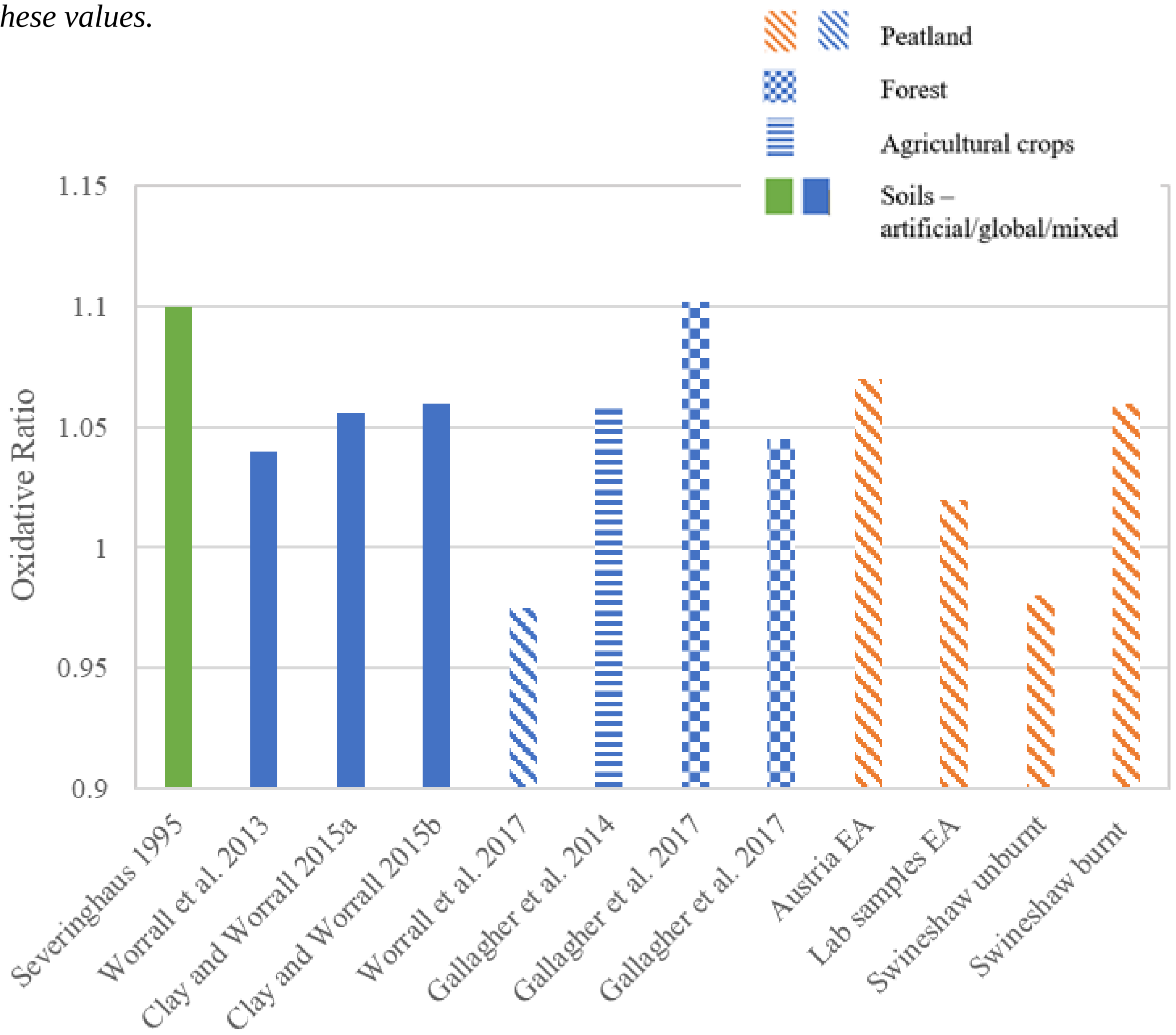
6.3 Principal findings and conclusions

The findings of the research can be summarised as follows:

- Gaseous flux analysis measured OR values of 50.71 and 2.34 in field and artificial laboratory peatland ecosystems respectively. Both values are above the range of accepted OR values as a result of a higher magnitude O_2 flux relative to CO_2 flux measured.
- The method of OR measurement by gaseous flux analysis using this IRGA system has been developed here; when dark conditions preceded light conditions an OR of 0.86±0.70 was measured. Measurement of OR by this method may not be routinely feasible unless for highly active photosynthetic systems over long [> 25 minute] time periods.
- Peatland OR measured by elemental analysis has returned values ranging from 1.10±0.01 in peat cores from Überlingmoos, Austria to 0.98±0.00 in unburnt soils from Swineshaw peatland, UK for whole peatland ecosystems.
- The value used by the IPCC and studies which calculate the global terrestrial C sink is at the maximum extent of those measured in this study and the range measured in this study extends significantly below that allowed by the IPCC's value. This value may not therefore be representative of all terrestrial environments.
- Figure 6.1 shows OR values measured in this study and others in a range of terrestrial environments. If, as suggested by the results of this and previous studies [e.g., Worrall et al. 2013], the OR_{terra} is less than the IPCC's value, then underestimation of the terrestrial carbon sink may be resulting from the use of this value. However, this study is based only on peatland environments, in order to assess global terrestrial OR, measurement of the value in substantially more environments and in more locations is required. The results of this study and others [e.g. Gallagher et al. 2014] suggest that a single value of OR_{terra} may not be globally representative and the value changes temporally and spatially.

- The value of OR varied significantly with the location and depth in the peat soil. OR of vegetation varied with type but not location of growth. However, trends observed in the value of OR are complex and require further study.
- Char samples are more oxidised [i.e. lower OR] than unburnt vegetation and soils which is in agreement with previous studies, however, burnt soils were more reduced than unburnt soils. Hence no consistent effect of burning on organic matter OR was observed.
- Other compositional indicators (e.g., Ω, H/C and C/N) provide more reliable information about peatland ecosystems. These relate to degree of burial and condensation reactions and vegetation types contributing to the peatland.

Figure 6.1: Oxidative ratios measured in other studies mentioned in this thesis (blue) plotted with those measured in this thesis (orange) for comparison. The 1.1 value being assessed in this study is in green. OR measured as described in Chapters 2 and 3 by gaseous flux analysis in a field and laboratory environment is not shown due to the difficulties in measurement of these values.



6.4 Limitations of the dataset

Some key issues affecting data across this thesis are discussed here:

- Measurement of OR by gaseous flux analysis at the Moor House field site could only be performed in 3 months of the 12 month study due to adverse weather and the remote location of the field site. Hence, changes in OR over a 12-month period cannot be assessed as was initially planned.

- Upon introduction of the longer measurement period of gaseous flux in May 2019, fewer complete OR measurements could be made in the field in one day. Hence not all gas collars in the Hard Hill Plots were analysed and any changes related to monitoring site may not have been identified.
- Conclusions drawn in this study are based solely on peatland environments. The OR of one ecosystem cannot be used to estimate a globally-accurate OR_{terra} value [Worrall et al. 2013].
- Peatlands analysed in this study do not extend beyond Europe. Hence comment on global peatland oxidation state and composition cannot be drawn from the results.
- Only one char sample was obtained from Swineshaw peatland. Hence any conclusions drawn about the oxidation state of surficial burn residues must be treated with caution.

6.5 Recommendations for future work

Some suggestions of further work have been made in individual chapters; here these are summarised and developed. The cause of the difference in O_2 and CO_2 fluxes measured by gaseous flux analysis in both Chapters 2 and 3 is unknown. Future research should measure photosynthetic gaseous flux by the methods presented here and by other methods such as the eddy covariance technique [Aurela et al. 2001, Lafleur et al. [2003] and the chamber technique [e.g., Whiting 1994, Bubier et al. 1998] to identify if this pattern is common and establish a cause there of. Measurement of OR by the Field-Portable Gas Analysis [FPGA] technique developed by Brecheisen et al. [2019] should also be investigated as a method of measurement by gaseous flux.

Future research should continue to assess the OR of individual ecosystems to compile a value and range representative of all ecosystems. Other ecosystems previously identified to be underrepresented in the global OR database include tropical rainforests as well as savannas and shrublands [Worrall et al. 2013; Clay et al. 2018]. The OR values measured by this study represent European peatlands, hence to assess global peatland OR it is necessary to increase the sampling extent.

The use of different compositional analysis techniques on the peatland ecosystems considered in this study and others would aid understanding of the humification processes which occur during burial, and perhaps provide insight to changes in the oxidation state and OR observed with depth in the peat profile. Analysis techniques which could be used include Fourier transform infrared spectroscopy [e.g., Artz et al. 2008] and UV/vis spectroscopy [e.g., Blackford and Chambers 1993]. To better understand compositional changes occurring in peat soils in the transition from vegetation to litter and with burial, thermogravimetric analysis [TGA] would be useful as it provides insight into molecular changes [e.g., Worrall et al. 2017]. TGA measures the composition of a whole sample, unlike many compositional analysis techniques, which is useful for the purposes described here as the entire peat soil composition would be investigated as opposed to individual components.

Future research should investigate any trends in OR values following burning and any conclusions that can be drawn about effect of wildfire on soil oxidation state. Long-term effects of burning on soil composition including pre- and post-burn measurements would allow time of recovery of soils to be assessed. Thermogravimetric analysis of the Swineshaw samples used in this study might provide insight to chemical changes which occur with burning [e.g., Worrall et al. 2017]. The OR of emissions products of peat soil fires should also be investigated as the composition of material that is lost may influence the biosphere-atmosphere C balance [McMahon et al. 1980].

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Appendices

The Appendices are provided on a CD. A brief outline of each appendix is provided below:

Chapter 2 Appendix:

- Concentration change and flux calculations from Moor House National Nature Reserve on each field day.

Chapter 3 Appendix:

- Concentration change and flux calculations from laboratory growth tent peat cores.
- Elemental analysis results of growth tent peat cores and derived variable calculations.

Chapter 4 Appendix:

- Elemental analysis results of Austrian peat cores and derived variable calculations.

Chapter 5 Appendix:

- Elemental analysis results of Swineshaw peat cores and surface samples and derived variable calculations.