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A Primer on Gas Phase CO_2 Production and Transport in Peatland Soils

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Abstract

CO_2 sequestered by peatlands is accounted for and offset against national emissions. Observational and modelling studies are used to estimate emission factors that dictate the rate of CO_2 emissions or removals from peatlands accounted for within the Landuse and landuse change including forestry (LULUCF) sector and often use simple Tier 1 emission factors found in the IPCC (1996) guidebook. However, the current estimates are predominately based off peatland surface fluxes measured using either chamber methods or eddy covariance techniques. These methods do not focus on sub-surface conditions while this information may prove useful in understanding efflux rates and conditions that influence them. To help assess the potential significance of subsurface dynamics in overall CO_2 efflux rates from peatlands this study proposes to review the literature dealing with subsurface conditions. The review found that the production of CO_2 in the sub-surface layers was often uncoupled from emissions and that on short time-scales the storage of CO_2 in soil pores and dissolved in soil water may account for this. The rate of production was found to be influenced by decomposition rate, vegetation type, nutrient availability and peat depth. The review also found that the mechanism of transport of CO_2 within the sub-surface was important in accounting for efflux rates. While diffusion is often assumed the most significant form of transport, the quantification and dynamics of other non-diffusive transport methods were found to also be important and further research is required to ascertain the drivers of both diffusive and non-diffusive transport.

Keywords: peatlands, carbon, greenhouse gas emissions, land-use

1. Introduction

Peatlands play an important role in the global carbon cycle – particularly in regulating carbon sequestration (Clymo, 1992; Zoltai and Martikainen, 1996; Clymo et al., 1998; Dean, 1999; Hilbert et al., 2000; MacDonald et al., 2006; Bhatti and Tarnocai, 2009; Beilman et al., 2009; Yu, 2011). However, it is becoming increasing apparent that these systems can be degraded by anthropogenic activities and climate change. As a result, their normal dynamics are being disrupted which in turn diminishes the ecosystem services such as services like climate and water regulation or supporting services like habitat for biodiversity, soil formation, nutrient cycling (Rosenzweig et al.,2007; Kimmel and Mander, 2010). Peatlands ability to sequester carbon mean it is an important instrument in the mitigation of anthropogenic climate change. Additionally, they have up to one third of global soil organic carbon have accumulated in peatlands (Gorham, 1991; Turunen et al., 2002) and they have potential to sequester 20–30g C m^{-2} yr^{-1}. Alternatively, they also represent potentially large flux sources of carbon if disturbed. For instance, Parish et al. (2008) has reported annual emissions from degraded peatlands (including fires) of 2-3 Gigatonnes CO_2 per year.

On an annual basis, peatlands may fluctuate between net sources and net sinks of carbon (Alm et al., 1999; Holden et al., 2006; Roulet et al., 2007; Sottocornola and Kiely, 2005; Laine et al., 2006). Studies have also found that this may be associated with hydro-meteorological variations (e.g. changing in precipitation or water table level (McVeigh et al., 2014) indicating that changing climatic patterns in temperature and precipitation are significant factors controlling the net sequestration / efflux rates of peatlands. Therefore the degradation of peatlands resulting in the reduction of peatland area or its potential to sequester carbon has impacts on the ability of these ecosystems to mitigate climate change and increasing its vulnerability to climate change. Hence, it is important to understand the gaseous dynamics of peatlands and also how they are influenced by climate and environmental parameters.

The purpose therefore of this review is to provide information regarding the system dynamics, methodologies and challenges in successfully monitoring and modelling soil respiration in addition to exploring the wider implications related to climate change. The growing importance of GHG fluxes from terrestrial ecosystems mean that internationally accounting for emission in peatlands and other soils must be accurately constrained. This is driven by legislative changes like the Land use and forestry regulation for 2021-2030 (Regulation (EU) 2018/841) which will require European Member States to account for and offset land use emissions by equivalent removals over the 2021-2030 period (European Commission, 2018).

2. Sub-Surface Overview

Many studies relating to the carbon dioxide fluxes in peatlands focus on the surface fluxes of carbon dioxide (Hommeltenberg et al, 2014; McVeigh et al., 2014, Nilsson et al.2008, Wu et al 2013., Roulet et al. 2007, Olson et al 2013) but fewer studies look at the contribution of sub surface dynamics and the roles played in the production, transport and sub-surface changes in carbon dioxide concentrations. However, we argue that studies including sub surface dynamics may improve our ability to represent carbon dynamics within peatlands via improved knowledge of system functioning and therefore may enhance CO_2 efflux modelling and predictions. For instance, does increased CO_2 gas-phase concentration in the sub-surface affect the rate of emission at the surface? If so, is production of CO_2 the main driver of emissions or do other factors affect emission rates.

To date, studies focusing on the sub surface have recognised what occurs in the sub surface to be an important component in understanding carbon efflux. For instance, Wright et al. (2011) found that the production of CO_2 from sub surface peat was a significant component of the net efflux of CO_2, implying that accounting for changing in the rate of production may improve emission/removal estimates a(Hoyos-Santillan et al., 2016). and investigating how production changes due to anthropogenic influences like climate change and/or draining can provide insights into how peatlands may fluctuate between sources and sinks into the future.

Accounting for sub-surface carbon dynamics is not without its own challenges. For example, sub-surface have been found to display complex and non-linear trends. Dorrepaal et al. (2009) found that warming occurred both as a result of short-term (plant-related) and longer-term (peat soil-related) carbon respiration. Dorrepaal et al. (2009) also found that at least 69% of the increase in respiration rates originated from carbon in peat towards the bottom (25–50 cm) of the active layer above the permafrost. This complexity cannot be represented using methods like open and closed chambers and eddy covariance (EC) methods. Further, observations need to collected at high temporal frequency and a large number of variables have been identified in previous studies like atmospheric pressure and wind(Rey, 2015), soil water balance (Holden, J., 2005) in addition to CO_2 effluxes and sub surface concentrations.

Conceptually, a simplified carbon efflux cycle within the peat sub surface can be visualised according to Figure 1. CO_2 efflux from soil begins with production, defined as the aggregate respiration from roots, microbes, and soil fauna within the soil profile. CO_2 concentrations within the soil profile may increase until transport is instigated via diffusive or non-diffusive mechanisms and results in emission from the soil surface. However, several other pathways may exist. For instance, instead of a gradual accumulation of CO_2 within the sub-surface, CO_2 may be transported near-instantaneously to the surface (Maier et al., 2010). Alternatively, high CO_2 concentrations in soil do not necessarily relate to high effluxes (Maier et al., 2010). For instance, Maier et al. (2012) summarised that rain pulses in summer can stimulate respiration and lead to and increased sub surface concentrations both because of increased respiration and because saturated soil inhibits diffusion. This implies that several pathways exist whereby the residence time of CO_2 in the sub surface varies. Importantly, the process outlined in Figure 1 can be categorised via biotic and abiotic factors. Production is dominated by biotic factors however efflux itself is governed mainly by abiotic factors such as soil moisture, temperature and the CO_2 gradient between soil and atmosphere (Maier et al., 2012).

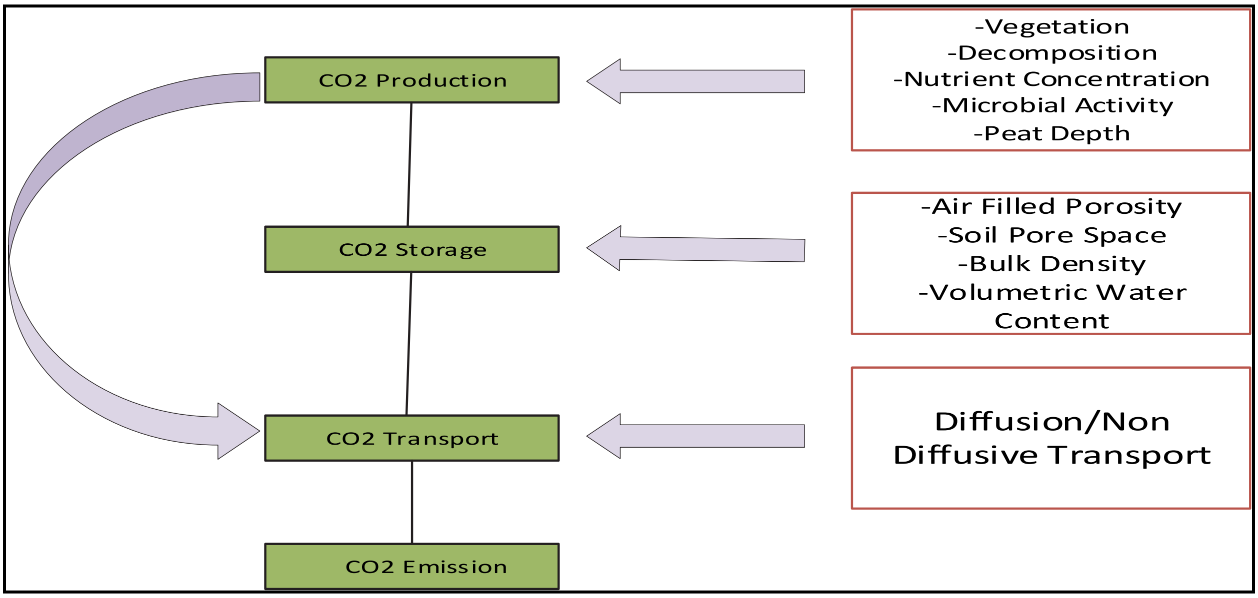

Figure 1. Conceptual emission model of peat CO_2 production and transport

2.1 Production of Carbon Dioxide

Figure 2 shows a simplified illustration of CO_2 production as a result of aerobic and microbial decomposition (Sánchez-Cañete et al.,2018). Intermediate steps in this process such as the steps between decomposition and production of CO_2 are likely driven by multiple parameters such as the Dissolved Organic Carbon (DOC) role in fuelling microbial activity (Tranvik, 1992). However, we do not further discuss DOC as we limit our review to CO_2 gas-phase fluxes. Rates of decomposition are in turn influenced by the population and status of microbiota and the water table level. Factors that affect microbial populations include climatic factors and nutrient availability which in turn is affected by the litter quality and vegetation.

Quantifying CO_2 production is necessary for several reasons. Firstly, on longer time scales, many studies assume that emissions from a peatland are likely to approximately equal what is produced (Maier et al., 2012). However, aqueous phase partitioning, calcite dissolution reactions, gravitational percolation due to a higher density dissolution of CO_2 and CO_2 dissolution in xylem water have been identified as significant CO_2 loss pathways within terrestrial systems (Sánchez-Cañete et al.,2018) meaning that assumption may need further investigation. Secondly, given that temperature and moisture are linked to increased production of CO_2 (Sánchez-Cañete et al.,2018), changing climatic regimes may change the rate of CO_2 production with warmer climates leading to higher emissions. For example, Hoyos-Santillan et al. (2016) found that this lack of understanding was significant enough to limit predictions of how tropical peatlands CO_2 and CH4 emissions will respond to environmental change (such as climate change) and land use change (such as changing peatlands to agricultural lands or forestry)

While Figure 2 shows a linear process, this distinctly non-linear system is further controlled by many known and unknown factors including abiotic factors like soil moisture where even small changes can result in significant changes in concentrations of gas phase CO_2 (Orchard and Cook, 1983). Moreover, Daly et al. (2008) found that near-surface soil CO_2 gas-phase concentrations followed a monotonically decreasing pattern interrupted by large increases induced by rainfall events. However, disaggregating reduced emissions caused by soil moisture and increased production remains a challenge. Additionally, many studies have focussed on decomposition, litter quantity and quality, nutrient profiles and microbial population (Moore and Dalva, 1997; Klotzbücher et al., 2011; Cotrufo et al., 2015; Joabsson & Christensen, 2001; Konnerup et al., 2010; Wright et al., 2011; Couwenberg et al., 2010; Hooijer et al., 2012). However, from a systems perspective these parameters are not independent of each other. As one parameter varies, incremental or abrupt changes can follow in other parameters. However, representing many of these parameters is difficult and building this wholistic representation of the peatland system remains extremely challenging.

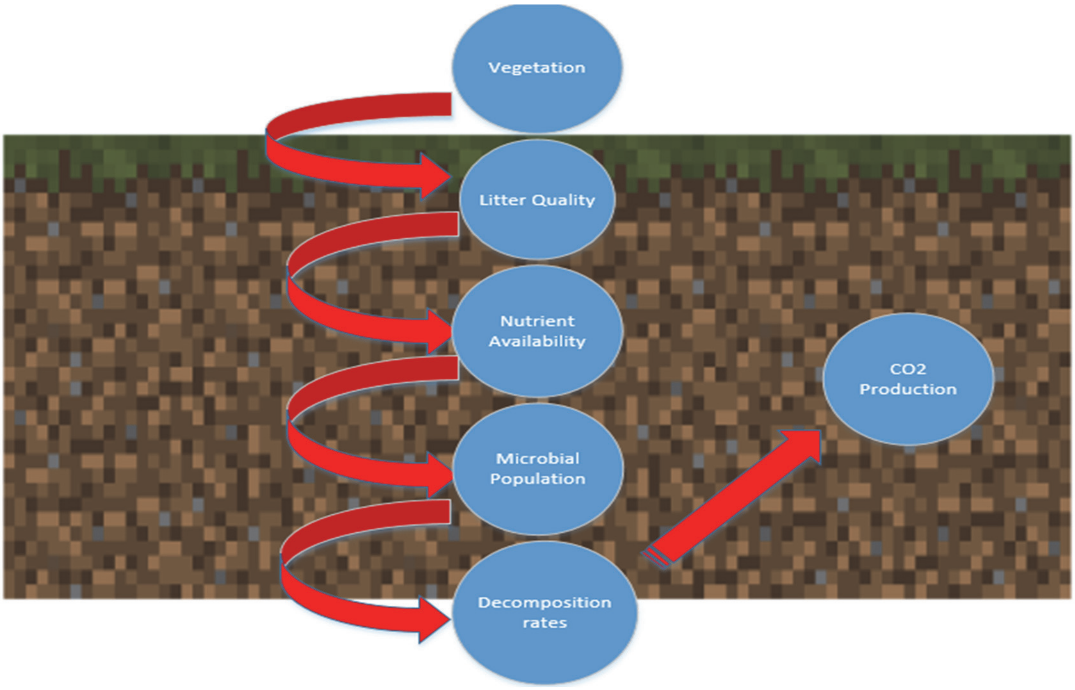

Figure 2. Parameters Influencing Production of CO_2 In Sub-Surface. Decomposition

2.1.1 Decomposition

CO_2 release during aerobic decomposition occurs above the water table and it is likely that it has a seasonal component given the tendency of peatlands to be near saturation during all but the warmer months in boreal and temperate peatlands (Jauhiainen et al., 2005). CO_2 release from anaerobic decomposition occurs via microbial breakdown of methane via methanogenic bacteria (Le Mer & Roger, P., 2001).

Wright et al. (2011) found that substrate temperature, moisture content and nutrient status affected rates of decomposition. Hoyos-Santillan et al. (2016) found that the depth of the peat was the primary driver of decomposition rates with lower peat decomposition rates being observed deeper in the peat profile. Differences between plant substrate materials were found to be likely responsible for this (Hoyos-Santillan et al., 2016; Cotrufo et al., 2015; Hogg et al., 1992). For instance, the progressive decay of carbohydrates relative to lignin with depth were found in multiple climate systems such as sub-tropical (Orem et al., 1986; Krull et al., 2004) and alpine (Grover & Baldock, 2010). The ability of microbes to decompose different plant material is reflected in the production of CH4 and CO_2. For example, in temperate peatlands, surface peat layers produce up to 12 times more CO_2 than deeper peat layers (Hogg et al., 1992). However, no clear consensus has been reached and Zhang et al. (2008) noted that it was likely that a combination of these factors determined the decomposition rates in soil.

2.1.2 Vegetation and Litter Quality

Vegetation was identified as playing a major role in decomposition and therefore CO_2 production (Moore and Dalva, 1997; Nilsson and Bohlin, 1993; Vancampenhout et al., 2008; Graça and Santos, 2007; Hoyos-Santillan et al., 2016; Grover & Baldock, 2010; Cornwell et al. 2008; Zhang et al. 2008). These studies found that the proportion of plant inputs that are incorporated and stabilized into Soil Organic Matter (SOM) versus the amount that is mineralized was more important to the long-term net ecosystem C balance. Other studies have also found that inputs from vegetation were important in driving C fluxes (Sebacher et al., 1985; Joabsson & Christensen, 2001; Konnerup et al., 2010). Several studies also found that vegetation was important because substantial below ground inputs of labile C from vegetation might contribute to the high in situ CO_2 and CH4 fluxes in the sub-surface (Joabsson & Christensen, 2001). For instance, vegetation type may also influence decay rates in sub-surface decomposing matter. Further to this point, Chimner and Ewel (2005) and Yule and Gomez (2009) found that greater lability of the vegetation increased decomposition rates and therefore increased C fluxes. Reasons for the importance of litter quality may be explained by the ratio of lignin to cellulose – in situations where a higher ratio of cellulose is found – decomposition rates are faster than areas where higher rations of lignin exist (DeBusk and Reddy, 2005). The type of vegetation is therefore an important component in understanding differences in CO_2 production within peatland profiles and differences between peatlands with different vegetation types and large scale vegetation surveys may explain variation in CO_2 efflux rates.

In addition to the contribution of microbial respiration and aerobic decomposition, root respiration is also a source that promotes the release of CO_2. However, the importance of root respiration varies from site to site. For instance in boreal, temperate and tropical locations estimates for root respiration suggest it equates to as much a. 50 % of production (Andrews et al.,1999). While Crow and Wieder (2005) found that root respiration accounted for 17 - 24 % of the total peat CO_2 efflux in a boreal peatland in Canada. To further complicate the role of root respiration, variation between ecosystems was found to be 10 to 58% (Larionova et al., 2003). In addition, Vries et al. (2019) found that root exudates collected from plants that had experienced drought respired more than exudates from un-droughted plants indicating that root respiration can vary in importance depending on climatic conditions. Clearly, information regarding vegetation type and status are important in understanding microbial decomposition and root respiration. However, field studies like vegetation surveys are time consuming and can only provide snap shots of vegetation type (geographically) and status (temporal) at very coarse intervals.

2.1.3 Nutrient Availability

In addition to litter quality, vegetation type and status contribute towards nutrient input and therefore its availability. Nutrient Availability in turn plays an important role in CO_2 production (Philips et al.,1997; Sjojgersten et al., 2011; DeBusk and Reddy 2005; Wang et al. 2010). As decomposition has been found to be an important contributor to sub-surface carbon fluxes (Hoyos-Santillan et al., 2016), conditions that alter decomposition in turn; effects carbon fluxes (Tiemann and Billings, 2012.) Studies have found that decomposition rates are influenced by microbial activity in peatlands (Phillips et al., 1997; Sjögersten, et al., 2011) while in turn, microbial activity is influenced by nutrient availability (Borken and Matzner, 2009). For instance, Tiemann and Billings (2012) found that nitrogen availability appeared to be an important component in protecting microorganisms from fluctuating osmotic potentials (Kempf and Bremer, 1998; Schimel et al., 2007). Nutrient concentrations and availability are influenced by depth with deeper soil profiles having lower concentrations.

For instance, Hogg et al. (1992) found that Total phosphorus, potassium and total non-structural carbohydrate (TNC) each showed strong decreases with peat depth. Additionally, the leeching of nutrients was found to be a significant factor in nutrient availability (Qiu et al. 2002; Yule and Gomez 2009; Schreeg et al. 2013; Millard 1988; Berlin et al. 2005) however its unclear if this applies to some or all nutrients. However, understanding how rainfall drives leeching is complicated by the characteristics of the individual nutrients, particularly given future rainfall changes that are projected under various climate change scenarios.

Nutrients like nitrogen and phosphorus have different residence times and are absorbed by plants and microbes at different rates. For instance, nitrogen is more resilient to leeching as it is held in slowly degrading complex organic molecules within litter (Millard 1988; Berlin et al. 2005). In addition, the ratio of C:N was also found to account for 70.2 per cent in the variation in the litter decomposition rates (Zhang et al., 2008). Monitoring nutrient concentrations at high spatial and temporal resolution is limited by the lack of low cost sensors. Currently, analysing many of the variables can only be achieved through laboratory analysis therefore limiting the ability to assess relationships between CO_2 fluctuations, microbial activity and nutrient concentrations. However, mesocosm studies (Laine et al., 2013) may provide insight into the importance of nutrient availability and CO_2 fluxes.

2.1.4 Microbiological Community

Microbial communities contribute to carbon fluxes in a number of ways; ranging from heterotrophic respiration which is likely to be related to soil composition (e.g. substrate quality) and also environmental stresses on the soil. As microbial populations play a role in regulating and controlling methane and carbon dioxide emissions in peatlands, factors which stress populations (such as drought) are significant in influencing carbon production. For instance, drought or lowering of the water table may cause changes in osmotic stress resulting in protective solutes being rapidly released to the environment (Kempf and Bremer, 1998; Halverson et al., 2000; Tiemann and Billings, 2012). Owen et al., (2007) demonstrated that nutrient availability and microbial decomposition have an effect on CO_2 fluxes by reducing the rate that methane released deep in the soil profile by converted it to CO_2 as it passes through methanotrophic (methane consuming) bacterial communities. Microbes can also be a source of CO_2 (Figure 3) and NH4+ emissions as a result of bacterial survival strategies where microorganisms rapidly catabolize C and N containing solutes and then release them in mineral form as CO_2 and NH4+ (Fierer and Schimel, 2003; Williams and Xia, 2009; Tiemann and Billings, 2012). Understanding and parameterising this relationship between microbial activity and pulse like CO_2 emissions resulting from stressful conditions requires long term observations and high temporal resolution measurements of water table level and other parameters.

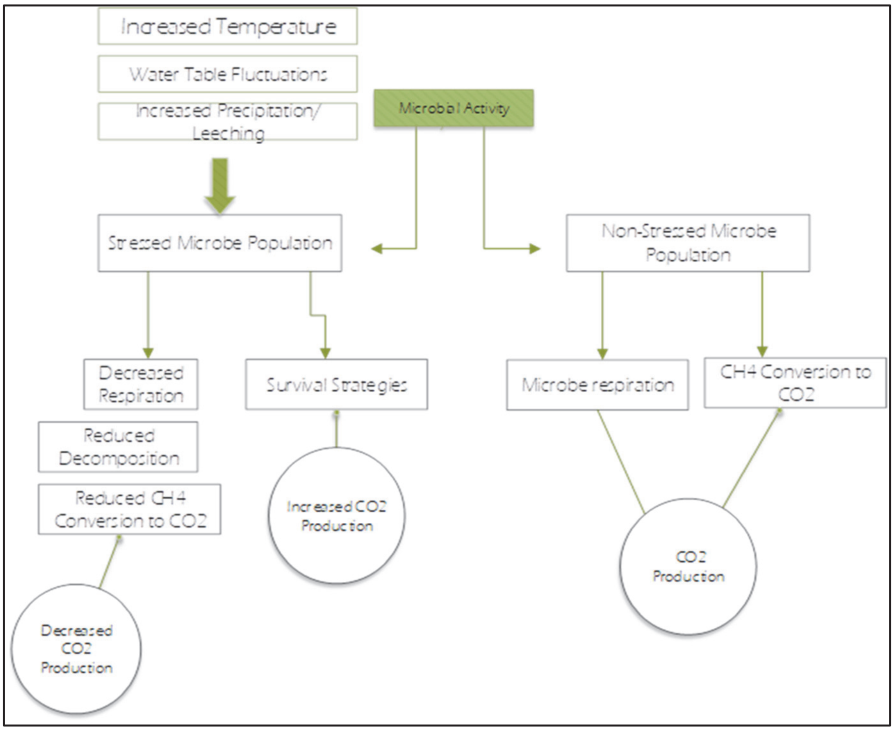

Figure 2. Pathways Influencing CO_2 Production from Microbiological Activity

2.2 Transport of Carbon Dioxides

The transport of CO_2 from the soil sub-surface to the surface in a wide range of soils is influenced by environmental conditions. Heavy rainfall events can result in large volumes of CO_2 (exceeding average daily fluxes) being emitted over the course of several minutes (Daly et al., 2008). Soil Temperature increases can promote production and subsequent emission (Maier et al., 2012). In order to understand how transport mechanisms influence surface carbon fluxes in peatlands, the land factors controlling the type and rate of transport need to be identified and the relationships need to be described (e.g. the relationship between pressure fluctuations and efflux). While several studies have investigated many of the factors governing sub-surface transport, several questions remain. For instance, Hamamoto et al. (2015) found that the controlling processes of CO_2 efflux were diffusion and advection but conditions that initiate either process are not well constrained. Other studies identified possible mechanisms that influence transport to include soil structure (Iiyama & Hasegawa, 2005; Clymo and Bryant, 2008), water table (Boon et al., 2013; Romanowicz et al., 1993) or peat chemistry (Beer and Blodau, 2007). As several competing explanations for the rate and cause of gaseous transport exist, it is currently unclear which are more capable of representing the actual drivers of CO_2 efflux.

However, taking a simplified top down approach to the calculation of transport, it is useful to categorise transport into three main mechanisms. These includes diffusion (Riveros-Iregui et al., 2008; Maier et al., 2011; Vargas et al., 2010), non diffusive transport (Ganot et al., 2014; Takle et al., 2004; Bain, et al., 2005; Rey et al., 2012;Rey et al.,2013; Kuang et al.,2014; Elberling et al., 1998) and storage (Maier et al.,2011). Using this approach, it is possible to conceptualise system dynamics that are governed by multiple pathways which are in turn controlled by both CO_2 production, concentration and temperature gradients, surface energy and water balance constraints.

2.2.1 Diffusion of Carbon Dioxide

Gas-phase diffusion in porous media is an important factor in transport in the soil sub surface (Webb and Pruess, 2003). Diffusion affects the rate of movement of gases in soils (Massman et al., 1997) and a number of factors contribute to the rate of diffusion. The media (in this case peat) through which gas diffuses controls the rate of diffusion. CO_2 diffuses at a slower rate through soil than air due to the tortuosity of the soil and because solid particles in soil occupy a large cross-sectional area (Shackelford and Daniel, 1989). Also, the rate of diffusion is determined by the product of a concentration gradient (a property of an individual species) and a co-efficient of diffusivity (a property of the mixture) (Massman, et al., 1997). Diffusion occurs where the total pressure is uniform as long as there is a spatial difference in the chemical potential, normally represented by differences in concentration gradients (Massman, et al., 1997).

In considering these factors, developing methods capable of representing the process of diffusion, involves understanding soil characteristics like bulk density, pore space and volumetric water content and real time longitudinal observations on CO_2 gradients. In the past, continuous monitoring of the CO_2 gradient was difficult given the remote nature of peatlands, expense of suitable sensors, adequate power supply and communication demands. In the last decade, as new sensors became available, continuous measurements were more frequently used (Vargas et al., 2010). This resulted in an increase in studies looking at gas transport and production in many different land types such as oak-grass savanna's (Tang et al., 2003), peanut fields (Pingintha et al., 2010), pine stands (Sullivan et al., 2010) and agricultural fields (Wolf et al., 2011).

These studies utilised a variety of techniques that facilitated the monitoring of CO_2 fluxes in the sub-surface. These methods all required the establishment of a sampling system, determination of the diffusivity profile and the calculation of CO_2 fluxes. To achieve this, many studies have used the Gradient Method (GM). The GM method was formally described by DeJong and Schappert (1972) and was often combined with Chamber measurements to partition vertically the soil gas flux. The GM is based on the assumption that molecular diffusion dominates gas transport in soils, therefore gas fluxes can be calculated from the gradient of soil gas concentration and the effective gas diffusivity of the porous medium (Maier, M. & Schak-Kirchner, H, 2014). This method has been used to study soil respiration (Davidson et al., 2006; DeJong and Schappert, 1972; Schack-Kirchner et al., 2011), CH4 fluxes (Dörr et al., 1993; Dunfield et al., 1995; Wolf et al., 2011) and N2O fluxes (Burford and Stefanson, 1973; Massman et al., 1997; Pihlatie et al., 2007). The method has been used in other applications like methane emissions from landfills (Bogner et al., 1995) and CO_2 gas transport in the vadose zone to a depth of 36m (Wood et al., 1993; Wood and Petraitis, 1984).

As diffusion is assumed to be the dominating gas transport process in Soil (Maier, M. & Schack-Kirchner, H., 2014), it can be estimated using Ficks law (eqn 9.)

Eqn 9. $F(z)= -D_s\ (dc/dz)$ (Jaynes and Rogowski, 1983)

where F is the gas (µmol m-2 s-1), Ds the effective gas diffusion co-efficient of the gas species (m2 s-1), C the trace gas concentration (µmol m-3) and z (m) the vertical position.

The GM provides an opportunity to monitor CO_2 production and transport within the peat profile (DeJong and Schappert, 1972; Maier, M. & Schack-Kirchner, H, 2014; Risk et al.,2008). Using the GM method, the rate of CO_2 diffusion and production can be estimated for a peatland area. In non-peatland soils, diffusion is considered the primary driver of CO_2 efflux while studies investigating CO_2 efflux in peatlands do not typically include the sub surface, the ratio of diffusive transport compared to non-diffusive transport is currently not well understood. Using the GM method in conjunction with a chamber system, it is possible to identify the rate of diffusion to non-diffusion driven efflux. Additionally, this also enables the calculation of CO_2 storage.

2.2.2 Non-Diffusive Transport of Carbon Dioxide

Non-diffusive transport is classified as transport of CO_2 that is not the result of diffusion. These exchanges of gases within soils are also caused by (1) variations in atmospheric pressure at the soils surface (Buckingham,1904; Massman,2006) (2) water infiltration that induces an air pressure waves ahead of the wetting front (Vachaud et al., 1974) and (3) temperature gradients that result in natural convection (Kamai et al.,2009; Nachshon et al., 2008);. Detecting non-diffusive efflux can be accomplished using a combination of the GM and chamber methods with the chamber accounting for total efflux, the GM method accounting for diffusion only and non-diffusive transport being the difference between the two.

2.2.3 (a) Variations in Atmospheric Pressure at the Soils Surface

Surface pressure variations induce gas movement (known as pressure pumping) between the atmosphere and the subsurface. Where atmospheric pressure decreases, gases are transported upward towards the atmosphere and in situations where atmospheric pressure increases air is compressed into the soil surface (Buckingham, 1904). Several studies have identified and described the relationship between atmospheric pressure and sub surface gas efflux. For example, field studies completed by Hirsch et al. (2004), Flechard et al. (2007) and Maier et al. (2010) showed that high frequency pressure fluctuations on the order of tens of millibars (Massmann and Farrier, 1992) caused by frontal systems moving across the surface can strongly influence soil gas concentrations. For instance, high pressure systems can exert a downward pressure on soil gas thereby reducing non diffusive transport. Alternatively, in low pressure systems the pressure gradient between the soil gas and atmosphere is reversed whereby higher pressure in the sub surface promotes gas exchange within the soil profile and to the atmosphere.

In order to understand how and why atmospheric pressure contributes to non-diffusive gas transport, it is important to understand conditions that enhance or promote pressure pumping. While studies have identified some potential drivers of vertical advective effluxes, uncertainty still exists. For example, competing explanations have been proposed to account for pressure driven advection ranging from gas permeability of soils (Massmaann and Farrier, 1992) soil water content (Rey et al., 2012) and wind (Tackle et al., 2004; Nachshon et al., 2012; Rey et al., 2012). In addition, it is still unknown if the drivers are interrelated. For example, high soil water content reduces the gas permeability of soil by reducing the connectivity of soil pores (Smith et al., 2003).

2.2.4 (b) Water infiltration

Holden, J. (2005) observed in 2005, virtually no research had focused on the effect on CO_2 of water movement through soil. While many studies acknowledge that soil air can be displaced where water infiltrates soil (Hammecker et al., 2003; Ying et al., 2011), the proportion of CO_2 emitted remains poorly constrained. Relationships have been identified between the rate that water infiltrates and air escapes (Hammecker et al., 2003) supporting the hypothesis that water infiltration plays a role in the release of CO_2 emissions. However, hydrological regimes differ to an extent that affects how water infiltrates, this may be an important component of understanding the rate and magnitude of CO_2 efflux. For example, (Holden and Burt,2002) found that pipeflow response was variable in peatlands of different depth.

Peatlands existence depends upon its ability to retain water (Labadz et al., 2010). However how water is transported within the peatland will determine if changing soil water concentrations are associated with changing carbon effluxes. Characteristics like climate, topography, soil type, and vegetation determine how water infiltrates the soil profile. If a peatland is rainfed (ombrotrophic), dominant flow paths are close to or over the surface (Labadz et al., 2010). Transport at the surface may be determined by a number of hydrological resulting from of a range of runoff production (Holden, J.,2005). For example, Holden J. (2005) found that infiltration-excess overland flow was produced where rainfall intensity was greater than the infiltration rate, and the overland flow therefore consists of water that has not been within the soil. However, the existence of pipes and hillslopes (macropores within the soil) mean that water rapidly percolates into the sub-surface. Saturation excess occurs at lower rainfall rates where the water table and surface water both contribute to overland flow (Holden, J., 2005). As water infiltrates the soil profile, air can be displaced and results in its transport to the surface (Vachaud et al., 1974; Wang et al., 1998). This has clear implications for CO_2 efflux particularly for rain fed blanket peatlands where water table levels are high and diffusion may be inhibited.

Air is displaced as a result of a subsurface pressure increase from water infiltration and the resulting compression of soil air. Soil air ahead of the wetting front reaches the surface only when sufficient pressure has built up and results in its eruption (Wang et al., 1998). In order for this to happen air pressure within the soil profile must exceed that of the static pressure created by the infiltrating water (Wang et al., 1998). As soil air is compressed, water infiltration is reduced until the soil air is compressed to a degree that it very rapidly releases CO_2 (Vachaud et al., 1974). Several studies have identified the role of water infiltration in the evasion of soil air (Poulson and Sharma, 2011; Wang et al., 1998; Vachaud et al., 1974; Hammecker et al., 2003; Maier et al.,2011; Holden and Burt, 2003) however to date the magnitude and rate of CO_2 evasion remains poorly understood (Holden, J., 2005). Understanding this transport mechanism is relevant as it may explain abrupt ebullition of CO_2 to the surface and also highlights the importance in understanding how changing precipitation rates and hydrology affects gas transport.

In particular, the ratio of diffusive CO_2 efflux to non-diffusive transport may prove an important distinction in understanding how CO_2 efflux may change under land management or climate change scenarios. For instance, if non-diffusive transport plays a greater role in transport and emission of CO_2, models operating under the assumption that diffusion is the main mechanism of CO_2 efflux may result in the efflux being overestimated or under estimated. Failing to account for parameters like projected changes in wind patterns, precipitation rates and the impact that longer dry seasons may have on infiltration and percolation may limit our ability to project how peatland CO_2 efflux may change. However, the sensitivity of the peatland to these conditions remains poorly understood. In other soil types, pulse-like effluxes were observed (Daly et al., 2008) and the impact this may have on large carbon stores in addition to its global warming potential remain poorly understood. Future studies should aim to investigate the proportions of CO_2 emissions from diffusive and non-diffusive transport.

2.3 Storage of Carbon Dioxide

CO_2 respiration and efflux do not always correspond due to the transient storage of CO_2 in soil pores. Over long periods, this assumption may be valid but in the short term CO_2 soil concentrations has been found to deviate from soil respiration (Maier et al. 2011). Pore space was found to act as buffer for CO_2 where changes in the concentration of CO_2 in pore space (storage) changes the actual CO_2 efflux (Flechard et al., 2007; Maier et al., 2010; Hirsch et al.,2004). Soil water content was found to be important in controlling soil storage capacity. Soil water content also decreases the soil bulk transport/diffusion coefficient (Schullssler, 1996). In addition, CO_2 tends to accumulate in a wet soil, until ultimately respiration is inhibited where $_2$ supply is reduced by waterlogging (Blagodatsky and Smith,2011). Maier et al. (2010) found that the storage flux can reach a significant proportion of the soil respiration, e.g. up to 20% after an intense rainfall (Maier et al., 2010). In a subsequent study, Maier et al. (2011) found after a rainfall in July, CO_2 efflux reached 60% of soil respiration; 40% of CO_2 was temporarily stored in the soil pore space. Studies focusing on the storage of CO_2 in the soil range from 20 to 40% of soil respiration with up to 60% of respired soil resulting in an emission. The implications of this remain unclear especially as in the longer term, CO_2 respiration and efflux are likely to correspond. However, given the aforementioned uncertainties with regards to transport mechanisms and factors influencing production, the ramifications are difficult to predict. Even small inaccuracies may accumulate especially where common methods are applied such as the IPCC greenhouse gas emission inventories guidebook (1997).

3. Conclusion

Sub-surface CO_2 dynamics is often not estimated when studying CO_2 effluxes from peatlands. Traditional methods use either chamber studies or eddy covariance methods. While these methods are useful and necessary, our understanding of peatland carbon dynamics could be enhanced if a greater number observational and modelling studies accounted for sub-surface CO_2 dynamics. However, considerable equipment and expertise is required to set up systems capable of working over long periods. For instance, the system must be automated, independently powered with low power consumption and it is optimal if this system is capable of sending and receiving information over the internet reducing both the risk of losing data in extreme weather events.

The review provided an overview of the types of parameters that have been identified as important in the production and transport of CO_2. Parameters influencing CO_2 production ranged from vegetation type and status, nutrient availability, microbiological community and peatland depth. Production is an important parameter and it has been demonstrated that the CO_2 produced in the sub-surface is not always released to the atmosphere. Future studies should seek to ascertain which of these parameters has the greatest impacts on CO_2 production, delineate the pathways and identify relationships and synergies that most accurately describe CO_2 production in the sub surface peatland ecosystem. In addition, more exact quantification of the response of peatlands to changes in production rates would enable both more accurate predictions under climate change scenario's and provide more information regarding the best way to restore peatlands.

Factors governing the transport of CO_2 in the sub surface also need to be more fully constrained. Emphasis should be placed on not only calculating CO_2 efflux as a result of diffusion but also non-diffusive mechanisms. In addition, the meteorological, physical and chemical parameters relationship with transport rates should be investigated with particular attention to the non-linear events (such as pulse events). Partitioning diffusive and non-diffusive transport of CO_2 with the aim of quantifying the overall contribution of each transport process would reduce uncertainty in soil respiration estimates.

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