Peat Biogeochemistry and Greenhouse Gas Emissions during Peat Use in Horticulture

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Abstract

Peatlands cover only 3% of the world's land cover, but in the northern hemisphere they store up to a third of organic carbon (C). The organic matter stored in peat bogs, known as peat, is highly sought-after as a growing medium for horticulture and agriculture in controlled environments. Peat extraction involves draining the natural peat bog and extracting the peat over several decades. The peat extracted is generally acidic and low in nutrients, so nutrients, limestone to raise the pH and other horticultural additives are added to enhance plant growth. Peat to which horticultural additives are added is called growing medium. Peat decomposition rates are relatively well known. However, data on the biogeochemical properties and decomposition rates of peat-based growing substrates are scarce but necessary to facilitate ongoing debates on the carbon footprint of peat use in horticulture. The aims of this thesis are i) to characterize growing substrates and compare how they differ from raw peat ii) to measure the decomposition rate of growing substrates iii) to explore the role of horticultural additives in increasing the decomposition rate of growing iv) analyze the decomposition rate of growing substrates on a Canadian scale and report the emission factor (EF) of peat use in horticulture and v) quantify the role of horticultural plants in increasing the decomposition rate of growing substrates. My work combines a variety of measurements ranging from Greenhouse Gas (GHG) flux measurements, $\delta^{13}C$, radiocarbon measurements, microbial analysis, soil biogeochemistry and modeling to arrive at the set objectives. I measured that the biogeochemistry and decomposition rates of growing substrates vary considerably from those of peat. To understand the causes of this increased decomposition rate in growing substrates, I show, using factorial experiments, that limestone added to increase pH increases the decomposition rate of growing substrates. Extrapolation of the values to a national scale shows that current IPCC Tier 1 emissions overestimate emissions from peat used in horticulture, and I suggest a revision to Intergovernmental Panel on Climate Change (IPCC) Tier 2 values. Growing lettuces and petunias in peat-based growing substrates in a controlled environment, I report on the different components of plant and soil respiration. Using radiocarbon measurements, I show that plant roots increase peat decomposition, but this could be species dependent. The results of this thesis help to revise the EFs related to the use of peat in horticulture in Canada and to improve the understanding of horticultural peat.

Résumé

Les tourbières ne couvrent que 3 % de la couverture terrestre mondiale mais, dans l'hémisphère nord, elles stockent jusqu'à un tiers du carbone (C)organique. La matière organique stockée dans les tourbières, appelée tourbe, est très recherché pour être utilisée comme substrat de culture pour l'horticulture et pour l'agriculture en environment contrôlé. L'extraction de la tourbe implique l'assèchement de la tourbière naturelle et l'extraction de la tourbe pendant plusieurs décennies. La tourbe extraite est généralement acide et pauvre en nutriments.Des nutriments, du calcaire pour augmenter le pH et d'autres additifs horticoles sont donc ajoutés pour éclairer la croissance des plantes. La tourbe à laquelle on ajoute des additifs horticoles est appelée substrat de culture. Les taux de décomposition de la tourbe sont relativement bien connus. Cependant, les données sur les propriétés biogéochimiques et les taux de décomposition des substrats de culture à base de tourbe sont rares mais nécessaires pour faciliter les débats en cours sur l'empreinte carbone de l'utilisation de la tourbe dans l'horticulture. Les objectifs de cette thèse sont i) de caractériser les substrat de culture et de comparer en quoi ils diffèrent de la tourbe brute ii) de mesurer le taux de décomposition des substrats de culture iii) d'explorer le rôle des additifs horticoles dans l'augmentation du taux de décomposition des substrats de culture iv) d'analyser le taux de décomposition des substrats de culture à l'échelle canadienne et de rapporter le facteur d'émission (FE) de l'utilisation de la tourbe en horticulture et v) de quantifier le rôle des plantes horticoles dans l'augmentation du taux de décomposition des substrats de culture. Mon travail combine une variété de mesures allant des mesures de flux de gaz à effet de serre (GES), du $\delta^{13}C$, des mesures de radiocarbone,

de l'analyse microbienne, de la biogéochimie du sol et de la modélisation afin d'atteindre les objectifs fixés. J'ai mesuré que la biogéochimie et les taux de décomposition des substrats de culture varient considérablement de ceux la tourbe. Pour comprendre les causes de cette augmentation du taux de décomposition dans les substrats de culture, je montre, à l'aide d'expériences factorielles, que le calcaire ajouté pour augmenter le pH accroît le taux de décomposition des substrats de culture. L'extrapolation des valeurs à l'échelle nationale montre que les émissions actuelles de niveau 1 du GIEC surestiment les émissions provenant de la tourbe utilisée dans l'horticulture et je suggère une révision vers les valeurs de niveau 2 du Groupe d'experts intergouvernemental sur l'évolution du climat (GIEC). En cultivant des laitues et des pétunias dans des substrats de culture à base de tourbe dans un environnement contrôlé, je fais état des différentes composantes de la respiration des plantes et du sol. En utilisant des mesures de radiocarbone, je montre que les racines des plantes augmentent la décomposition de la tourbe, mais cela pourrait dépendre de l'espèce. Les résultats de cette thèse permettent de réviser les FE liés à l'utilisation de la tourbe en horticulture au Canada et d'améliorer la compréhension de la tourbe horticole.

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AR – Autotrophic Respiration

BG- β-D-glucosidase

BX- β-D-xylosidase

C – Carbon

CH_4 - Methane

CO_2 - Carbon Dioxide

DOC- Dissolved Organic Carbon

ER – Ecosystem Respiration

FT-MIR- Fourier transform-mid infrared

GPP – Gross Primary Production

HI- Humification index

HR – Heterotrophic Respiration

IPCC- Intergovernmental Panel on Climate Change

LOI- Loss on Ignition

MBC- Microbial Biomass Carbon

MBN- Microbial Nitrogen

N- Nitrogen

N_2O- Nitrous oxide

NAG- N-acetyl-β-D-glucosaminidase

NEE – Net Ecosystem Exchange

PHOS- Acid Phosphatase

SOC- Soil Organic Carbon

SOM – Soil Organic Matter

TDN- Total Dissolved Nitrogen

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Contribution to original knowledge

This thesis contributes to our understanding of horticultural peat by exploring the biogeochemistry of the peat and respiration dynamics. By combining experimental data and extrapolating them at a Canadian scale, this thesis provides a firsthand report of greenhouse gas emissions, and particularly CO_2 emissions when peat is used in horticulture. This thesis contributes to the fundamental knowledge of peat decomposition and is relevant to the current global dialogue on peat harvesting and sustainability of peat use. It provides important experimental evidence for assessing C footprint of peat use. Specifically:

In Chapter 3, I present the biogeochemical properties and decomposition rate of growing media. I compare them with peat biogeochemistry and conclude that growing media exhibit significant differences compared to peat due to horticultural additives that are added in preparation of growing media. Using $\delta^{13}C$ measurements, I show the indirect and indirect influence liming has on increasing CO_2 emissions in growing media. This finding will be useful in guiding future research in limed agricultural soils.

In Chapter 4, using a controlled experiment I demonstrate that the biogeochemical and decomposition rate changes that are caused by horticultural additives. Among four different additives (lime, NPK, perlite and surfactants)- I report that the lime causes the most significant impact in terms of biogeochemical properties as well as decomposition rates of peat. Using microbial analysis, biogeochemical properties and $\delta^{13}C$ measurements, I explore the question of C cycling through multiple lenses.

In Chapter 5, I extrapolate the findings from Chapter 3 and show the implication of the measured decomposition rate for growing media at Canadian scale and quantify the contribution of CO_2 emissions from peat use. I propose that the current use of Tier 1 emissions factors for horticultural peat use needs to be updated to Tier 2 values that accurately captures the nature of horticultural peat decomposition. In addition, using different future peat extraction scenarios, I present what the future emissions from peat use might look like until 2050.

In Chapter 6, I introduce two horticultural plants to the growing media and report GHG emissions and biomass measurements over four months. Using radiocarbon measurements that I partition out ecosystem respiration into autotrophic and heterotrophic components and investigate the influence of roots in increasing C losses from used peat.

Contribution of authors

This thesis is presented in manuscript-based thesis format. This thesis is arranged around four main results Chapters (3-6), which has been written as manuscripts to be submitted for publication in journals. The thesis also contains an introduction (Chapter 1) and literature review (Chapter 2) at the beginning and the concluding chapter (Chapter 7) at the end. It is an original work of Bidhya Sharma with a few exceptions. I have developed scientific questions, carried out the experiment, analyzed the results and wrote the manuscripts as a lead author. Co-supervisors Dr. Nigel Roulet and Dr. Tim Moore provided expert advice on development of research questions, formulating the project as well as editing all the manuscripts and the thesis. Measurements and analysis on FTMIR result on chapter 3,4 were provided by Henning Teickner and Dr. Klaus- Holger Knorr. Dr. Peter Douglas assisted in use of isotopes and analysis of results in Chapters 3, 4 and 6. I worked with Dr. Hongxing He in chapter 5 and benefitted greatly from his insight in writing the manuscript.

Chapter 1: Introduction

1.1 Research background

In less than 3% of the global land cover, peatlands in the northern hemisphere store up to one-third of organic carbon (Hugelius et al., 2020). It occurs as the result of plant productivity being greater than decomposition, which is inhibited by a combination of anoxic conditions, cold temperature, vegetation composition and low pH (Laiho, 2006; Limpens et al., 2008). This has resulted in accumulation of significant amount of organic matter since the last ice age and, hence peatlands are a long term net sink of carbon (C) (Frolking & Roulet, 2007; Gorham, 1995). This organic matter in peatlands is known as peat. Peat is rich in organic carbon and has high calorific value. It has been used since pre-industrial times for agriculture, after drainage, (Qiu et al., 2021; Wüst-Galley et al., 2019) and starting in early 20th century peat is extracted for fuel (Schilstra, 2001; Tcvetkov, 2017; Warner & Buteau, 2000). More recently peat has been extracted for horticulture purposes (Waddington & Price, 2000; Warner & Buteau, 2000). Use of peatland and peat, combined with other anthropogenic disturbance in peatlands (Harris et al., 2021) has resulted in loss of extensive peatlands areas in northern European peatlands and, to a lesser extent, in North America (Fluet-Chouinard et al., 2023).

In over the past 50 years of peat use in horticulture, its properties in terms of efficiency for plant growth, e.g. cation exchange capacity, water holding capacity and so on have become well known (Leiber-Sauheitl et al., 2021; Schmilewski, 2008; Vandecasteele et al., 2020). In Europe and North America peatlands are easily accessible; therefore making peat an economical growing media with excellent productivity yields (Barrett et al., 2016). In Europe and Russia, on average, a combined amount of 21 Million tons (Mt) of non-energy peat is extracted every year (Hirschler & Osterburg, 2022). In Canada, extraction average is around 1.5 Mt yearly (Natural Resource Canada, 2022). Less than ~0.03% of the Canadian peatland coverage is affected by extraction (CSPMA, 2017). Globally horticultural peat use in controlled environment agriculture (CEA) is projected to increase four-fold between 2017 and 2050 (Blok et al., 2021).

The search for an alternate growing media is increasing. Compost, biochar, rockwool, coconut coir or wood fiber having the potential to replace peat completely or partially in volume (Chrysargyris et al., 2019; Leiber-Sauheitl et al., 2021; Montagne et al., 2015; Steiner & Harttung, 2014; Zanin et al., 2011). Alternative growing medias that could replace peat need to have similar attributes of accessibility and cost, and ensure equal plant productivity (Barrett et al., 2016; Leiber-Sauheitl et al., 2021; Miserez et al., 2019). While the search for an alternate media goes on, professional horticulture is still dominated by use of peat. It is estimated that up to ~80% of the growing media is peat in the EU (Altmann, 2008) its complete phase-out seems implausible.

Peatlands provide intangible ecological and economic values, store C that goes back to millennia and are potentially a nature-based solution for climate change (Drever et al., 2021). On the other hand, a large portion of peatlands are facing numerous anthropogenic threats around the world (Fluet-Chouinard et al., 2023; Harris et al., 2021). Furthermore, peat use in horticulture and its decomposition is a significant direct contributor to GHG emissions (Cleary et al., 2005). Currently, GHG emissions from peat, continued use of peat extraction for horticulture use now faces national and international scrutiny (Alexander & Bragg, 2014; Barrett et al., 2016). Peat extraction contributes to wetland degradation, reduction in C storage function of peatlands

(Harris et al., 2021; Waddington & Price, 2000) and as contributor to GHG emissions during extraction (Clark et al., 2023; He et al., 2023; He & Roulet, 2023) and post extraction during the use phase (Cleary et al., 2005; Vandecasteele et al., 2023).

As a party to the Convention on Climate Change (UNFCCC) and the Kyoto Protocol, Canada is required to report greenhouse gas emissions (GHG) to the International Panel on Climate Change (IPCC). Currently emissions related to the peat use in horticulture are reported under Tier 1 calculations, which first developed for fuel use of peat, that do not accurately represent the nature of peat use in horticulture and largely overestimate the related emissions. Therefore, development of Tier 2 or Tier 3 emission factors is urgent. Therefore, quantifying the C footprint for horticulture is imperative for several reasons. i) To report emission factors (EF) stemming from horticultural peat use for Canada (Environment & Climate Change Canada, 2023). ii) For peat extraction companies and horticultural producers to assess and potentially mitigate the industry footprint as Canada moves to net-zero emissions target by 2050; iii) to compare alternative growing media with or without peat; and iv), to use the numbers generated by EFs from peat use in horticulture to assess the timeframe required for extracted peatlands to reach C-neutral conditions (Nugent et al., 2019).

To address this, I quantified CO_2 emissions from peat that is used in horticulture by incubating peat based growing media. Later, to have a larger experimental control, I conducted a factorial experiment in laboratory conditions and measured soil biogeochemical properties and decomposition rates over time. In the final experiment, to mimic horticultural system better, I introduced horticultural plants to the system and measured the peat respiration rates as well as explored the role of introduced plants in increasing peat decomposition. In addition, I extrapolated the experimental findings to Canadian scale to construct EF from peat use in horticulture.

1.2 Research objectives

Our understanding of peat in its natural environment, biogeochemical properties and decomposition processes are partially well-known. As peatlands receive wide recognition for their climate benefits, research on the climate impacts of degraded peatlands and their restoration is increasingly receiving scientific and policy attention (Drever et al., 2021). Even though peat use in horticulture is widespread and is at the forefront of policy debates in many countries, especially in Europe (Alexander & Bragg, 2014; Hirschler & Thrän, 2023), our understanding of horticultural peat and its EF's are limited. Therefore, the goal of the thesis is to understand the biogeochemical properties and CO_2 emissions from peat-based growing media. In addition, I aim to understand how growing media differs from the raw peat from peatlands and what does this difference mean in terms of C cycling. Following these measurements, I upscaled the findings to a Canadian scale to quantify the historical, present, and future emissions from peat use in horticulture. In addition, I look at the CO_2 emissions dynamics from peat-based growing medias with growing plants. The contributions of my individual thesis chapters are as follows.

Chapter 3:

Using incubations of peat and growing medias, I measured differences in short-term emissions and showed that when used in horticulture, because of horticultural additives, horticultural peat (growing media) behaves a different system. This difference can be observed in increased decomposition rate as well as in differences in biogeochemical properties.

Chapter 4:

Chapter 3 showed the differences between peat and growing media. To have a mechanistic understanding of the biogeochemistry of growing medias, I ran a controlled experiment. I did this by creating various types of growing medias with differing additives and quantified decomposition and biogeochemical properties from the mixtures. I hypothesized that the growing media mixtures would show higher microbial biomass, higher microbial activity, and more significant C loss over the incubation period than the control. I show that the lime, because it increases pH, causes the largest effect in C loss over the incubation period.

Chapter 5:

Using findings from chapter 3 and 4, I upscaled the emissions measured from growing media to the peat extracted in Canada at present and in the past since the initiation of peat extraction for horticulture in Canada. Based on various peat extraction and decomposition scenarios, I projected the emission scenarios until 2050 and estimated what the emissions would mean for future circumstances.

Chapter 6:

While previous attempts for quantification only noted soil heterotrophic respiration, horticultural peat is ultimately used for plant growth. Using lettuce and petunia, which represent food production and ornamental horticulture sector respectively, I quantified the CO_2 emission components once plants are introduced to the system. Using radiocarbon signature as a tracer, I quantified the role of plant roots in increasing soil decomposition. Furthermore, I calculated the biomass accumulated in plants over the experiment period and compared it to the heterotrophic loss in the same period.

1.3 Thesis structure

This thesis comprises seven chapters including this introduction. In chapter 2, I present a literature review on the current state of knowledge on natural peatlands and their role in regulating global climate. Next, I discuss ongoing threats to peatlands globally and in Canada, with a focus in horticultural peat extraction. I further add on our current knowledge of controlled environment agriculture and their dependence on peat as a growing media, alternatives that are currently available and what the future scenario for peat use looks like. Encompassing peat use in horticulture from both ends of peatland's degradation and horticultural dependence on peat, I shed light on why the topic is receiving importance in legislative, public, and environmental debates. The main body of the thesis is structured into four research chapters, which are under review or are being prepared for submissions to peer-reviewed journals. Chapter 7 summarizes the main conclusions of this thesis and proposes future research directions.

Chapter 2: Literature Review

2.1 Peatlands

Most peatlands are low-lying areas in waterlogged conditions that have built up the organic matter of more than 30 – 40 cm thickness or as defined by a country (Rydin & Jeglum, 2005). Depending upon the source of water and nutrients, they are classified into nutrient poor, precipitation-derived bogs, or fens that also receive water and nutrients from the adjacent landscape. Fens can exhibit both nutrient poor and rich conditions depending upon where the inflow of water comes from (Clymo, 1984; Rydin & Jeglum, 2005). Globally, peatlands extend over approximately 4 million km^2 areas with the major proportion (~80%) in boreal and sub-arctic areas of the northern hemisphere (Xu et al., 2018).

Northern peatlands occupy 3% of the global area and store up to 500 to 1055 Gt of carbon (C) (Nichols & Peteet, 2019; Yu et al., 2010) amounting to more than 30% of the C stores in the global soil pool (Yu et al., 2010). The high amount of accumulation of organic C results from the small difference between the productivity and the decomposition rate in peatlands. The slow decomposition rate is mostly attributed to a combination of anoxic conditions, cold temperature, vegetation composition and low pH conditions in the region (Laiho, 2006). The slight difference of productivity over decomposition (Limpens et al., 2008) has resulted in the accumulation of several meters deep of organic matter since the last ice age and, hence peatlands are a net sink of carbon in the long-term (Frolking & Roulet, 2007).

The accumulation of C in peatlands started after deglaciation of the northern hemisphere and the maximum amount of C accumulation as observed from vertical peat profiles occurred

8,000- 10,000 yrs ago. It could have occurred because of high summer insolation and pronounced seasonality that facilitated higher productivity in summer but reduced decomposition in the winter (Yu et al., 2010). Even though the rate of C accumulation in peatlands changed with warming and cooling of the earth's surface and to some extent with the atmospheric CO_2 concentration, on average more than 5 Gt C per century entered the long term C sink in peatlands (Yu et al., 2010) impacting global C cycle since millennia (Frolking & Roulet, 2007). The development of peatlands has resulted in a significant lowering of atmospheric CO_2 and the water-logged conditions imply an increase in of CH_4 emissions (Frolking & Roulet, 2007). CH_4 losses from peatlands of 3.7 ± 0.5 g C m^{-2} yr^{-1} (Roulet et al., 2006) are small but a considerable source as compared to the long-term C accumulation rate of 20-30 g C m^{-2} yr^{-1}. Similarly, export of dissolved organic C from peatlands remains an important pathway of C loss from the system (Koehler et al., 2011).

2.2 Decomposition of peat

The value of average aboveground net primary productivity (NPP) for *Sphagnum* peatlands between 30 to 1,660 g C m^{-2} yr^{-1} is lower than most of the other ecosystems for example, Mangroves have an aboveground NPP of 1000 to 4,599 g C m^{-2} yr^{-1} (Reddy et al., 2022). Since the C mineralization rate in peatlands is slow, a higher fraction of NPP enters the long-term soil C accumulation pool. The mass loss or mineralization per year of *Sphagnum* peat is higher in fresh plant tissues from mosses and nutrient-rich leaves. It ranges from 3 to 30% (Moore & Basiliko, 2006) in the top layer of peatlands, acrotelm, where a high amount of easily degradable media is available. Once the slightly decomposed plant materials reach to lower cateotelmic layer, the decay rates are much lower than i.e. < 0.01 per year (Clymo, 1984).

Climatic conditions, litter chemistry and biogeochemical controls dictate the decompositions of organic matter in peatlands (Davidson & Janssens, 2006; Freeman et al., 2004; Laiho, 2006; Moore & Basiliko, 2006). When decomposition is reduced to below the net primary productivity a vertical build up and intact storage of peat over millennia could be insured. The inhibiting conditions of water-saturation, refractory plant materials made of predominantly *Sphagnum* moss, higher phenolic built up, lower pH, nutrient scarcity and low temperature conditions supress the microbial activity (Freeman et al., 2004; Pinsonneault et al., 2016a). In addition, water logged conditions in peatlands, especially in lower permanently saturated catotelm, favour methanogenesis as the anaerobic C degradation that is less efficient process and results in formation of CH_4, in addition to smaller amount of CO_2 (Schlesinger & Bernhardt, 2013). Therefore, a large amount of world's C is tightly held by different sets of environmental variables interacting with each other which are vulnerable to environmental changes that could cause cascading effects on the peat C stored and the net C sink function of peatlands (Davidson & Janssens, 2006; Limpens et al., 2008). For instance, around the world peatlands have been heavily drained (Fluet-Chouinard et al., 2023), used for agriculture (Qiu et al., 2021) and could face disproportional risk from an increase in global temperatures with climate change (Olefeldt et al., 2021).

Once the environmental controls of decomposition are reduced in peatlands and in peat, i.e. drainage (Freeman et al., 1992; Moore & Dalva, 1997) and increased temperature (AminiTabrizi et al., 2022; Pinsonneault et al., 2016b); enhanced mineralization and release of C is observed. Long-term nutrient addition, following increased deposition affects the vegetation structure in peatlands to increase vascular plants and decrease moss growth (Bubier et al., 2007). This changed litter chemistry, with less *Sphagnum* moss might in turn enhance peat decomposition (Moore et al., 2019). A similar impact on peat decomposition following nutrient or limestone addition in agricultural peatlands could be expected (Andersson & Nilsson, 2001; Andersson et al., 2000; Li et al., 2022).

The litter chemistry and the environmental conditions together determine the decomposability of peat. Several parameters and proxies are used to measure the degree of decomposition, which is a function, as well as a controller, of the inherent decomposability of the peat. The state of peat, degree of decomposition (or decomposability), and the environmental conditions interactively govern the rate of decomposition. Quantifying the rate of decomposition can be obtained using different methods ranging from litter bags to incubation of peat, but measurement of the effect of environment from that of the composition of peat requires the measurement of degree of decomposition of peat. In peat and peatland studies, quantification of the degree of decomposition is important for both mechanistic understanding of rate of decomposition observed as well as to predict the fate of different degree of decomposed peat towards future anthropogenic changes (Craine et al., 2010; Fissore et al., 2009; Hodgkins et al., 2018; Plante et al., 2011). Measures of degree of decomposition ranges from simple qualitative von Post scale (Rydin & Jeglum, 2005) to more analytical measurements that elucidate the chemical composition of different organic factors (Wilson & Tfaily, 2018). The use of analytical measurements using Fourier-transform ion cyclotron resonance and carbon 13- nuclear magnetic resonance are invaluable but are limited in use because of their cost and availability of the instruments. Other simpler measurements like Fourier transform mid- infrared spectroscopy (FT-MIR), carbon to nitrogen ratio(C:N), bulk density and stable isotope signatures have been shown to be good proxies of decomposition (Biester et al., 2014; Broder et al., 2012; Drollinger et al., 2020), although they have limitations and care must be taken in their interpretation. Decomposition indices calculated using FT-MIR have been shown to elucidate smaller differences in degree of decomposition in peat by using humification indices of FT-MIR provides on detailed chemical compounds pertaining to each of acrotelm, mesotelm and catotelm layer. Interestingly, FT-MIR could precisely detect changes in humification indices before and after a short-term incubation of 75 days (Tfaily et al., 2014).

2.3 Peatland degradation and peat use

Land use change in peatlands for agriculture and forestry practices, drainage for peat extraction, and use in horticulture and fuel are the major alterations to natural peatlands. It is estimated that around 14-20% of global peatlands are threatened through direct anthropogenic activities of agricultural practices, mining, forestry and infrastructure development (Leifeld & Menichetti, 2018; Rowland et al., 2021; Urák et al., 2017). In addition, climate change induced increased temperature, fluctuating weather patterns and increased peatland fire threatens the peatlands in the northern hemisphere (Coogan et al., 2019; Gibson et al., 2018; Helbig et al., 2022). Peatland degradation means that the biodiversity and the C sink of peatlands are lost and that the ecosystems turn into hotspots of CO_2 and N_2O emissions, contributing to positive climate feedback (Tiemeyer et al., 2016).

Canada contains one-fourth of the world's northern peatlands, storing ~150 Gt of C stock (Xu et al., 2018). Estimates of threats to peatlands in Canada are limited and significantly underestimated where 12,200 km^2 of 1.1 million km^2 is currently disturbed (Harris et al., 2021). Of the disturbances, agricultural land, mining, and forestry on drained peatlands are the largest disturbances for Canadian peatlands (Harris et al., 2021). Peat extraction in Canada covers 350 km^2 of peatlands and is one of the smaller human disturbances, affecting only 0.03% of the total peatland area in Canada (CSPMA, 2017; Environment & Climate Change Canada, 2023). Historically, extracted peat in Europe and Canada was primarily used for energy (Tcvetkov, 2017; Warner & Buteau, 2000). While the energy use of peat still continues in some parts of Europe, in Canada extracted peat is almost exclusively used for horticulture (Environment & Climate Change Canada, 2023; Warner & Buteau, 2000).

Horticultural peat extraction involves draining and removal of vegetation from a natural peatland (Waddington & Price, 2000). Water is drained through drainage ditches placed throughout the extraction site and once a peatland is opened, the process of removal of peat happens at a decadal timescale (Clark et al., 2023). During the process, extraction fields are net source of CO_2 (Clark et al., 2023; He et al., 2023; He & Roulet, 2023) and a source of CH_4 that is more pronounced in the drainage ditches (Clark et al., 2023). Each year, depending on the weather conditions, a few cm of peat is extracted and stored in stockpiles in the fields. Before the peat is sent to professional and amateur horticulturists, peat is mixed with horticultural additives as peat is often extracted from bogs that are low in pH and nutrients (Alexander & Bragg, 2014; Schmilewski, 2009). This typically involves, but is not limited to, limestones to raise the pH, nutrients, inert minerals like perlite, vermiculite, wetting agents and so on. The additives could differ widely within extraction companies depending on the targeted use of the product.

2.4 Importance of peat as a growing media in horticulture

Horticulture production in a controlled environment that do not use traditional cropping practices use growing media and a substrate for growing plants. These systems offer benefits of cost-effectiveness, higher yields and offer higher water and nutrient efficiencies as compared to traditional agriculture (Barrett et al., 2016; Grafiadellis et al., 2000; Gruda, 2022; Rezaei Nejad & Ismaili, 2014). For instance in Canada, soil-less agriculture in mushroom production, greenhouse flowers and plants have a farm gate value of more than 3 billion CAD (Agriculture and Agri-Food Canada, 2023a, 2023b).

Driven by performance of plants, economic cost and accessibility of peat, peat use in these soil-less media has been dominant both historically, and up to present day (Schmilewski, 2009). A global estimate of 37 million m^3 of growing media is used annually (Kern et al., 2017) and expected to rise by 422% by 2050 (Blok et al., 2021). Approximately 80% of the growing media is peat (Schmilewski, 2009) and an increase in demand for growing media would mean an increase in demand for peat (Blok et al., 2021). More research on alternatives to replace peat completely or partially is being done. Decomposition of peat while it is used in horticulture is one of the largest source of CO_2 emissions for the horticulture industry (Cleary et al., 2005). If use of peat alternatives is of equal value for the horticultural production and of lower emissions, it could be a useful way for the horticulture industry to reduce their emissions. However, the alternatives need to provide equal or superior physical, chemical and biological properties for plant productivity as that of peat (Barrett et al., 2016). These properties would include, but not limited to, shape, size, texture, bulk density of the particles, nutrient status, phyto-toxicity, water holding capacity, pH, cation exchange capacity, pathogens, useful microbes and biological stability (Hirschler & Thrän, 2023; Leiber-Sauheitl et al., 2021; Montagne et al., 2015; Pot et al., 2022). Coconut coir, wood fibre, biochar, compost, rock wool and rice hulls are some of the potential peat replacements that are often discussed in the literature. For example, measured plant performances while replacing peat with rice hulls, the authors found a 50% reduction in peat did not affect chicory production, but this reduction was not suitable for tomato and pepper production (Zanin et al., 2011). In ornamental *Poinsettia* experiment replacement of peat up to 75% by pine tree media ensured better biomass as compared to the 100% replacement of peat (Jackson et al., 2008). This suggests that the choice of complete or partial peat replacement and the resulting effect on productivity is species dependent.

In addition to their properties, the alternatives should be economically viable and environmentally less damaging (Barrett et al., 2016; Hirschler & Thrän, 2023). For instance, coir as a waste product of coconut industry possess biological, chemical and physical properties similar to peat, but its production is limited to tropical areas and therefore for use in Canada the transportation cost and emissions will make it an unsuitable for peat replacement (Schmilewski, 2009). Interviews with German growing media producers on peat replacement showed even if peat-free and peat-reduced media were available, economic advantage of peat meant that replacement of peat in near future was unlikely (Hirschler & Thrän, 2023).

2.5 Peat extraction for National and International GHG reporting

Using the guidelines developed by the IPCC, parties to the United Nations Framework Convention on Climate Change (UNFCCC) and the Kyoto Protocol are required to report greenhouse gas emissions (GHG). The IPCC guidelines provides methodologies on calculating and reporting national GHG emissions for different sectors. These methodologies are divided into three Tiers based on complexity, accuracy and data requirements (IPCC, 2013).

To estimate the national and global emissions from use of peat in horticulture, emission factors (EFs) that reflect the conditions need to be developed. Current, default Tier 1 EFs for extracted peat that are used were first developed for fuel use and consider 100% of peat lost in a single year of extraction (Eggleston et al., 2006). For reporting of emissions from peat extraction, Canada currently uses Tier 1 values; even though almost all the peat extracted in Canada is used for horticultural use (Environment & Climate Change Canada, 2023). When peat is used for horticulture, the C decomposes slowly and remains in the biosphere for a long time, therefore it is important to reflect the adequate scenario by developing Tier 2 EFs. Revising emissions factors by accurately capturing the temporal trend of emissions from peat decomposition is important for designing policy development and mitigation measures.

2.6 Conclusions from literature review

In this literature review I highlighted the current state of peatlands and their degradation in general, their role in maintaining global climate over millennia. As peatland degradation increases globally and has important repercussions in the future of climate change, I discuss the nature of continued and implication of degradation of peatlands with an emphasis on horticultural peat extraction. In addition, I presented the ongoing and increasing future demand for peat use in horticulture. The major focus of my thesis is to address the issue by first ascertain the CO_2 emissions attributed from peat use in horticulture, so that the current EF could be revised. I calculate the EF through incubation and plant growth experiments and upscale the findings at national scale, to shed the light on what current extracted peat use means in terms of the past, present and future CO_2 emissions for Canada in the horticulture peat use section.

In the next Chapter, I will present the research on biogeochemical properties of peat and growing substrate and presents the results of rates of their decomposition.

Chapter 3: Horticultural additives influence peat biogeochemistry and increase short-term CO_2 production from peat

Bridging statement to chapter 3

Early on it became evident that growing media, with added nutrients and other horticultural additives, could represent a completely different system compared to peat from a bog.

For this work, I therefore worked closely with peat extraction companies in understanding what the growing media constitutes. Collaborating with the companies on their practices, I first identified the properties of growing media and compared them to that of the peat. To do that, I obtained samples from extraction companies and measured biogeochemical properties in the laboratory and conducted lab incubation experiments to measure the decomposition rates. This chapter introduces the difference in CO_2 emissions from peat and growing substrate. The difference is due to the addition of horticultural additives in the latter. Comparing the biogeochemical between the two groups, we show that the growing substrates short-term CO_2 emissions are twice as large as that of peat. Nutrient and pH status change and this could potentially govern the C losses. Using $\delta^{13}C$- CO_2 as a tracer, we show that limestone additives contribute on average 21% to the total CO_2 emissions. To account for peat-based emissions only, the CO_2 emissions arising from dissolution of limestones should be considered.

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Note: The heading, figure and table numbers for chapter 3 are adjusted to follow the table of contents for the thesis.

3.1 Abstract

Peat is used as a major ingredient of growing media in horticulture. Peat extracted from bogs can be acidic and low in nutrient availability and is therefore mixed with liming agents, nutrients, surfactants, perlite and so on. This study aims to estimate the rates at which raw peat and the modified peat ('growing media') decompose to release carbon dioxide (CO_2), to estimate the release of carbon (C) from liming agents and to estimate how peat biogeochemistry is changed. We obtained 28 and 24 samples of raw peat and growing media from four peat extraction companies in Canada. Growing media were treated with horticultural additives. We incubated the samples under laboratory conditions, measuring CO_2 production, tracer using $\delta^{13}C$- CO_2, pH, C, nitrogen (N) content and humification indices (HIs) from infrared technology called Fourier transform-mid infrared (FT-MIR). C:N ratio, pH, dissolved organic carbon, bulk density and C content differed significantly ($P < 0.05$) between raw peats and growing media. There was more than a doubling of total CO_2 production from growing media compared to raw peat. HIs show higher values for the growing media, which could result from spectral band shifts in the growing media because of increased cation availability. $\delta^{13}C$- CO_2 as a tracer showed an average 22% of the total CO_2 production originated from added carbonate materials. Our results provide the rates ($0.15\pm 0.017 mgCO_2\text{-}Cg^{-1}d^{-1}$) at which horticultural peat decomposes and on the source of emitted CO_2. This will improve current estimates CO_2 emissions from horticultural peat.

3.2 Introduction

Peatlands are prominent features of the Canadian landscape, storing about 147 Gt Carbon (C) (Tarnocai et al., 2002). Of the estimated 1.14 million km^2 of peatlands in Canada (Xu et al., 2018), around 0.03% are being actively extracted for use in horticulture (CSPMA, 2017)with an annual average dry peat extraction of 0.9 Mt yr^{-1} between 2015 to 2022 (Natural Resource Canada, 2022). Assuming 50% of the peat extracted is C, 0.45Mt C are removed from Canadian peatlands each year. As not all the C extracted is emitted back to the atmosphere, what happens to this irrecoverable C remains an important question to accurately account the C lost from horticulture peat use. Compared to other human disturbances in Canadian peatlands, peat extraction for horticulture is one of the smallest disturbances in terms of area coverage in Canada (Harris et al., 2021). Extracted horticultural peat is used by professional and amateur growers for food production, ornamental plants, gardening, landscaping and mineral soil improvement, among other purposes. The use of peat is common and in demand in horticulture, and is in increasing demand due to its well-known and favourable properties and a current lack of viable alternatives (Alvarez et al., 2018).

In their C accounting, the Intergovernmental Panel on Climate Change assume all the peat C harvested to be instantaneously released back to the atmosphere (Eggleston et al., 2006). While the rapid loss of peat C might be accurate if the peat is used as fuel, peat decomposition follows an exponential decay, with the C released slowly over time. A significant fraction of greenhouse gas (GHG) emissions from peat extraction is due to peat decomposition over time (Cleary et al., 2005). How much of the extracted C is emitted to the atmosphere and in what time frame becomes important, allowing accurate reporting of emissions from peat use for the horticultural sector. This could allow to quantify if subsequent accumulation of C in restored peatlands compensates for the loss of extracted peat (Nugent et al., 2019) and it permits comparison of the C footprint of peat with that of alternative growing media like coconut coir and wood fiber.

In the extraction process, peatlands are drained, and the vegetation is removed. The aerobic conditions created by the process accelerate heterotrophic respiration compared to anaerobic conditions (Laiho, 2006). Peat is then extracted using vacuum harvesters and stored in stockpiles in the extraction fields. As peat extracted from ombrotrophic bogs can be acidic and low in available nutrients, several nutrients, horticultural additives can be mixed to optimize its physical and biogeochemical properties for plant growth in horticulture. After mixing with additives, peat is called a growing media. Additives may be limestone/dolomite, inorganic fertilizers, perlite and surfactants. Once the additives are mixed in, the growing media are often bagged and shipped to professional and amateur growers to use in horticulture. As conditions are made optimal for plant growth, the rate of decomposition is potentially altered compared to raw peat. Several studies have shown that the decomposition rate of peat varies with both intrinsic biogeochemical properties (e.g. pH, nutrient availability and organic matter 'quality') as well as extrinsic factors (e.g. temperature and particularly degree of saturation) (Andersson & Nilsson, 2001; Blodau et al., 2004). As a result of aerobic conditions, raised pH, and improved nutrient availability, higher microbial activity and decomposition rates are expected in growing media than in raw peat. Consequently, the faster cycling of C in growing media would potentially translate into more decomposition, because of the stimulating effect of horticultural additives on microbial activity (Pot et al., 2022).

Several studies have measured biogeochemical properties and/or decomposition rates of peat with one or more components of horticultural additives (Andersson & Nilsson, 2001; Li et al., 2022; Pinsonneault et al., 2016b). However, the set of horticultural additives differs among companies and for products within the same company. Studies available on growing media often focus on how media quality improves plant growth and usually analyze only a single type of growing media sourced from one company (Leiber-Sauheitl et al., 2021; Lévesque et al., 2018). Therefore, a more comprehensive understanding of growing media properties and decomposition rate remains desirable for use in C accounting. The primary objective of this study is to measure emissions from growing media and compare them to emissions from raw peat. The 'recipes' to make growing media are numerous and vary among and even within the companies depending on the targeted use of the product. Therefore, to put the measurements of emissions in context, we investigated if the emissions can be explained by the measured biogeochemical properties.

The growing media pH is raised using calcitic [$CaCO_3$] or dolomitic [$CaMg(CO_3)_2$] limestone, which when dissolved in acidic water, releases carbon dioxide (CO_2). In previous studies with limed soils, direct CO_2 emissions from the lime are persistent and remain over a long period (Biasi et al., 2008). Liming in agricultural soil is a common practice in acidic soils, and lime-based national emissions are accounted for in agricultural emissions in Canada (Environment & Climate Change Canada, 2023). Therefore, partitioning the emitted CO_2 into biotic (peat-based) and limestone sources needs to be addressed for accurate measurement and reporting of biotic emissions from growing media. The stable isotopic composition of CO_2 can be used to separate the CO_2 flux into abiotic and biotic components owing to the different ^{13}C abundance in peat and limestone, using a two-way mixing model (Fry, 2006).

Recently, FT-MIR derived humification indices (HIs) have been widely used to characterize peat properties and have been linked to several decomposition proxies (Broder et al., 2012; Drollinger et al., 2020; Harris et al., 2023). Previous studies have used FT-MIR results to detect short-term changes in the chemical properties of peat following incubation (Tfaily et al., 2014). Given the ease and low cost of FT-MIR analysis, we wanted to explore the usability of HIs in the horticultural peat context to assess peat decomposition.

Previous attempts to model climate impact of peatland restoration on peat extraction sites excluded the C removed from the systems (Nugent et al., 2019). Yet, removal of peat C and its decomposition in *ex situ* environments are previously reported to be the largest source of GHG emissions for the Canadian peat industry (Cleary et al., 2005). Our measurements of CO_2 emissions from decomposing growing media allow more accurate upscaling and budgeting of CO_2 emissions from Canadian horticultural peat extraction.

3.3 Materials and Methods

3. 3. 1 Sample collection and Preparation

In July 2020, we contacted four peat harvesting companies based in Quebec and Alberta and requested samples of raw peat from harvesting sites and growing media (horticultural additives added to the raw peat) ready for sale. We asked for variations in peat and growing media and received 28 peat samples and 24 growing media samples. Each company had its definition of 'peat quality', so we reclassified the grade groups based on the von Post scale that ranged in our case from 3 to 8 (Table 3.1) (Rydin & Jeglum, 2005). Samples were divided into triplicates and stored at 4^{o}C before laboratory analysis. Measurements of incubation for CO_2 and $\delta^{13}C$-CO_2 were done on triplicate sub-samples, whereas all other analyses were done on a representative single sub-sample only.

Table 3. 1: Samples divvied into groups using type (peat or growing media) and a measure of peat quality (using von Post groups). Sample size is the number of samples in that sub-group.

Type	Quality	Sample size
Peat	von Post 3-4	*n= 10*
	von Post 5-6	*n= 9*
	von Post 7-8	*n= 9*
Growing media	von Post 3-4	*n= 12*
	von Post 5-6	*n= 6*
	von Post 7-8	*n= 6*

3.3.2 Laboratory Analysis

Gravimetric moisture content was based on mass loss from 10 g of fresh peat samples upon oven drying at 105 ^{o}C for 24 h. Loss-on-ignition (LOI) was determined using 1- 2 g of oven-dried samples ignited at 550 ^{o}C for 4 h (Heiri et al., 2001). Our measurement of LOI represents organic matter content. A higher temperature of combustion is needed to combust inorganic compounds (Heiri et al., 2001). In hindsight it would have been useful to obtain a measure of inorganic carbon content, but we did not. The peat pH was measured in water with 1:35 dry mass to water mass ratio (Nilsson et al., 1995). Bulk density was calculated as ratio of dry mass of a known volume of 50 cm^3 peat that was obtained in peat bags. Samples were oven-dried at 60°C for 120 h and ground to a fine powder for total C, total N, and Fourier transform mid-infrared (FT-MIR) spectroscopy. For the analyses of C, N, solid $\delta^{13}C$, FT-MIR, to remove added carbonates finely ground samples were treated in 1M HCl, left in the oven to evaporate and treated with deionized water until the pH of the peat and water solution was circum-neutral (raw peat samples were not treated with HCl). We evaporated the excess acid and DI water, instead of decanting excess solutions, to ensure that the soluble fractions of C are not poured off (Hélie, 2009). C and N were measured using direct combustion (900C) with an elemental analyzer (Flash EA 1112 CN ThermoFinnigan, Waltham, MA, USA). We performed the isotopic measurements on solid peat with a Micromass model Isoprime 100 isotope ratio mass spectrometer coupled to an Elementar Vario MicroCube elemental analyser in continuous flow mode (GEOTOP, Montreal). Two internal reference materials ($\delta^{13}C$ = -28.74± 0.02‰ & -11.80 ± 0.03‰) were used to normalize the results on the NBS19-LSVEC scale. A third reference material ($\delta^{13}C$=-17.06 ±0.02‰) was analyzed as an unknown to assess the exactness of the normalization. Results are given in delta units (δ) in ‰ vs Vienna Pee Dee Belemnite (VPDB). The overall analytical uncertainty (1σ) was better than ±0.1‰.

For FT-MIR, 2 mg of powdered sample was mixed with 200 mg KBr (FTIR grade, Sigma Aldrich, St. Louis, MO, USA), and spectra were obtained using a Cary 660 FTIR spectrometer (Agilent, Santa Clara, CA, USA). With a resolution of 2 cm^{-1}, spectra were recorded from 600 cm^{-1} to 4000 cm^{-1} and then baseline corrected (Beleites & Sergo, 2021) and normalized with the irpeat package (Teickner & Hodgkins, 2020) to estimate the relative heights of specific peaks. Humification indices (Broder et al., 2012) were computed to analyze relative abundances of groups of molecular structures relative to the absorption band at 1090 cm^{-1} (assumed to be caused predominantly by polysaccharides in this case because of low mineral contents):

1420/1090 Hi_1: phenolic and aliphatic structures / polysaccharides

1510/1090, Hi_2 : aromatic $C = C$ or $C = O$ of amides / polysaccharides

1630/1090, Hi_3: aromatic $C = C$ and COO^-, protein NH_2 and $C=O$ /polysaccharides

1720/1090, Hi_4: carbonylic and carboxylic $C = O$ / polysaccharides

3.3.3 Incubation Experiments

We incubated triplicates of peat and growing media samples (~10g) in 250 mL Mason jars after removing large roots and twigs. After adjusting the water content to 60% volumetric moisture, samples were stored at 4°C for one week to avoid the initial disturbance and brought out at room temperature for 48 h. Incubations to determine CO_2 emissions were done aerobically at a temperature of 23°C. Since the jars were not completely closed during the settling down period for nine days (one week at 4 °C and two days at 23 °C days), we assume that aerobicity in the bottles was maintained during the sampling period. Gas samples (5 mL) were collected from each jar using stopcocks attached to rubber tubes in the jar lids, and before sample collection, the headspace air was mixed by flushing the syringes. After 48 h incubation at 23°C, gas samples were collected at 0, 6, 24 and 48 h and CO_2 concentrations were measured on a Shimazdu GC-2014 gas chromatograph equipped with a methanizer and flame ionization detector. N_2 was the carrier gas, the SRI column temperature was 70°C and the flame ionization temperature detector (FID) was at 110 °C. Three to five standards of 5000 ppm were run through the GC before, during and after the sampling period. Five mL of ambient air were added to the jars after each sampling, and rates of CO_2 production by samples were calculated from the rates of change in concentration within the headspace and corrected for the dilution because of the 5 mL ambient air addition. For quality control, only measurements with $r^2 > 0.8$ were used. Less than 10% of the data were discarded after the control. Production rates were expressed per mass of organic C (org C) in the peat or growing media, as the samples had varying C content.

3.3.4 Separation of CO_2 sources based on stable isotopic composition.

Sub-samples of four peat samples, one from each company, and of all growing media were incubated as above in triplicate to measure the $\delta^{13}C$ (V-PDB) signature of CO_2 emissions. 25 mL of headspace gas was sampled at 0, 2, 4 and 6 h and 5 mL were used to measure CO_2 concentration, as above, and 20 mL was used to determine $\delta^{13}C$- CO_2 in a G2201-i CRDS Isotopic Analyzer system (Picarro, Santa Clara, CA). After each sampling, 25 ml of CO_2-free gas was refilled in the Mason jars. During each sampling period, two replicate CO_2 standards of 850 ppm and -28.5‰ VPDB and an ambient air sample were run through the instrument. Measurements on the standards had a standard error of < 0.4‰ throughout the sampling period. The Picarro instrument was calibrated prior to the measurement period with two additional isotopic standards (100% CO_2) with $\delta\ ^{13}C$ values of -15.6 and -43.2‰ VPDB (Stix et al., 2017).

The $\delta^{13}C$ of emitted CO_2 was calculated using Keeling plots (Keeling, 1958). Intercepts of $\delta^{13}C$ values of CO_2 were accepted when the regression coefficient was >0.90 and when the coefficient of variation was less than 10%. Around 10% of sub-samples had a regression coefficient of less than 0.90, for these samples only two replicates were used in calculations. In addition, 5% of the samples had coefficient of variation larger than 10% and were removed from subsequent analyses in order to achieve high confidence in measurements of $\delta^{13}C$ values. Intercept values for each sample and standard errors calculated from the triplicates can be found in Table S1. These quality check controls are similar to other studies using Keeling plots (Biasi et al., 2008; Pataki et al., 2003; Soper et al., 2017).

The $\delta^{13}C$ signature was used to divide the total CO_2 flux into lime- and peat-based sources for the growing media. From the horticultural peat extraction companies, we requested samples of their commercially used limestone products. We received seven different limestone and dolomite products in total. For lime $\delta^{13}C$ signature measurement aliquots of typically 100–150 µg of powdered samples were analyzed on a Nu Instruments Perspective™ isotope ratio mass spectrometer equipped with a NuCarb™ online carbonate preparation device at the McGill University, Geotop Stable Isotope Laboratory. On this instrument, carbonate powders are reacted in orthophosphoric acid at 70ºC and analyzed via dual inlet following double distillation of the evolved CO_2 gas. Based on regular analysis of an in-house standard (UQ6), reproducibility is better than 0.1‰. One sample was removed for large variability between replicates. Measured average $\delta^{13}C$ value of lime was -0.03‰ (0.28‰) and individual $\delta^{13}C$ value for solid peat in a two-pool mixing model equation (Biasi et al., 2008; Fry, 2006; Wild et al., 2023).

$$f = \frac{\delta - \delta_0}{\delta_1 - \delta_0}$$

Here, f is the fractional contribution of lime to total flux, δ is the isotopic signature for CO_2 emitted from growing media, δ_0 is the isotopic signature of solid peat and δ_1 is the isotopic signature of lime.

3.3.5 Dissolved organic carbon (DOC), total dissolved nitrogen (TDN) and phenolic concentration

After the incubation, two grams of sample were mixed with 20 mL of distilled water for 1 h at 200 rpm in a shaker. After filtration with 0.45 µm filter papers (Macherey-Nagel, Düren, Germany), concentrations of DOC and TDN were determined using a Shimadzu TOC-TN analyzer

(Shimadzu Corp., Kyoto Japan). Because of significant differences in C content among samples, DOC and TDN are expressed per g solid org C.

For phenolic concentration we adopted the method from Alshehri et al. (2020). Briefly, 5 g of the incubated sample were mixed with 40 mL of DI water in 50 mL centrifuge tubes and thoroughly mixed by shaking for 24 h at a speed of 200 rpm. Afterwards, samples were centrifuged at 5000 rpm for 30 minutes on a Sorvall ST16R centrifuge (Thermo Fisher, Altricham, UK). The samples were then filtered through 0.45 µm Macherey-Nagel filter papers. In a separate 2 mL centrifuge tube, 1 mL of filterate was added, followed by 50 µm of Folin-Ciocalteau phenol reagent and 0.15 mL of Na_2CO_3 (200 g L^{-1}) to buffer the reaction. A range of standards of phenol compounds between 0.5 to 30 mg L^{-1} was prepared in a similar way. After 1.5 h, 300 µm of each sample and the standard were transferred to wells of a clear 96-well microplate. Absorbance was measured at 750 nm on an Epoch Microplate Spectrophotometer (BioTek Instruments Inc., Winooski, Vermont) and converted the values into phenol concentration per g org C.

3.3.6 Statistical Analysis

Peat with horticulture additives in them are growing media, presumably differing depending on the specific additions. We lack information required to match each growing media sample with the respective original peat, we treat peat and growing media as independent groups. Furthermore, we make the assumption that the differences we observe are due to horticultural additives, even though differences in the peat material can also contribute to some of the differences. The statistical analyses were conducted in R, version 4.1.0 (R Development Core Team, 2021). We first discuss the differences between peat and growing media for each variable and then compare the results with the degree of decomposition for peat and growing media individually. Finally, we highlight the difference between peat and growing media within each von Post class. Both the independent variables, peat or the growing media and the von Post groups are treated as categorical variables and the interaction between the two variables is also considered.

We used the generalized least squares (gls) model in R package "nlme" for statistical comparison between the groups (Pinheiro, 2009). Whenever the residuals of the models demonstrated heteroskedasticity, we used the varIdent variance structure in the gls model as it handles differences in variances of different groups (Supplementary information Section A). The choice between the model with equal and unequal variances was guided by a likehood-ratio test, comparing the models. Results from the models where residuals demonstrate homoscedasticity and higher log-likelihood values are reported. Post hoc comparisons among the groups were made using the package "emmeans", which used the Tukey method to adjust for multiple comparisons. Unless otherwise stated, 10% is used as the significance level, to capture any potential trends and differences in the data. For comparing $\delta^{13}C$- CO_2 between peat and growing media, we used two sample t-test with unequal variance. We report Spearman correlation coefficients to estimate correlations between the variables, Correlations coefficients for significant relationships are termed moderate when r is between ± 0.3 to ± 0.5 or strong when $|r| > 0.5$. Results are presented as the average ± one standard error.

3.4 Results

We first describe the pooled differences between peat and growing media for biogeochemical properties and CO_2 emissions. As the measured variables in each group (peat and growing media) also differ by the degree of decomposition, we present the results along the von Post gradient within each group. Finally, we report the differences in biogeochemical properties and overall and peat specific C emissions between the two groups (peat and growing media) within each von Post class.

3.4.1 Biogeochemical Properties

There were differences in biogeochemical properties between peat and growing media in their average pH, bulk density, water-soluble phenolic concentration and LOI (Table 3.2, Figure S3.1). The peat samples were more acidic than the growing media, with mean pH values of 4.16 (±1.2) and 5.78 (±0.16) respectively. Within peat, the pH of von Post class 7-8 was highest followed by class 5-6 and 3-4 respectively. This trend was not present for the growing media. When compared between peat and growing media in each von Post class, growing media always had a higher pH. On average, the growing media also had a higher bulk density than peat (0.09 ±0.007 and 0.07 ±0.003 g cm^{-3} for growing media and peat respectively). This difference in average appeared to be driven by growing media von Post class 7-8 which had the largest bulk density of all the groups.

Water soluble phenolic concentration was on average higher for growing media than for peat (0.58 ±0.56 and 0.61 ± 0.06 mg g^{-1} org C respectively). Peat samples did not demonstrate any observable patterns along the von Post scale, whereas for growing media, there was a decrease in phenolic concentration with increasing von Post class (Table 3.2, Figure S3.1). LOI was significantly lower and more variable for growing media (80.3 ± 2.08 % than for peat (94.02 ±

1.06 %, P<0.001). LOI tended to decrease with an increase in von Post class, with LOI in peat for von Post class 7-8 being significantly different from classes 3-4 and 5-6 (P = 0.04 and P = 0.06 respectively). There was no observable pattern in LOI of the growing media along the von Post scale. Growing media LOI was lower than for peat in each von Post class.

Similar to LOI, there was an overall significantly higher organic C content (%) in the peat samples than in the growing media (means of 50.9 ± 0.51 and 43.96 ± 1.07 %, respectively) (Table 3.2, Figure S3.2). In contrast to the C content, N concentrations did not differ significantly between the two groups (1.11 ± 0.06 for peat and 1.17 ±0.06 for growing media) or between each von Post group (Table3.2, Figure S3.2). However, within peat, N concentrations were larger for more decomposed samples than for less decomposed samples. Similarly, growing media also had a larger N content for more larger von Post classes, with group 7-8 having the highest average LOI. The differences in C and N contents translated into a higher average C:N ratio for peat (50.44 ± 3.04 than the growing media (39.45 ± 2.01, P = 0.001). As expected, a decrease in C:N along the decomposition gradient was observed for peat as the C:N for von Post classes 3-4, 5-6 and 7-8 averaged 62.6 ± 2.44, 47.8 ± 3.11 and 30.8 ± 3.33 respectively, and all the groups were statistically significantly different from one another (P= 0.02 between 3-4 and 5-6; P< 0.001 between 3-4 and 7-8 and P<0.001 between 5-6 and 7-8 group) (Table 3.2, Figure S3.2). This gradient was less pronounced for growing media as only the von Post class 7-8 was statistically different from the other von Post classes. The average δ^{13}C-solid for peat samples was lower than for growing media (-26.88 and -27.37 ‰, respectively, P < 0.001) (Table 3.2, Figure S3.2). Along the von Post scale, there were no trends in δ^{13}C-solid for peat samples, whereas for growing media, average δ^{13}C-solid decreased with larger von Post class, but no statistical difference was observed (P > 0.5 between all von Post group comparisons). Contrasting peat and growing media among each von Post class, statistically significant differences are observed for von Post class 5-6 (P = 0.005, difference of 0.7 ‰).

Average DOC in the growing media was higher than for peat (0.64 ± 0.04 and 0.5± 0.04 mg g^{-1} org C respectively, P = 0.02) (Table 3.2, Figure 3.1). For both peat and growing media, DOC decreased with increasing von Post class. On the other hand, TDN was, on average, 3 to 5 times larger in the incubations of growing media than in the incubations of peat (0.484 ± 0.06 and 0.10 ± 0.005 mg g^{-1} org C respectively ,P < 0.001) (Table 3.2, Figure 3.1). Similar to the overall difference between peat and growing media this relationship held for each of von Post class 5-6 and 7-8 (P = 0.04 and P = 0.02, respectively). These differences in TDN also resulted in a large difference in average DOC: TDN values between peat and growing media (5.08 ± 0.76 and 13.09 ± 0.86 , respectively, P< 0.001) (Table 3.2, Figure 3.1). This ratio tended to decrease along increasing decomposition for peat, with class 7-8 having the on average lowest values compared to class 3-4 (P=0.04) and group 5-6 (P=0.02). This trend along von Post scale was also similar for growing media, but the differences were not statistically different (all P >0.14). Consistent with overall differences, DOC: TDN for peat and growing media differed statistically in each von post class (P= 0.08, P<0.001 and P= 0.03 for 3-4, 5-6 and 7-8 groups.

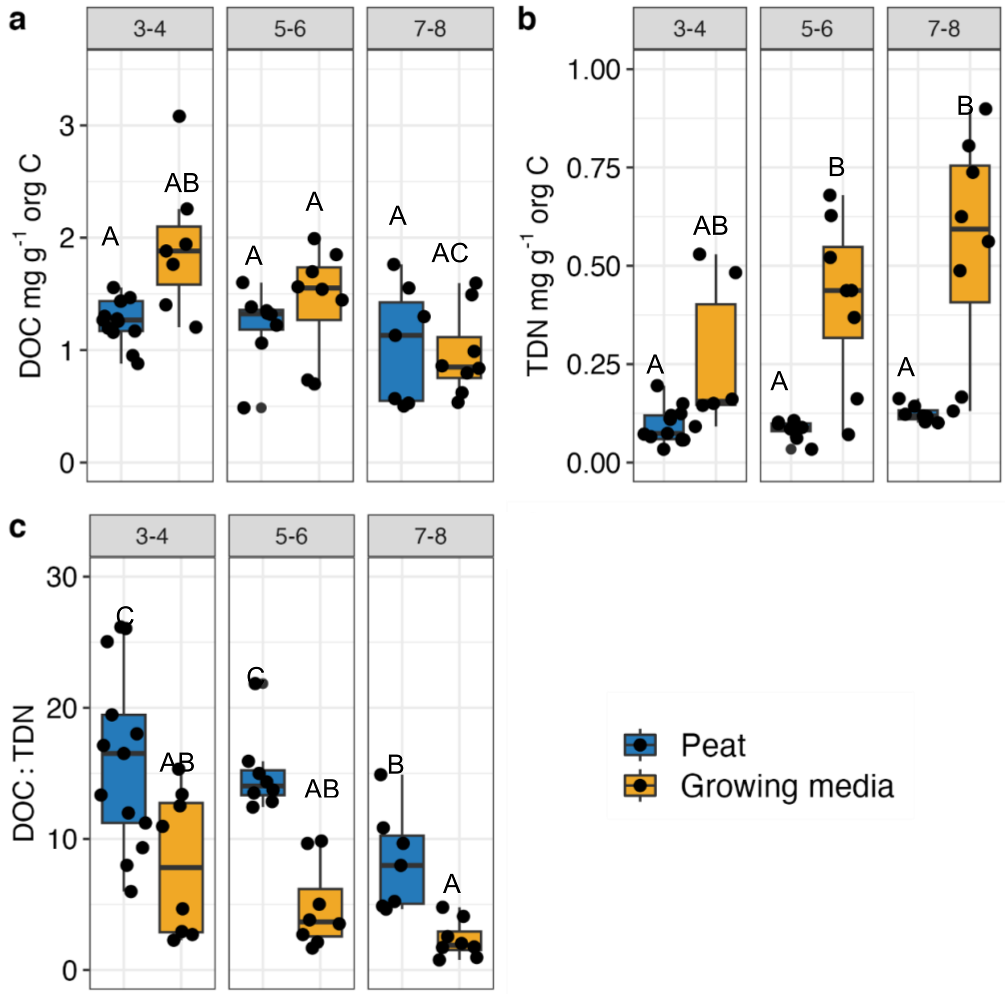

Figure 3. 1: Values of a) DOC, b) TDN and c) DOC:TDN are shown for peat and growing media across different von-post class. Letters above each box represent significant difference as compared to other groups, where differing letters denote statistical difference.

Table 3. 2: *Biogeochemical properties mean (± se) of peat and growing media in each von post groups. n=28 for peat and n=24 for growing media.*

Group	Von Post	pH	LOI (mass-%)	Bulk density (g cm^{-3})	Phenolic (mg g^{-1} org C)	Carbon (mass-%)	Nitrogen (mass-%)	C:N (g g^{-1})	$\delta^{13}C\text{-}solid$ (‰)
Peat	3-4	3.83 (0.01)	96.87(0.09)	0.07(0.001)	0.54(0.02)	52.08(0.15)	0.86(0.01)	62.57(0.93)	-27.00 (0.02)
	5-6	3.86(0.02)	95.84(0.41)	0.067(0.001)	0.73(0.04)	51.22(0.28)	1.09(0.02)	47.88(0.93)	-26.65(0.03)
	7-8	5.1(0.10)	86.63(0.93)	0.009(0.002)	0.48(0.04)	48.39(0.43)	1.60(0.04)	30.83(0.73)	-26.91(0.09)
Growing media	3-4	5.78(0.09)	72.36(1.26)	0.074(0.001)	0.84(0.03)	41.88(0.72)	0.94(0.02)	45.00(1.06)	-27.16(0.04)
	5-6	5.33(0.09)	89.46(0.67)	0.085(0.004)	0.62(0.03)	45.56(0.50)	1.09(0.03)	42.92(0.88)	-27.27(0.04)
	7-8	6.21(0.10)	79.00(0.81)	0.12(0.004)	0.37(0.02)	44.45(0.73)	1.49(0.02)	30.44(0.91)	-27.57(0.04)

Group	Von post	DOC (mg g^{-1}org C)	TDN (mg g^{-1} org C)	DOC: TDN	Hi1	Hi2	Hi3	Hi4
Peat	3-4	1.25(0.01)	0.09(0.003)	16.02(0.52)	0.51(0.003)	0.33(0.004)	0.67(0.005)	0.61(0.005)
	5-6	1.21(0.04)	0.08(0.003)	14.95(0.37)	0.60(0.006)	0.46(0.008)	0.84(0.012)	0.71(0.005)
	7-8	1.04(0.07)	0.12(0.003)	8.30(0.54)	0.91(0.02)	0.84(0.02)	1.30(0.02)	0.80(0.01)
Growing media	3-4	2.13(0.10)	0.48(0.06)	8.09(0.68)	0.57(0.008)	0.39(0.008)	0.76(0.01)	0.41(0.01)
	5-6	1.44(0.05)	0.41(0.03)	4.79(0.40)	0.70(0.009)	0.52(0.01)	0.99(0.01)	0.64(0.004)
	7-8	0.96(0.05)	0.55(0.03)	2.33(0.17)	1.02(0.02)	0.89(0.02)	1.42(0.02)	0.76(0.009)

Table 3. 3: Correlation values following Spearman rank correlation and associated p-values for assessing relationship between different measured variables. *All the* variables that are associated at 10% significance level are presented in bold *(in next page)*

	Peat-CO_2	pH	LOI	Bulk density	DOC	TDN	DOC:TDN	C	N	C:N	Hi1	Hi2	Hi3	Hi4	Phenolic Conc.
pH	**0.38**														
	0.004														
LOI	**-0.47**	-**0.76**													
	<0.001	<0.001													
Bulk density	0.11	**0.46**	**-0.37**												
	0.41	<0.001	0.006												
DOC	**0.43**	-0.13	-0.11	**-0.32**											
	0.001	0.3	0.41	0.01											
TDN	**0.46**	**0.65**	**-0.59**	**0.31**	0.15										
	<0.001	<0.001	<0.001	0.04	0.26										
DOC: TDN	**-0.32**	**-0.68**	**0.52**	**-0.38**	0.22	**-0.88**									
	0.01	<0.001	<0.001	0.005	0.1	<0.001									
C	**-0.52**	**-0.72**	**0.7**	**-0.28**	-0.04	**-0.63**	**0.57**								
	<0.001	<0.001	<0.001	0.04	0.7	<0.001	<0.001								
N	-0.01	**0.38**	-0.2	**0.27**	**-0.48**	0.19	**-0.43**	-0.16							
	0.93	0.004	0.14	0.04	<0.001	0.15	0.001	0.24							
C:N	-0.19	**-0.64**	**0.48**	**-0.33**	**0.37**	**-0.44**	**0.61**	**0.53**	**-0.89**						
	0.16	<0.001	<0.001	0.014	0.006	0.003	<0.001	<0.001	<0.001						
Hi_1	0.11	**0.57**	**-0.48**	**0.55**	**-0.35**	**0.31**	**-0.47**	**-0.4**	**0.65**	**-0.67**					
	0.42	<0.001	<0.001	<0.001	0.009	0.02	<0.001	0.002	<0.001	<0.001					
Hi_2	0.10	**0.53**	**-0.43**	**0.51**	**-0.39**	**0.23**	**-0.42**	**-0.34**	**0.73**	**-0.7**	**0.97**				
	0.44	<0.001	<0.001	0.001	0.004	0.09	0.001	0.012	<0.001	<0.001	<0.001				
Hi_3	0.11	**0.56**	**-0.466**	**0.53**	**-0.37**	**0.38**	**-0.44**	**-0.4**	**0.66**	**-0.67**	**0.98**	**0.97**			
	0.42	<0.001	<0.001	<0.001	0.006	0.04	0.001	0.003	<0.001	<0.001	<0.001	<0.001			
Hi_4	**-0.25**	0.07	0.01	**0.5**	**-0.51**	-0.13	-0.07	0.07	**0.55**	**-0.38**	**0.69**	**0.71**	**0.71**		
	0.06	0.59	0.93	<0.001	<0.001	0.34	0.57	0.58	<0.001	0.005	<0.001	<0.001	<0.001		
Phenol	0.17	-0.11	-0.002	-0.16	**0.53**	**-0.28**	0.18	0.018	-0.22	0.18	**-0.26**	**-0.24**	**-0.28**	**-0.28**	

	0.22	0.42	0.98	0.23	<0.001	0.04	0.19	0.89	0.1	0.19	0.06	0.07	0.04	0.04	
δ^{13} C- Peat	-0.09	**-0.5**	**0.42**	**-0.52**	0.2	**-0.38**	**0.48**	**0.35**	-0.06	0.2	**-0.29**	**-0.25**	**-0.25**	-0.08	0.08
	0.5	<0.001	0.001	<0.001	0.14	0.004	<0.001	0.009	0.67	0.15	0.03	0.07	0.06	0.53	0.56

In general, humification indices derived from FT-MIR differed along the von Post scale and between peat and growing media in each von Post class (Table 3.2, Figure 3.2). For Hi_1, Hi_2 and Hi_3, average growing media values always were larger values than for peat (P = 0.005; P = 0.08 and P = 0.003 respectively). However, Hi_4 was on average smaller for growing media than for peat (P<0.001). Humification indices Hi_1, Hi_2 and Hi_3 differed along the von Post scale for both peat and growing media. For Hi_1 and Hi_3, only peat and growing media in class 5-6 differed (P = 0.07 for both), and for Hi_2, none of the groups differed significantly (all P> 0.2). Average Hi_4 of growing media in each von Post class always were smaller than for peat, and the differences were significant for class 3-4 (P = 0.005) and class 5-6 (P = 0.02).

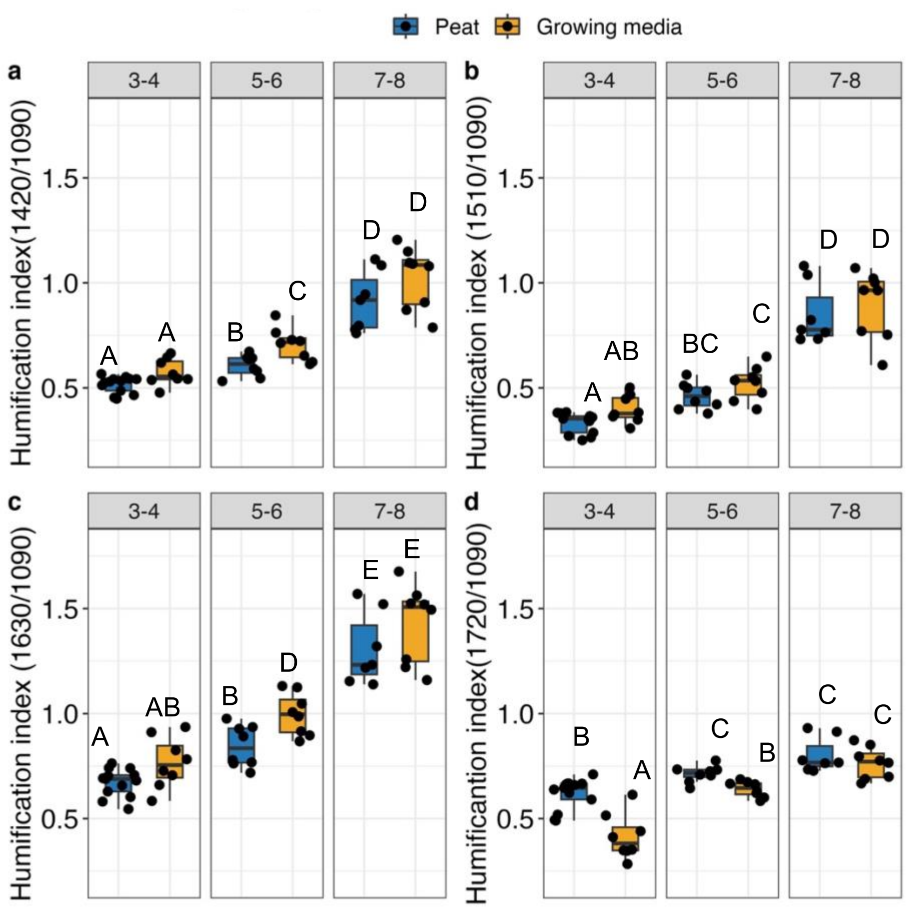

Figure 3. 2: Humification indices a) 1420/1090 b) 1510/1090 c) 1630/1090 and d) 1720/1090 between peat and growing media across different von Post classes. The ratios are referred as Hi_1, Hi_2, Hi_3 and Hi_4 respectively. Letters above each box represent significant difference as compared to other groups, where differing letters denote statistical difference.

3.4.2 CO_2 emissions and $\delta^{13}C$- CO_2 measurements

Total CO_2 emitted from peat was on average three times larger for growing media than for raw peat (0.063 ± 0.004 and 0.19 ± 0.02 mg CO_2-C g org C^{-1} day^{-1} respectively, $t= 5.90$, $df= 23$, $P< 0.001$). Variability in values, measured as the coefficient of variation of total emitted CO_2, was larger for growing media than for peat (0.54 and 0.38, respectively). Neither for peat nor for growing media did the total CO_2 emissions differ statistically significantly along the von Post scale. Comparison within von Post classes showed larger and significantly different CO_2 emissions for class 3-4 ($t = 3.96$, $df = 7.42$, $P = 0.03$) and class 5-6 ($t = 4.15$, $df = 7.33$, $P = 0.03$), whereas the difference was not significant for class 7-8 ($t = 2.02$, $df = 9.12$, $P = 0.3$) (Figure 3.3a).

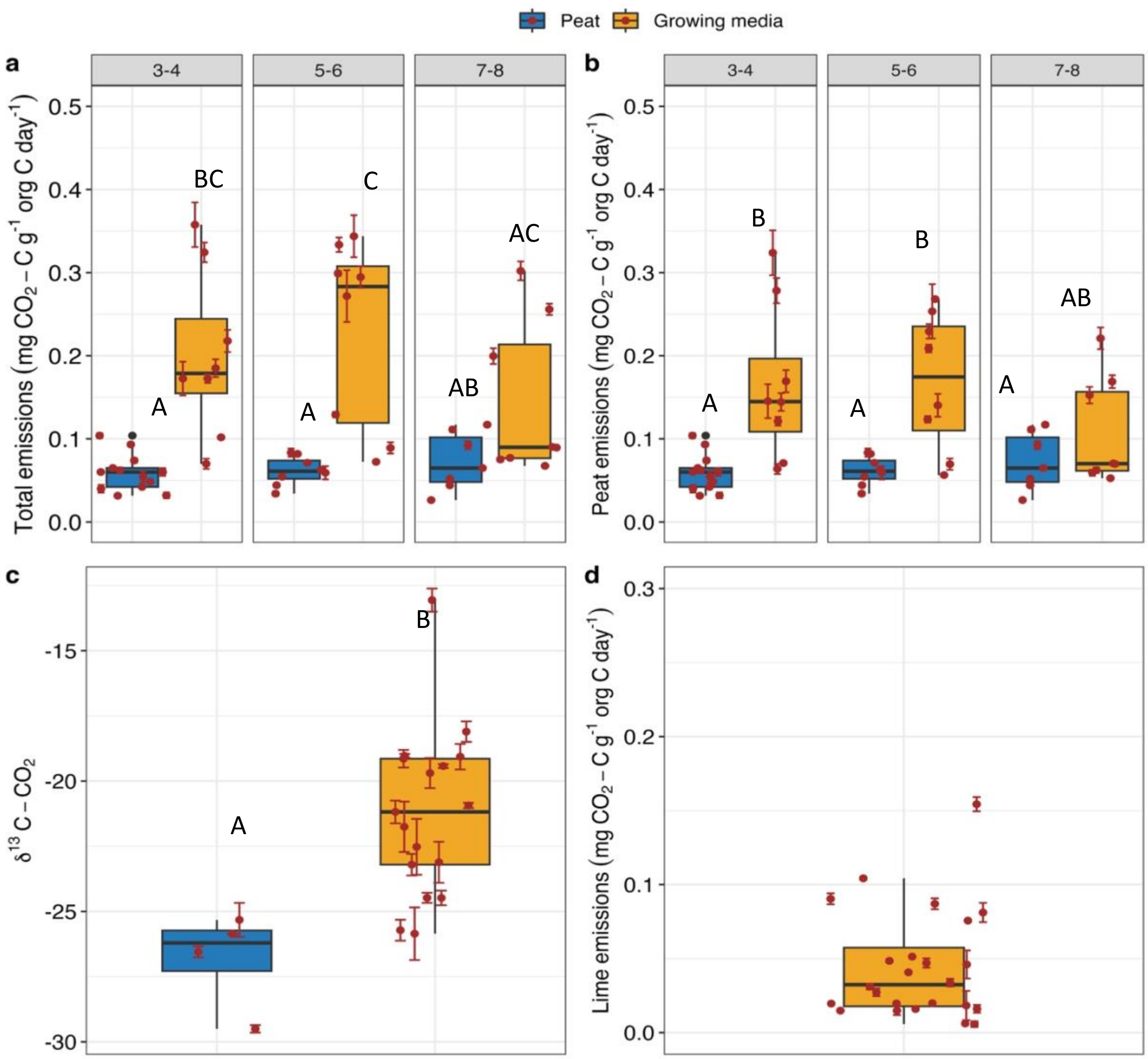

Figure 3. 3: a) Total CO_2 emissions, b) is the CO_2 emissions after lime contribution has been removed for the growing media, c) $\delta^{13}C$ of the emitted CO_2, and d) CO_2 emissions from peat only. The bottom right graph in (d) emissions from lime in growing media. Numbers in the panel represent von Post classes. Differing letters above each box represent significant difference as compared to other groups.

Average $\delta^{13}C$- CO_2 values of peat were more negative than those of the growing media (mean of -26.80 and -21.22 ‰, respectively, P = 0.001), indicating the contribution of carbonates (relatively enriched in ^{13}C) to the total emitted CO_2 in growing media (Figure 3b). The average fraction of carbonate emissions in the total flux from growing media was 22.3%, 0.05 mg CO_2-C g org C $^{-1}$ day^{-1} (Figure3. 3c). After subtracting the direct contribution of carbonates in growing media emissions (Figure 3c and 3d), peat-based emissions in growing media were still larger than in peat (0.063 ± 0.004 and 0.15 ± 0.017 mg CO_2-C g org C $^{-1}$ day^{-1} respectively, t = 4.62, df = 22.9, P < 0.001) (Figure 3.3d). The peat-based CO_2 emission did not differ significantly along the von Post scale for either peat or growing media. However, differences between peat and growing media in peat flux were significant, except for von Post class of 7-8 (P= 0.09, P=0.05 & P= 0.74 for classes 3-4, 5-6 and 7-8 respectively).

3.4.3 Correlation between variables

The combined correlation matrix and their associated *P*-values are shown in Table 3.3, and significant associations of CO_2 emissions with explanatory variables are expanded in Figure S3.3. Most importantly, there was a moderate and significantly positive correlation of the peat-borne flux with pH (r_s= 0.41, P= 0.002), TDN (r_s = 0.55, P<0.001) and DOC (r_s = 0.39, P=0.0013). Similarly, peat-borne C emissions show a moderate and negative association with C content in solid peat (r_s = -0.52, P < 0.001), with LOI (r_s= -0.49, P < 0.001), with DOC:TDN (r_s= -0.36, P < 0.007), and low and negative association with Hi4 (r_s = -0.34, P = 0.01).

Hi_1, Hi_2 and Hi_3 were associated positively and significantly with pH, bulk density, N, and negatively with C:N, DOC, TDN, LOI and weakly with phenolic concentration. While dividing the correlation matrix into two groups for peat and growing media, differing relationships were observed (Table S3.2 and S3.3). CO_2 emissions for peat tended to increase with increasing δ^{13} C-Peat (r_s = 0.39, P = 0.03). For growing media, CO_2 emission tended to increase with increasing DOC (r_s = 0.36, P = 0.08) and tended to decrease with increasing N content (r_s = -0.37, P = 0.02) and increasing C content (r_s = -0.37, P = 0.07).

3.5 Discussions

3.5.1 Biogeochemical differences between peat and growing media

Peat pH, LOI, C:N, phenolic content are within ranges and similar to the values reported for bog peat and for peat extracted for horticulture. For instance, from the data collected from undisturbed Ontario bogs the estimated 99% CI of i) pH ranged from 4.72 to 4.9, ii) LOI from 93.93 to 94.78% and iii) C:N from 32.62 to 35.56 (Riley, 1994). The addition of horticultural additives affected several biogeochemical properties. Values of LOI, C:N, $\delta^{13}C$- C, bulk density, phenolic concentration in a natural peatland are often used as a proxy for the decomposition stage; for example lower C:N signifies a more mineralized peat (Biester et al., 2014). However, most of these biogeochemical measures in growing media would be influenced by added inorganic fertilizers, lime and other inorganic buffers, therefore they would not be reflective of the degree of decomposition or biological origin of peat anymore (Figure 2 and 3). The bulk density measurements on the compacted samples received in peat bags do not reflect bulk density as measured in natural peatlands. Although lower LOI in a natural peatland may suggest increased mineralization (Chambers et al., 2011) in our investigation, the lower LOI measured for growing media is potentially influenced by inert perlite and other added inorganic substances. However, it remains unclear from this study whether the addition of perlite to peat directly impacts C mineralization.

3.5.2 CO_2 emissions and influence of liming

CO_2 emitted from raw peat (0.026 to 0.12 mg CO_2-C g org C^{-1} d^{-1}) measured in this study is on the lower end but within the ranges reported for other raw peat soils where total C is almost exclusively organic C. Glatzel et al. (2004) measured emissions from 0.027 to 0.7 mg CO_2-C g g C^{-}

^{1} d^{-1} in a horticultural peat extraction site and a pristine bog. Similarly, Scanlon and Moore (2000) report emissions from 0.07 to 0.36 mg CO_2-C g C^{-1} d^{-1} from a Canadian bog at 14°C. Potentially more similar conditions to our study are from Clark et al. (2023), where CO_2 emissions from incubation of peat from actively extracted peatlands in Quebec ranged between 0.006 and 0.03 mg CO_2-C g C^{-1} d^{-1}, with C being predominantly organic.

Total CO_2 emissions for growing media in our study (0.055 to 0.35 mg CO_2-C g org C^{-1} d^{-1}) are similar in magnitude with what has been reported for agricultural organic soils that are limed and fertilized in Finland with values ranging from 0.12 to 0.47 mg CO_2-C g C^{-1} d^{-1} (Biasi et al., 2008). As we did not consider dissolved CO_2 in water, considering that our setup volume was 250 mL and assuming a typical representative concentration of CO_2 in the headspace in the observed ranges of pH, we underestimated CO_2 production rates by a maximum of 20% depending on the exact pH (Stumm & Morgan, 2012) for both peat and growing media.

Values of $\delta^{13}C$-CO_2 for peat in our study (-24.66 to -26.9 ‰) are similar to values reported for unlimed plots in agricultural organic soils in Finland (-25.32 to -29.5 ‰) (Biasi et al., 2008). Values of $\delta^{13}C$- CO_2 of growing media (-13.06 to -29.50 ‰) are also within the range reported for limed and fertilized plots by Biasi et al. (2008). The contribution of lime-derived CO_2 to the total flux is on average 22.3%. Uncertainty in this measure could arise from the fractionation between solid peat and resulting CO_2, or between the lime carbonate and the resulting CO_2. A substantial fractionation between carbonate and the resulting CO_2 has been inferred in soils at higher pH and with significant HCO_3^{-1} leaching (Schindlbacher et al., 2015) but, we argue that at lower pH and with no HCO_3^{-1} leaching in our closed incubation, fractionation of carbonate from dissolution and exsolution would likely be either neligible or similar to the fractionation that occurs in biotic respiration. However, even if the most extreme value of the fractionation value of 12‰ were to be considered in this study (Schindlbacher et al., 2015), on average it will alter the fractional contribution of carbonate from 0.22 to 0.39. In this scenario, the average biotic emission for growing media will decrease from 0.15 to 0.11 mg CO_2-C g org C^{-1} d^{-1}, but still validate our results that emissions for growing media almost twice as high as that for peat. Therefore, even while accounting for the uncertainties associated with lime-derived $\delta^{13}CO_2$, we demonstrate that without partitioning the total flux into peat-based and lime-based, emissions from growing media would have been overestimated.

The measurements of at least twice as much biotic CO_2 emissions for growing media compared to peat might be due to the indirect influence of additives that increased the pH and lowered the C:N ratio (Figures S1 and S2 and Table 3) and availability of DOC and TDN (Figure 1 and Figure S3). These soil properties have been shown to impact microbial structure and activity, which in turn control the decomposition rate (Ren et al., 2018). For instance, limed-peat media had a different microbial community structure than unlimed-peat media (Pot et al., 2022) and increased C mineralization as a function of pH (Montagne et al., 2015). Thus, increase in pH following liming been shown to increase respiration rates and microbial activities in incubation samples where lime was applied in field conditions (Andersson & Nilsson, 2001; Andersson et al., 2000). In addition, the direct contribution of added lime-derived CO_2 has also been demonstrated even after several years of lime addition (Biasi et al., 2008). After portioning lime-derived CO_2, the biotic emissions from growing media in our study (0.05 to 0.32 mg CO_2-C g org C^{-1} d^{-1}) fall into the range of what has been reported for disturbed agricultural peatlands (0.012 to 0.57 mg CO_2-C g C^{-1} d^{-1} by Säurich et al. (2019)). Incubation at 20°C of peat from a forest, cropland and grassland in Switzerland which has comparable pH, SOC and C:N ratio as to our study report an average emissions of 0.18 mg CO_2-C g C^{-1} d^{-1} (Cédric Bader et al., 2018). Even though the biotic peat-based emissions are twice as large for growing media than for peat, current IPCC reporting (Eggleston et al., 2006) that 100% of peat extracted for horticulture is lost in a single year is over-estimated. For instance, an average 0.45 Mt C per year of peat is removed from Canadian peatlands (Natural Resource Canada, 2022). Assuming a single average value (0.15 ± 0.017 mg CO_2-C g org C^{-1} day^{-1}) for growing media decomposition; extrapolation from our results show that on the first year of extraction, a resulting amount of 0.024 Mt C (95% CI 0.019 to 0.03 Mt) is released back to the atmosphere as CO_2 (Supplementary information, Text C). In the 18,000 ha of extracted peatland harvesting sites in Canada that are under restoration (Environment & Climate Change Canada, 2023), a long-term annual sink of 50 gC m^{-2} yr^{-1} following restoration (Nugent et al., 2019) means that only 0.009 Mt of C is sequestered into the restored peatlands. This amount of C sequestration that happens in currently restored peatlands is lower than what is emitted from peat extracted within a year of extraction (0.024 Mt C). In addition, if we consider the emissions from peat extracted over a longer timescale, the sequestration potential is small compared to the current level of extraction. However, the emissions that we report for growing media could differ once plants are introduced and compared to the after-use conditions to which the growing media is subjected. While the influence of plants could be important in shorter timescales, the after use conditions to which peat is subjected to is important at a longer time-scale. Future work on these topics would be important to further constrain the IPCC reporting to adequately represent horticulture use of peat.

3.5.3 Decomposition and humification indices

There are many different proxies for decomposition ranging from C:N, N, bulk density to $\delta^{13}C$, MIR-derived humification indices and DOC in peat (Biester et al., 2014; Broder et al., 2012; Drollinger et al., 2020; Tfaily et al., 2014). For our original peat, our data similarly indicated that more decomposed peat has larger humification indices, smaller C:N, C and increased N, resulting in a decreased C:N ratio. In contrast, growing media samples did not show such trends (Figure S1 and S2). In addition, correlations between peat properties within peat samples (Table S3) indicate that larger humification index values relate to C:N, C, N and bulk density measurements. However, except for the positive relationship with TDN, none of the variables correlated with $\delta^{13}C$ values in peat samples. This could be because the range of $\delta^{13}C$ values in our study is quite narrow (1.4 ‰) and, in addition, our samples have peat that is sourced from different companies in different geographic locations. Different vegetation that contributed to the isotopic signature may have played a greater role in controlling $\delta^{13}C$ values in our case than decomposition processes (Hornibrook et al., 2000).

Humification indices derived from FT-MIR has been shown to be sensitive enough to detect small changes in peat chemistry that occur in just over 75 days of decomposition (Tfaily et al., 2014). However, larger values in growing media Hi_1 (1420/1090) , Hi_2(1510/1090) and Hi_3 (1630/1090) in our study are potentially due to interactions of carboxyl groups with cations from the added lime (Ellerbrock & Gerke, 2021) and not mainly due to decomposition. Interestingly, lower values of Hi_4 (1720/1090) for growing media can also indicate the influence of added cations in the spectra (Ellerbrock & Gerke, 2021): The band at 1720 cm^{-1} is caused, to a large fraction, by C=O stretching in carboxylic acids and increasing the pH value by adding lime will cause deprotonation of COOH groups and will cause cation exchange of protons for Ca^{2+}, thus converting COOH groups into carboxylate COO^- groups with Ca^{2+} either bound electrostatically or as complex. This causes a decrease in absorption around 1720cm^{-1} (Ellerbrock & Gerke, 2021) and can explains lower Hi_4 (1720/1090) in growing media than in peat. The same mechanism may have caused an increase in absorption around 1630 and 1420 cm^{-1}, causing larger Hi_1 (1420/1090) and Hi_2(1630/1090) in growing media (Ellerbrock & Gerke, 2021). Even if there are differences in the relative amounts of carbohydrates and aromatics, the influence of cations on carboxyl groups is a plausible confounder which will hamper the interpretation of humification indices in decomposition between peat and growing media. However, the patterns in Hi_1 (1420/1090) , Hi_2(1510/1090) and Hi_3 (1630/1090) for both peat and growing media suggest that a rough overview of degree of decomposition can be obtained from FT-MIR analysis also for growing media, although changes over time in incubations are obscured.

3.6 Conclusion

We characterized the biogeochemical properties of peat and compared them with growing media across their different grades. Horticultural additives of lime and inorganic fertilizers in the growing media caused marked differences in their pH, bulk density, C:N, DOC and TDN. Due to favorable changes in the environment for microbes from liming, addition of fertilizers and direct chemical dissolution of carbonate-based additives, we measured twice larger CO_2 emissions from growing media than for peat. Even after accounting for the direct CO_2 emitted from chemical dissolution of carbonates (~22% of the total emission), the indirect effect of horticultural additives caused a doubling of the microbial respiration measured in growing media as compared to peat (0.063 ± 0.004 and 0.15 ± 0.017 mg CO_2-C g org C $^{-1}$ day^{-1}

respectively). This increased microbial respiration observed in growing media could be the result of the sub-optimal conditions of low pH, lack of N and other nutrients in raw peat where decomposition is impeded. Once, these conditions are altered in growing media, increase in CO_2 production is thus expected. FT-MIR based humification indices could not be used to infer on preferential use and loss of different C fractions because of the influence of cations from the added lime on absorbance of molecular structures of the growing media samples. This means that humification indices cannot be directly used to identify difference in decomposition between peat and growing media. However, trends of indices along the von Post gradient for growing media suggest that they could be used to obtain a rough overview on the degree of decomposition of the parent material and its inherent decomposability. While the role of horticultural plants and after-use conditions remain to be assessed our initial extrapolation, assuming the decomposition rate is substrate invariable, suggest that of 0.45 Mt C extracted from Canadian peatlands, ~0.024 Mt C (95% CI 0.019 to 0.030 Mt) is released back to the atmosphere in the first year of extracted peat use.

3.7 Competing interests

The authors have no relevant financial or non-financial interests to disclose.

3.8 Author contributions

Bidhya Sharma designed the study, collected data, ran initial data and wrote the first draft under supervision of Nigel Roulet and Tim Moore. Klaus Holger-Knorr and Henning Teickner contributed to FTIR analysis and to the final writeup of the paper. Peter Douglas contributed to the isotope measurements and to the final writeup. All authors read and approved the final manuscript.

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3. 11 Supplementary information

A. Formulas used for model development.

pH~ Amendment * von_post, weights = varIdent (form=~1|von_post* Amendment)

Bulk density ~ Amendment * von_post, weights = varIdent (form=~1|von_post* Amendment)

LOI ~ Amendment * von_post, weights = varIdent (form=~1|von_post* Amendment)

B. $\delta^{13}C - CO_2$ Measurements

Table S3. 1: Average values (± SD) of $\delta^{13}C - CO_2$ obtained after keeling plot method. Each value is an average of three replicates except for samples 27, 28,29, 51 and 52 for which only two replicates were used as regression coefficient were <0.9. Sample 44 is removed from subsequent analysis as the two sub-samples had regression coefficient less than <0.9.

Sample	Type	Intercept $\delta^{13}C - CO_2$ (‰)	SD (‰)
1	Peat	-26.54	0.37
5	Peat	-29.5	0.24
13	Peat	-25.86	0.01
37	Peat	-25.32	1.12
2	Growing media	-19.06	0.84
3	Growing media	-24.47	0.33
4	Growing media	-20.93	0.18
14	Growing media	-24.48	0.48
15	Growing media	-25.72	0.69
27	Growing media	-23.11	1.36
28	Growing media	-19.42	0.12
29	Growing media	-22.52	1.85
30	Growing media	-21.75	1.67
44	Growing media	-7.44	1.10
45	Growing media	-19.03	0.12
46	Growing media	-19.14	0.58
47	Growing media	-23.21	0.71
48	Growing media	-13.06	0.76
49	Growing media	-25.85	1.74
50	Growing media	-18.10	0.68
51	Growing media	-21.18	0.75
52	Growing media	-19.69	1.00

C. Extrapolation of CO_2 emissions to Canadian scale

Dry peat C extracted in Canada in 2023= 0.45Mt

Average CO_2 emission calculated for growing substrate = 0.15 ± 0.017 mg CO_2-C g org C $^{-1}$ day^{-1}

Decomposition rate (k)value per year= 0.0547 (± 0.0062)

Extrapolated CO_2 emissions for growing media in the first year of extraction

= extracted amount * k value

= 0.024 Mt [95% CI= 0.019 to 0.03 Mt]

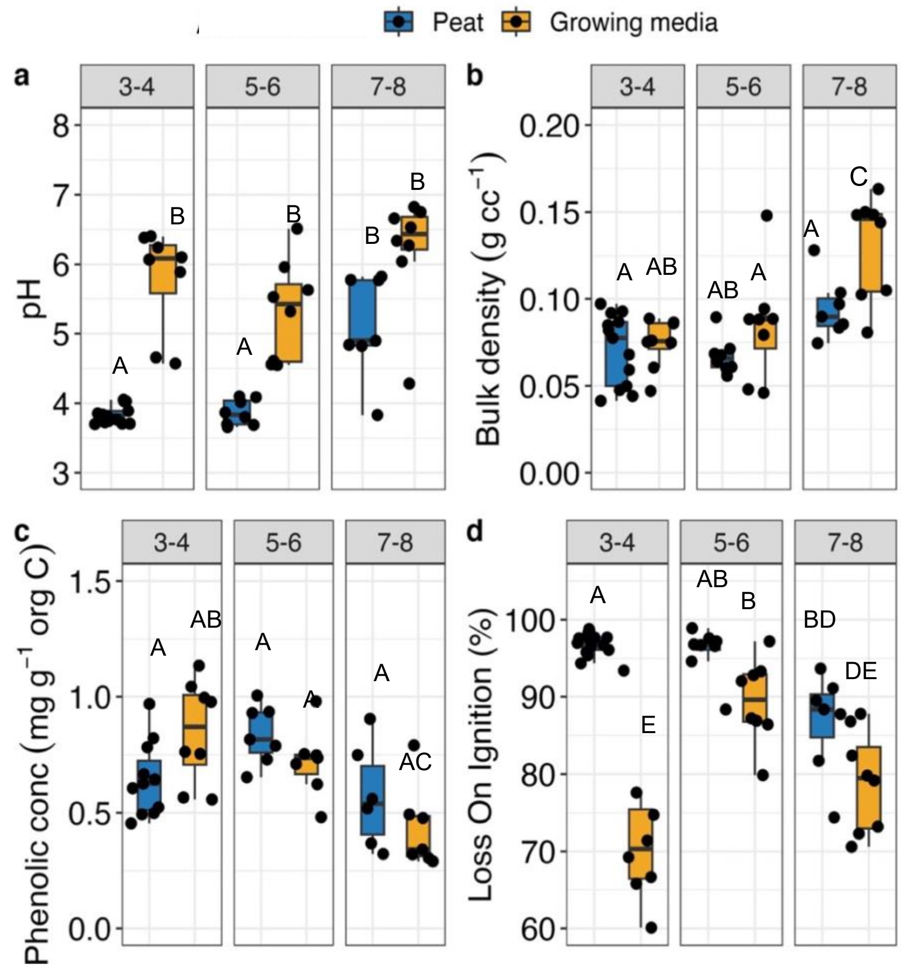

Figure S3. 1: Biogeochemical properties a) pH, b) bulk density (in the bags the samples were shipped in) c) phenolic concentration and d) LOI of peat and growing media classified across different von Post scale values.

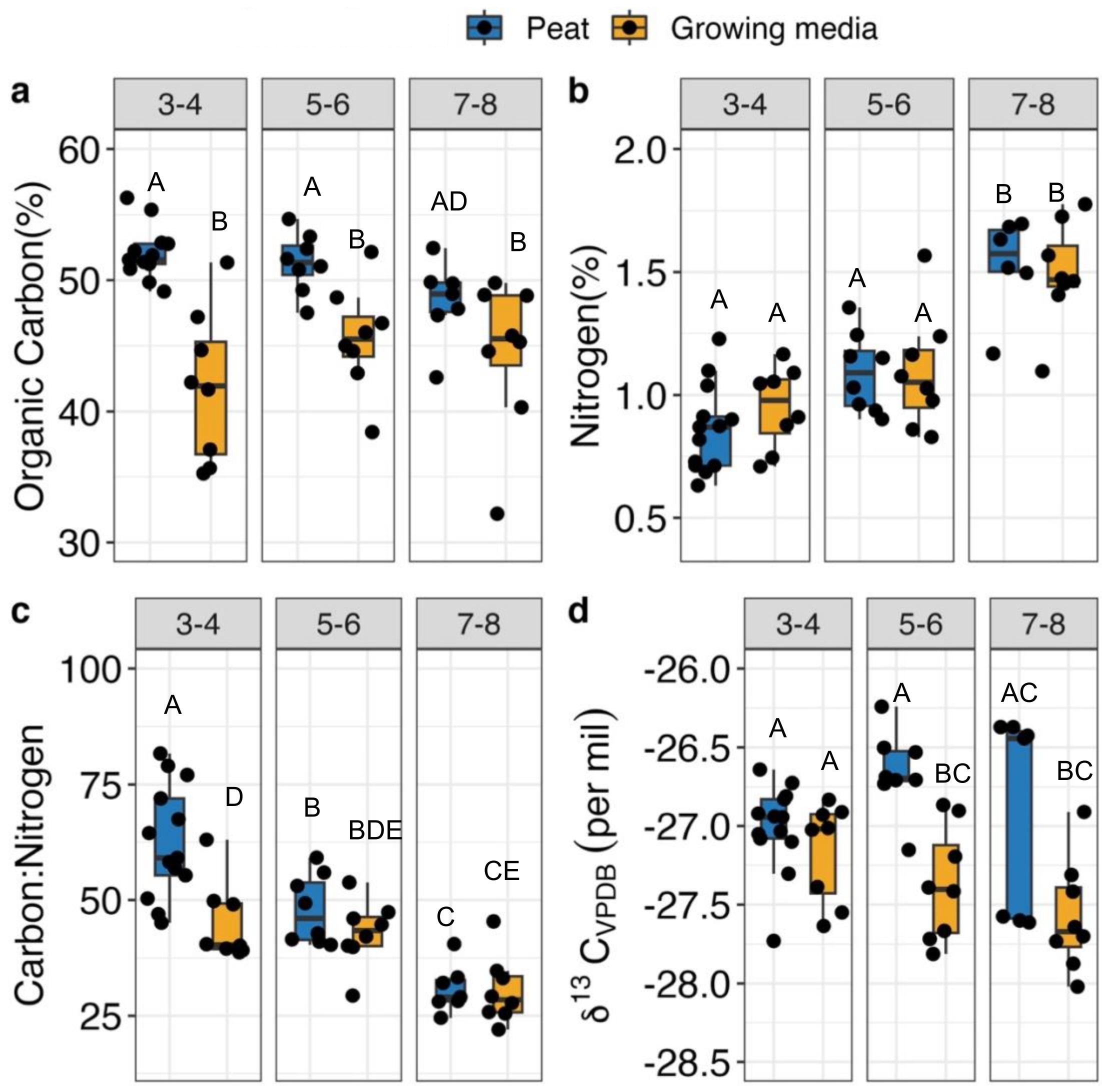

Figure S3. 2: a) Organic carbon (mass-%), b) nitrogen (mass-%), c) C:N ratio (g g^{-1}) and $\delta^{13}C$ values for peat and growing media across different von Post scale.

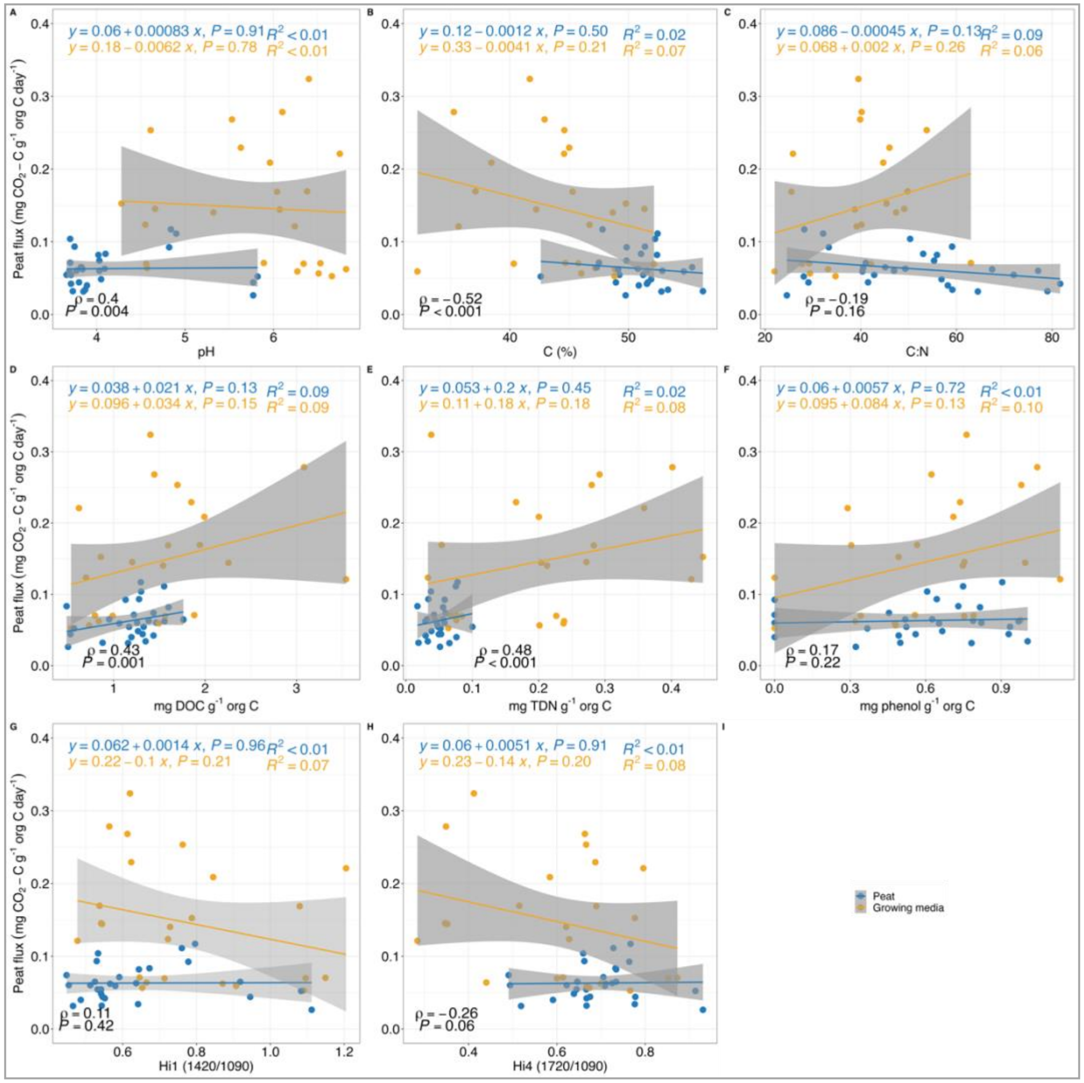

Figure S3. 3: Relations between peat-borne CO_2-C emission with a) pH b) C c) C:N d) DOC e) TDN f) phenolic concentration g) Humification index (1420/1090) and h) humification index (1720/1090). Equation, p-value and R^2 values represent the linear relationship between two variables for subset of peat and growing media. ρ and p-value at the bottom left of the graph represents spearman correlation and associated p-value for the whole dataset. The shaded area around the lines represents 95% confidence interval.

Table S3. 2: Correlation between variables for peat samples only. Symbols of *, ** and *** represent significance level at 0.1, 0.05 and 0.01 respectively.

	pH	LOI	Bulk density	DOC	TDN	DOC: TDN	Carbon	Nitrogen	C: N	Hi1	Hi2	Hi3	Hi4	Phenolic conc.	δ^{13}C- Peat
LOI	-.64***														
Bulk density	0.19	-.46**													
DOC	-0.15	-0.07	-0.04												
TDN	.34*	-0.1	0	0.1											
DOC: TDN	-.47**	0.11	0.04	.41**	-.80***										
Carbon	-0.29	.38**	-0.14	0	-.33*	.37*									
Nitrogen	.40**	-.42**	0.19	-0.3	0.25	-.52***	-.35*								
C: N	-.41**	.42**	-0.14	0.28	-.33*	.58***	.47**	-.98***							
Hi1	.52***	-.74***	.52***	-0.16	0.04	-0.23	-.45**	.65***	-.63***						
Hi2	.55***	-.72***	.44**	-0.17	0.04	-0.25	-.47**	.78***	-.77***	.96***					
Hi3	.53***	-.73***	.48***	-0.17	0.05	-0.25	-.47**	.69***	-.69***	.99***	.98***				
Hi4	.49***	-.71***	.56***	-0.18	-0.02	-0.19	-.37*	.60***	-.57***	.97***	.93***	.95***			
Phenolic conc.	-0.12	0.16	0.05	0.31	-0.18	0.29	0.19	0.04	0.05	0.01	0.09	0.06	0.08		
δ^{13}C- Peat	-0.07	0.09	-0.14	0.31	.37*	-0.14	-0.18	0.21	-0.25	0.08	0.1	0.12	-0.01	0.09	
CO_2 emission	0.05	-0.05	0.19	0.31	0.08	0.11	-0.15	0.24	-0.26	0.09	0.19	0.09	0.06	0.09	.39**

Table S3. 3: Correlation between variables for growing media samples only. Symbols of *, ** and *** represent significance level at 0.1, 0.05 and 0.01 respectively.

	pH	LOI	Bulk density	DOC	TDN	DOC: TDN	Carbon	Nitrogen	C: N	Hi1	Hi2	Hi3	Hi4	Phenolic conc.	δ^{13}C- Peat
LOI	-.64***														
Bulk density	0.19	-.46**													
DOC	-0.15	-0.07	-0.04												
TDN	.34*	-0.1	0	0.1											
DOC: TDN	-.47**	0.11	0.04	.41**	-.80***										
Carbon	-0.29	.38**	-0.14	0	-.33*	.37*									
Nitrogen	.40**	-.42**	0.19	-0.3	0.25	-.52***	-.35*								
C: N	-.41**	.42**	-0.14	0.28	-.33*	.58***	.47**	-.98***							
Hi1	.52***	-.74***	.52***	-0.16	0.04	-0.23	-.45**	.65***	-.63***						
Hi2	.55***	-.72***	.44**	-0.17	0.04	-0.25	-.47**	.78***	-.77***	.96***					
Hi3	.53***	-.73***	.48***	-0.17	0.05	-0.25	-.47**	.69***	-.69***	.99***	.98***				
Hi4	.49***	-.71***	.56***	-0.18	-0.02	-0.19	-.37*	.60***	-.57***	.97***	.93***	.95***			
Phenolic conc.	-0.12	0.16	0.05	0.31	-0.18	0.29	0.19	0.04	0.05	0.01	0.09	0.06	0.08		
δ^{13}C- Peat	-0.07	0.09	-0.14	0.31	.37*	-0.14	-0.18	0.21	-0.25	0.08	0.1	0.12	-0.01	0.09	
CO_2 emission	0.05	-0.05	0.19	0.31	0.08	0.11	-0.15	0.24	-0.26	0.09	0.19	0.09	0.06	0.09	.39**

Chapter 4: Liming increases peat lability by reducing phenolic inhibition and increases CO_2 production in horticultural peat.

Bridging statement to chapter 4

In Chapter 3, we established a difference in CO_2 emissions between peat and growing media. Growing media had two times larger peat-derived CO_2 emissions than raw peat. In addition, chemical dissolution of carbonates caused direct contribution to the CO_2. We demonstrated that measurements of $\delta^{13}C$ of the emitted CO_2 allows partitioning of the total emission to peat-derived and carbonate-based emission. When measuring organic C based emissions in soils that are limed, not partitioning the sources will lead to an overestimation of the decomposition rate. Overall, the differences observed was attributed to horticultural additives. Our samples were a range of products that peat companies produced, but the additives and their amount were unknown to us. Therefore, to explore what additives have the largest impact, we conducted a controlled, factorial experiment combining a range of limestone, NPK fertilizers, surfactant, and perlite. The amounts added mimicked those used by the peat industry. We incubated the different treatments for 120 days and measured the changes in biogeochemical and microbial properties at the end of the experiment. Building on the results and observations established from the first experiment, we continued to measure $\delta^{13}C$ of the CO_2 into the two sources (peat and carbonate). Even after subtracting the direct carbonate-based emissions, added limestone was the largest factor in increasing indirect CO_2 emissions by making the peat more favorable to decomposition but the effect of nutrients, surfactant and NPK fertilizers were limited.

Note: The manuscript for the publication is currently under preparation and we aim to submit it to *Geoderma.*

4.1 Abstract

Peatlands store large amounts of carbon (C) in the form of organic matter- rich peat. Extracted peat is one of the chief growing media used in horticulture. Though peat extraction and its use come with a large CO_2 emission associated with its extraction and use, peat remains essential for use in horticulture. With a lack of feasible and suitable alternatives, its use is likely to rise in the future. While peat is used for horticulture, additives like lime, nutrients, surfactants and perlite are added to make peat conducive to plant growth. The impact of these additives on peat biogeochemistry and C turnover is not well-explored in the literature. In this study, by mixing different horticultural additives to peat, we elucidate the influence of these additives in C losses from peat. 11 different treatments of horticultural additives including the control were added to peat and incubated for 120 days at 23 °C and measured CO_2 production and δ^{13} C – CO_2. At the end of the incubation, we measured the biogeochemical and microbial properties of the peat. On average, over the incubation period treatments lost 0.27 ± 0.71 mg CO_2-C g^{-1} soil d^{-1}. A two-way mixing model using δ^{13} C – CO_2 showed that the total C lost included both biotic and abiotic CO_2. After controlling for abiotic C losses, an average of 0.07 ± 0.06 mg CO_2-C g^{-1} soil d^{-1} was lost from peat among all treatments. Therefore, not including lime-based CO_2 production overestimates heterotrophic soil respiration in limed soils. Over the incubation period, in all treatments, on average 6.86 mg CO_2-C g^{-1} soil was lost from peat for all the treatments. There was a significant impact of treatments on the amount of cumulative biotic CO_2 emission ($F_{1,10}$= 6.83, p<0.001), with limed treatments showing an average of twice the control. In contrast to liming, there was no significant effect of nutrients, perlite or surfactants on total C loss. Limed treatments also show larger Dissolved Organic Carbon (DOC) and smaller

phenolic concentrations, suggesting that reduction in phenolic inhibition and increased DOC availability might have contributed to larger CO_2 losses. In contrast to our expectations, measurements on microbial biomass and hydrolase enzyme activities did not offer mechanistic understanding of nutrient cycling processes in horticultural peat.

4.2 Introduction

Peatlands accumulate partially decomposed organic matter from decaying plant matter and although occupying approximately 3% of the land mass, 20% of the global soil carbon I is stored in peat (Xu et al., 2018). Peat is a crucial component of growing media in horticulture, forming 80% of the growing media in Europe, and its use is important for food production and ornamental horticulture (Alvarez et al., 2018; Barrett et al., 2016; Schmilewski, 2008). Peat extracted for horticulture is a small fraction of the total peat loss in Canada (Harris et al., 2021), but the demand for peat is predicted to increase up to four times in the near future (Blok et al., 2021). An annual average of 1.6 Mt yr^{-1} of peat between the years 2016-2022 was extracted from Canadian peatlands (Natural Resource Canada, 2022). Assuming 45% gravimetric moisture and 50% C fraction in the extracted peat (Cleary et al., 2005), on average 0.44 Mt of C is removed from Canadian peatlands to be used in horticulture every year (Natural Resource Canada, 2022) . The timeframe in which this extracted peat C ends up in the atmosphere as CO_2 has important implications: i) for understanding the C footprint of horticulture and peat extraction industries (He & Roulet, 2023) and ii) for ascertaining the net C recovery period required following restoration of extracted peatland areas (Nugent et al., 2019).

The decomposition of soil organic carbon is complex and is governed by environmental variables and intrinsic characteristics of the degrading material (Blodau, 2002; Davidson &

Janssens, 2006). Peat in natural peatlands has a slow decomposition rate because of interacting conditions of low temperature, anaerobic environment and intrinsic recalcitrance of peatland vegetation (Laiho, 2006). When peat is used in horticulture at warmer temperatures and in aerobic conditions, environmental variables are favourable to enhance decomposition. As peat extracted from bogs can be acidic and nutrient-limited, extracted peat is mixed with several additives (e.g. lime, nutrients, perlites, vermiculite) to make a more favourable environment for plant growth. While the impact of changes in environmental variables on peat decomposition is well-known in the literature (AminiTabrizi et al., 2022; Blodau et al., 2004; Davidson & Janssens, 2006; Pinsonneault et al., 2016b), how horticulture additives impact peat biogeochemical properties and its decomposition is less known.

In a natural peatland, the degree of decomposition of peat is estimated using proxies that range from organic C content, nitrogen (N) content, and C: N ratio to FT-MIR-based humification indices (Biester et al., 2014; Broder et al., 2012; Drollinger et al., 2020; Tfaily et al., 2014). The build-up of phenolic substances in peatlands contributes to the slow rate of peat decomposition (Alshehri et al., 2020; Dunn & Freeman, 2018; Dunn et al., 2013; Freeman et al., 2004), therefore with increased decomposition, the concentration of phenolic inhibitors can be expected to decrease (Naumova et al., 2013; Yule et al., 2016). A reverse relationship could also be true, reduced phenolic concentration could speed up decomposition or vice versa (Dunn & Freeman, 2018). In a natural peatland, a decrease in phenolic inhibitors following a disturbance in peatlands is linked with an increase in microbial extra-cellular hydrolase enzyme activity (Freeman et al., 2004; Min et al., 2015).

Limestone addition to increase soil pH is a common practice in acidic agricultural soils. Liming has been shown to increase microbial biomass and soil respiration (Andersson & Nilsson, 2001) by mobilizing labile dissolved organic carbon (DOC) fractions in soil (Andersson et al., 2000), but no significant increase in soil respiration after liming has also been shown (Biasi et al., 2008; Kunhikrishnan et al., 2016). Previous experiments with adding NPK fertilizers at the ecosystem level in peatlands have shown drastic results in changing the vegetation structure, but the effect on increasing decomposition is mixed and confounded with the changes from vegetation structure that affect the peat biogeochemistry (Biasi et al., 2008; Li et al., 2022; Moore et al., 2019). Surfactants are added to peat to decrease peat hydrophobicity and perlite, and an inert inorganic component is added to improve aeration and drainage (Barrett et al., 2016). While the impact of lime in microbial processing and CO_2 production is well known, how the combination of other horticultural products affects peat biogeochemistry is less well known.

To address the impact of additives on peat decomposition rates, we incubated peat with different horticultural additives for 120 d in laboratory conditions and measured CO_2 production during the incubations and biogeochemical and microbial properties at the end of the experiment. We hypothesize that the addition of nutrient, limestone and their combination i) increases peat-derived respiration over the incubation period, ii) increases microbial biomass C and N and consequently hydrolase enzyme activities, iii) increases the labile DOC available at the end of the incubation period and iv) peat will be more decomposed at the end of incubation period as revealed by increased humification indices from FT-MIR measurements and decreased phenolic concentration.

In addition to increased biotic CO_2 production following liming, adding limestone and dolomite compound causes abiotic CO_2 released from the dissolution of the carbonate fraction. Given the difference in the $\delta^{13}C$ of peat (-27 ‰) and lime (−9.6 ‰), measuring the $\delta^{13}C$ in the CO_2 produced allows for fractionating the total CO_2 into two sources using a two-way mixing model (Fry, 2006). In limed peat soils, not accounting for carbonate-based emissions overestimates the peat-derived CO_2 emissions (Biasi et al., 2008).

The findings from this study will enhance the understanding of the decomposition rates and the role of horticultural additives in the C mineralization of peat. As horticultural peat increases in demand, it becomes increasingly important to quantify the CO_2 emissions from its use.

4.3 Methods

4.3.1 Preparation of samples and experimental setup

We obtained horticultural grade peat without any additives sourced from a peat extraction company in Quebec. Large roots were separated, and the peat was stored at 4°C before the analysis. Values of biogeochemical properties before the incubation of peat samples are given in Table 1. We placed 3 replicates of 10g-dry weight samples of the peat per treatment into mason jars. Equal amount of water was added to each replicate to bring the volumetric water content to 50%.

There are a number of possible combinations of horticultural additives, and we consulted horticultural companies for the most important additives and the range in which they are used. Based on this, limestone to raise the pH, NPK nutrients, surfactant and perlite were chosen as important additives and 10 different treatments were added to the peat. Limestone and perlite were added in the dried form, whereas NPK were added in a solution form. Different treatments and their concentration are show in in Table 4.1.

Table 4. 1: Combination of different treatments and their concentrations.

Treatment	**Peat**	**Concentration**
Control	Peat only	
NPK1	Peat +NPK1	2.5 g kg^{-1} NH_4NO_3 1.16 g kg^{-1} K_2PO_4
NPK2	Peat +NPK2	5 g kg^{-1} NH_4NO_3 3.5 g kg^{-1} K_2PO_4
SF	Peat+ Surfactant	310 ml m^{-3}
PR	Peat +Perlite	25% by volume
L1	Peat + Lime 1	50g kg^{-1} $CaCO_3$
L2	Peat + Lime 2	100g kg^{-1} $CaCO_3$
L_2NPK_2	Peat+ NPK2+ Lime 2	5 g kg^{-1} NH_4NO_3 3.5 g kg^{-1} K_2PO_4 100g kg^{-1} $CaCO_3$
L_2NPK_2SF	Peat+ NPK2+ Lime 2 + Surfactant	5 g kg^{-1} NH_4NO_3 3.5 g kg^{-1} K_2PO_4 100g kg^{-1} $CaCO_3$ 310 ml m^{-3} Surfactant
L_2NPK_2PR	Peat+ NPK2+ Lime 2+ Perlite	5 g kg^{-1} NH_4NO_3 3.5 g kg^{-1} K_2PO_4 100g kg^{-1} $CaCO_3$ 25% by volume Perlite
L_2NPK_2SFPR	Peat+ NPK2+ Lime 2 + Surfactant+ Perlite	5 g kg^{-1} NH_4NO_3 3.5 g kg^{-1} K_2PO_4 100g kg^{-1} $CaCO_3$ 310 ml m^{-3} Surfactant 25% by volume Perlite

4.3.2 Measuring CO_2 production and $\delta^{13}C - CO_2$

We placed three replicates of 10 g-oven dry-weight samples of the peat per treatment into Mason jars and water was added to each replicate to bring the volumetric water content to 50%. Mason jars were closed with parafilm and partially closed with lids to allow gaseous exchange and were incubated for 120 d at a room temperature of 23°C.

Production rates of CO_2 and its isotopic composition were measured on the 1, 7, 30, 60, 90 and 120 d. On the days of sampling, jars were closed with air-tight lids and a short plastic tube fitted with a stopcock valved and sealed with epoxy. Jars were closed for 6 h and sampled at 0, 2, 4 and 6 h, by removal of 5 ml of headspace gas sampled with pre-flushed syringes and needles for measurement of CO_2 concentration, and 25 ml for CO_2 isotopic analysis. To maintain headspace gaseous pressure, 25 ml of CO_{2}- free air was backfilled into each jar after each sample was taken.

The concentration of the gas samples was analyzed in two gas chromatographs (Shimazdu 2014 GHG GC and SRI 8610 C GHG GC) within 5 h of collection. Column temperature and flame ionization detector temperature for SRI were 70 °C and 110 °C respectively and N_2 was the carrier gas. Three standards of 5000ppm CO_2, 20ppm N_2O and 5ppm CH_4 were run before, during and after the gas samples were analyzed. Measurements of ambient air and of the CO_2 standard of 500ppm demonstrated that there was no statistical difference between the two GCs. Dilution in headspace caused due to backfilling of CO_2-free air was corrected for and the CO_2 production values were calculated as a change in concentration over time. To determine

$\delta^{13}C - CO_2$ we used G2201-i Isotopic Analyzer system (Picarro, Santa Clara, CA) with standard to -28.5 ‰ at 850ppm.

4.3.3 Measurement of biogeochemical properties

At the end of the 120-d incubation, pH, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), phenolic concentration and FT-MIR-based humification indices were measured on all the samples. pH was measured in water with a 1:35 dry weight to water ratio. To removed added carbonates, samples were treated in 1M HCl, left in the oven to evaporate and treated with DI water until the pH of the peat and water solution were circum-neutral. 2 mg of powdered HCl-treated samples were mixed with 200 mg KBr (FTIR grade, Sigma Aldrich, St. Louis, MO, USA). Spectra were obtained using a Cary 660 FTIR spectrometer (Agilent, Santa Clara, CA, USA). With a resolution of 2 cm^{-1}, spectra were recorded from 600to 4500 cm^{-1}, baseline corrected (Beleites & Sergo, 2021) and normalized with irpeat package (Teickner & Hodgkins, 2020). Ratios of intensities at defined wavenumbers (humification indices) as described in (Broder et al., 2012) were computed as:

1420/1090 Hi_1: phenolic and aliphatic structures / polysaccharides

1510/1090, Hi_2 : aromatic *C = C* or *C = O* of amides / polysaccharides

1630/1090, Hi_3: aromatic *C = C* and COO^-, protein NH_2 and *C=O* /polysaccharides

1720/1090, Hi_4: carbonylic and carboxylic *C = O* / polysaccharides

To determine concentrations of DOC and TDN, 2 g of sample was mixed with 20 mL of deionized water for 1 h at 200 rpm in a shaker and after filtration with 0.45um Macherey-Nagel filter papers, were determined using a Shimazdu TOC-TN analyzer (Shimadzu Corp., Kyoto Japan). DOC and TDN are expressed as mg DOC or TDN per g soil.

We used a water extraction method for phenolic concentration analysis, similar the method described by (Chantigny, 2003). 5 g of the incubated sample was mixed with 40 mL of DI water in a 50 mL centrifuge tube and thoroughly mixed by shaking for 24 h at a speed of 200 rpm. Afterwards, samples were centrifuged at 5000 rpm for 30 minutes on a Sorvall ST16R centrifuge (Thermo Fisher, Altricham, UK). The samples were then filtered through $0.45\mu m$ Macherey-Nagel filter papers and analyzed for phenolic using a method adopted from Box (1983). In a separate 2 mL centrifuge tube, 1 mL of sample was added, followed by 50 µL of Folin-Ciocalteau phenol reagent and 0.15 mL of Na_2CO_3 (g L^{-1}) to buffer the reaction. A range of standards of phenol compounds between 0.5 to 30 mg L^{-1} was prepared in the similar way. After 1.5 h, $300\mu L$ of each sample and the standard were transferred to wells of a clear 96-well microplate. Absorbance was measured at 750 nm on a Spectramax M2espectrophotometer and converted the values into phenol concentration mg phenol g^{-1} soil mass.

4.3.4 Exo-cellular enzyme activity and microbial biomass

We determined extracellular hydrolase enzyme activity to establish the changes in microbial activity from substrate availability across treatments. We measured the activities of the five key hydrolase enzymes- β-D-glucosidase (BG), β-D-xylosidase (BX), N-acetyl-β-D-glucosaminidase (NAG) and Acid Phosphatase (PHOS). We used the assay protocol used by (Alshehri et al., 2020; Dunn et al., 2013) that utilizes 4-methylumbelliferone (MUF) labeled substrates with slight modifications. Hydrolytic enzymes were measured in peat slurries of 0.5g fresh weight, homogenized with 50mM sodium acetate buffer. Assays were done on the pH of the samples adjusted by adding HCl in the buffer. In a 96-well microplate, peat slurry, fluorescent substrate and MUF standard were added and potential enzyme activity was measured fluorometrically on a fluorometer. Excitation fluorescence was set to 365nm, and the emission intensity was set to 450nm (BioTek Instruments, Winsooki, Vt, USA). Enzyme activity results are presented as an activity nmol h^{-1} g^{-1}. Since a single enzyme activity can influence the cycling of multiple nutrients, we also show total hydrolase enzyme activity which is the sum of all the hydrolase enzymes (Margenot & Wade, 2023).

For measurements of microbial biomass, replicate 1 g samples from each peat were treated with 1 mL of ethanol-free chloroform ($CHCl_3$) for 24 h to kill and lyse microbial cells. A 0.25M K_2SO_4 the solution was used to extract the carbon from fumigated and non-fumigated samples, with extracts filtered (Macherey-Nagel glass fibre filters, 0.4 µm porosity) and measured for dissolved organic carbon and total dissolved nitrogen using a Shimazdu TOC-TN analyzer (Shimazdu Corp., Kyoto Japan). The difference in C and N content between fumigated and unfumigated samples gives an estimate of microbial biomass carbon (MBC) and nitrogen (MBN), expressed in per g organic matter because of differing organic matter content among the samples. An extraction efficiency of 0.45 for MBC and 0.54 for MBN was used as a correction factor (Brookes et al., 1985; Vance et al., 1987).

4.4.5 Calculations and Data Analysis

A two-way mixing model (Estop-Aragonés et al., 2022; Wild et al., 2023) was used to separate peat-derived and carbonate-derived respiration. $\delta\ ^{13}C$ of solid-peat was -27.9 ‰ whereas that of calcium carbonate was -9.6 ‰. These differences in their isotopic signature allowed partioning the sources of CO_2 production (carbonate and SOC). Fractional proportion of the respired peat was calculated by applying an isotopic mass balance using $\delta\ ^{13}C$ of the respired CO_2 mixture, and of the carbonate and peat end members.

$$f_{peat} = \left(\delta^{13}\ CO_2\ measured - \delta^{13}\ C_{CaCO_3}\right) / \left(\delta_{peat} - \delta_{CaCO_3}\right)$$

By multiplying the previously calculated CO_2 production rate with f_{soc}, we obtained the rate of peat respiration in horticulture-amended samples.

4.3.6 Statistical Analysis

All the statistical analyses were carried out in R (Version 4.1.0) (R Development Core Team, 2021) . We used one-way Kruskal Wallis test to understand the influence of the treatments on CO_2 production and biogeochemical properties at the end of the experiment. To identify the treatments that differ significantly from the control we used the Dunnet test. Mean ($\pm se$) are reported else otherwise mentioned. We used non-parametric tests to identify significant differences between groups, because of the smaller samples size that we have. We used scatterplots and Spearman correlation values to establish the associations between variables.

4.4 Results

4.4.1 Initial biogeochemical properties

The initial biogeochemical properties of peat before the incubation are given in Table 4.2. Representative of a bog peat, the initial conditions of peat were low pH (3.9± 0.07) and high C: N (60.81 ± 4.31).

Table 4. 2: Biogeochemical properties of peat samples before the start of the incubation

C (%)	N (%)	C:N	Hi_1	Hi_2	Hi_3	Hi_4	Phenol (mg g^{-1})	pH	DOC (mg g^{-1})	TDN (mg g^{-1})	DOC: TDN

52.17 ± 1.12	0.86 ± 0.04	60.81 ± 4.31	0.46 ± 0.01	0.26 ± 0.01	0.58 ± 0.04	0.53 ± 0.05	0.42 ± 0.01	3.9 ± 0.07	1.42± 1.26	0.29 ± 0.05	4.60 ± 0.68

4.4.2 CO_2 production and δ^{13} C- CO_2

For all treatments, total CO_2 production ranged from 0.013 to 4.85 mg CO_2-C g^{-1}soil d^{-1} following an exponential decay curve with higher values on Day 1 of incubation (1.20 $\pm$ 0.043 mg CO_2-C g^{-1}soil d^{-1}) and lower on day 120 (0.056 $\pm$ 0.0009 mg CO_2-C g^{-1}soil d^{-1}) (Figure 4.1a). On average, over the incubation period L_2NPK_2PR had the highest total CO_2 production (0.79 $\pm$ 0.087 mg CO_2-C g^{-1}soil d^{-1}), and NPK_2 had the lowest average CO_2 production (0.045 $\pm$ 0.001 mg CO_2-C g^{-1}soil d^{-1}).

Measuring δ^{13} C in emitted CO_2 showed that in treatments with added lime, CO_2 was sourced from the carbonate component as well as from peat. δ^{13} C- CO_2 in treatments with no lime ranged from -22.03‰ to -30.04‰, in treatments with lime1 ranged from -10.97 ‰ to -25.86‰ and in treatments with lime2 ranged from -9.82‰ to -27.16‰. In treatments with lime, the δ^{13} C- CO_2 values were more positive at the start of incubation and the value became increasingly negative towards the end of the experiment (Figure 4.1b) as the added carbonate depleted over time. Subtracting lime-based CO_2 values using two-way mixing models gave peat-derived emissions that ranged from 0.013 to 0.48 mg CO_2-C g^{-1}Soil d^{-1}. Peat-derived CO_2 production values in the lime-only treatments also followed an exponential decline (Figure 4.1c), with the highest average values on Day 1 (0.16 $\pm$ 0.003 mg CO_2-C g^{-1}soil d^{-1} and lowest on Day 30 (0.044 ± 0.0006 mg CO_2-C g^{-1}soil d^{-1}). L_2NPK_2PR had the highest average peat-derived CO_2 production (0.13 $\pm$ 0.007 mg CO_2-C g^{-1}soil d^{-1}).

In 120 days, incubation period, across all treatments, an average of 6.86 mg CO_2-C g^{-1} soil of peat-C was respired. and there was a significant difference across treatments ($F_{10, 21}$= 6.83, P< 0.001). On average, L_2NPK_2PR treatment lost the highest amount of peat-C (9.88 $\pm$ 0.15 mg CO_2-C g^{-1}soil), followed by L_2, L_2NPK_2SF, L_2NPK_2SFPR, L_1, Control, NPK_2, PR, SF and NPK_2 lost the least amount of peat-C (4.30$\pm$ 0.23 mg CO_2-C g^{-1}soil) (Figure 4.2). The L_2NPK_2PR lost 64% more peat-C than the control and was the only treatment that showed significant difference from that of the control (t=1.77, p= 0.07). On average, all the treatments with lime2 saw the highest peat-C loss with a mean of 8.55 mg CO_2-C g^{-1}soil, followed by lime1 treatment (7.48 mg CO_2-C g^{-1}soil), whereas treatments with no lime additions lost the least amount of peat-C (6.02 mg CO_2-C g^{-1}soil).

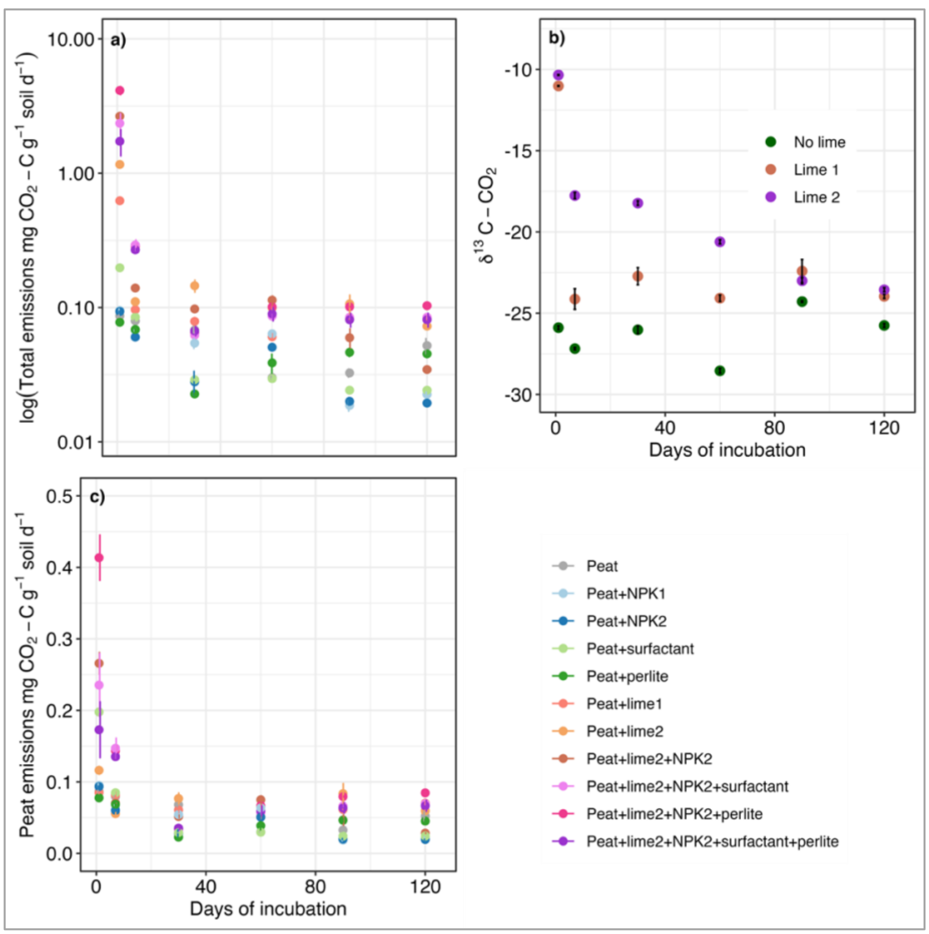

Figure 4. 1: Mean (se) of total emissions, that combines biotic and abiotic CO_2 produced, in a logged scale for all the treatments (a); δ^{13}C- CO_2 measurements over the incubation period for treatments with and without lime additions (b) and peat based biotic emissions only for all the treatments (c).

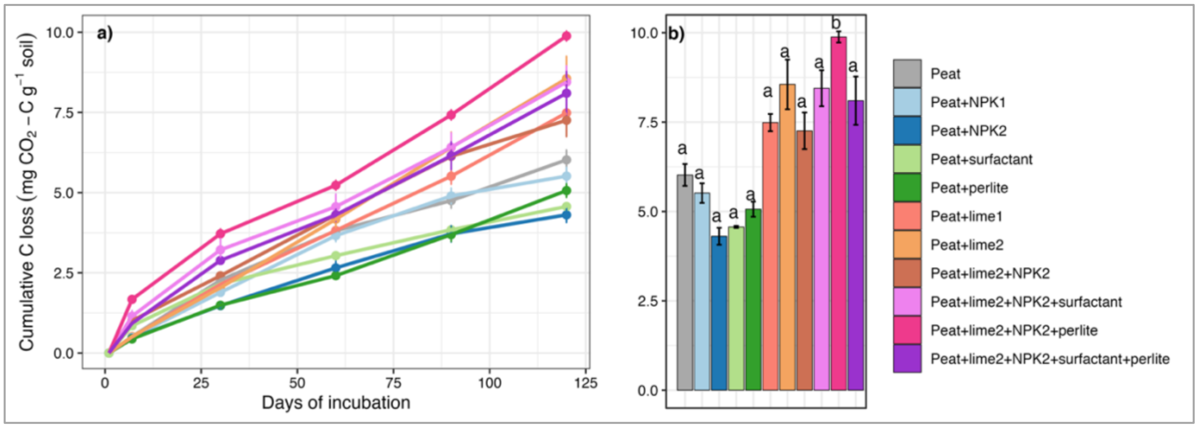

Figure 4. 2: Cumulative peat-CO_2-C production over time (a) and bar plot (mean $\pm$ se) showing total peat-C lost over the incubation period across all treatments, n=33. Different letters denote significant difference with the control at 0.05 level of significance.

4.4.3 Biogeochemical properties

At the end of the incubation period, pH ranged from 3.52 to 6.56. As anticipated, pH with lime2 treatments had the highest pH and the control had the lowest pH value. Correlating final measured pH values with total peat-C lost showed a positive significant relationship ($r_{s=}$ 0.78, P <0.001) (Figure 4.4a). Phenolic concentration varied significantly among the treatments (Table S1) with concentration increasing in the order L_2NPK_2PR > L_2 > L_2NPK_2SF > L_2NPK_2SFPR > L_2NPK_2 > NPK_1 > NPK_2 > PR > SF > control, with the control having twice the amount of phenolic concentration than L_2NPK_2PR (0.43 $\pm$ 0.01 mg g^{-1} soil and 0.2 $\pm$ 0.02 mg g^{-1} soil respectively) (Figure 4.3b).

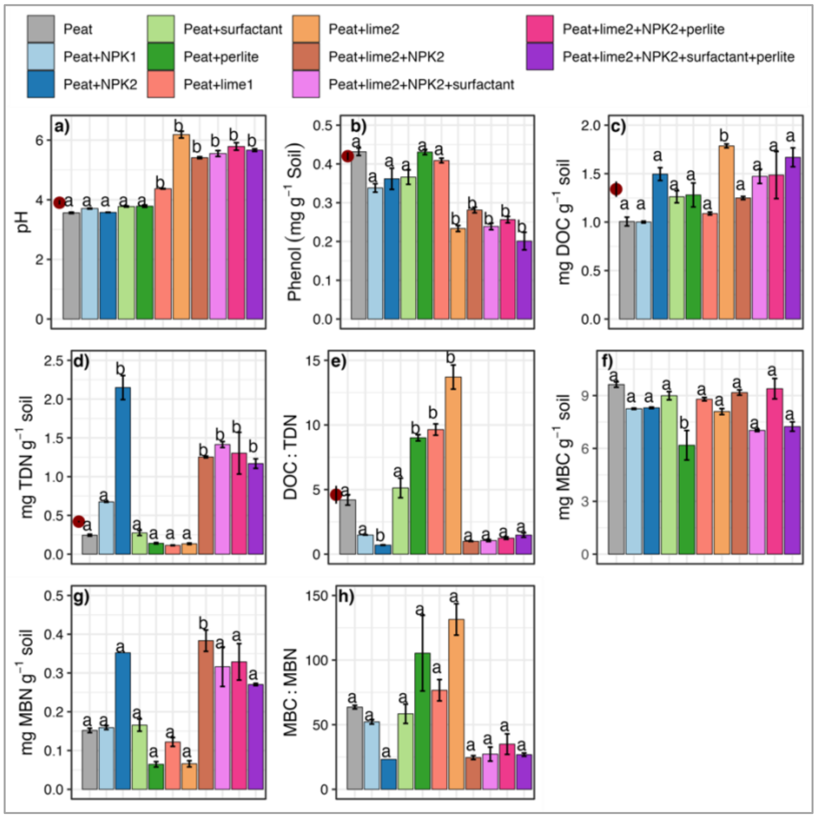

Figure 4. 3: Bar graph (mean +- se) showing a) pH b) phenolic concentration, c) DOC d) TDN e) DOC:TDN, f) microbial biomass carbon, g) Microbial biomass N and h) Microbial biomass C:N. Brown circle denote the values of the variables at the start of the incubation.

Phenolic concentration across all the samples showed a negative correlation with cumulative peat-C lost; that is, samples with larger C loss had lower phenolic concentrations ($r_{s=}$ 0.62, P <0.001) (Figure 4.4b). Compared to before incubation concentrations (1.34 ± 0.08 mg g^{-1} soil), DOC measurements decreased for all the treatments (Figure 4.3c). DOC concentration ranged between 0.83 and 2.27 mg g^{-1} soil, with highest average DOC in L_2 treatment (1.78 ± 0.02 mg g^{-1} soil) and the lowest average DOC in the control and NPK_1 treatment (1 mg g^{-1} soil for both). Results from one-way ANOVA show a significant difference between treatments exists at 0.1 significance level ($F_{10,21}$= 2.24, P= 0.06) (Figure 4.3c) but does not show any clear trends as DOC production and losses would have confounded together masking any discernible patterns. As expected, treatments with added NPK showed higher TDN and lower DOC: TDN values (Figure 4.3d and 4.3e).

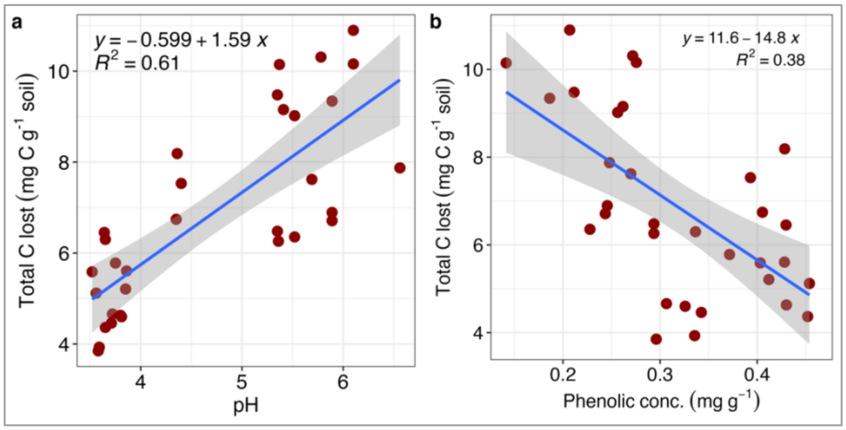

Figure 4. 4: Relationship between pH and total C lost over incubation period (a) and between phenolic concentration and total C lost (b).

4.4.4 Microbial biomass and microbial enzyme activity

MBC was highest for the control (9.63± 0.15 mg g^{-1}) and lowest for PR treatment (6.18 ± 0.83 mg g^{-1}) and differed significantly between treatments (Table S1.1). MBC tended to parallel exo-cellular hydrolase enzyme that act on bioavailable C, as MBC showed positive correlation with both β-D-xylosidase (r_s = 0.43, p= 0.06) and β-D-xylosidase (r_s = 0.49, P= 0.005). MBN was higher for treatments with added N. NPK_1 and NPK_2 had 1.45 and 2.9 times higher MBN than the treatments without the added N. Thereby, a positive strong association between MBN and TDN is observed (r_s=0.74, P<0.001).

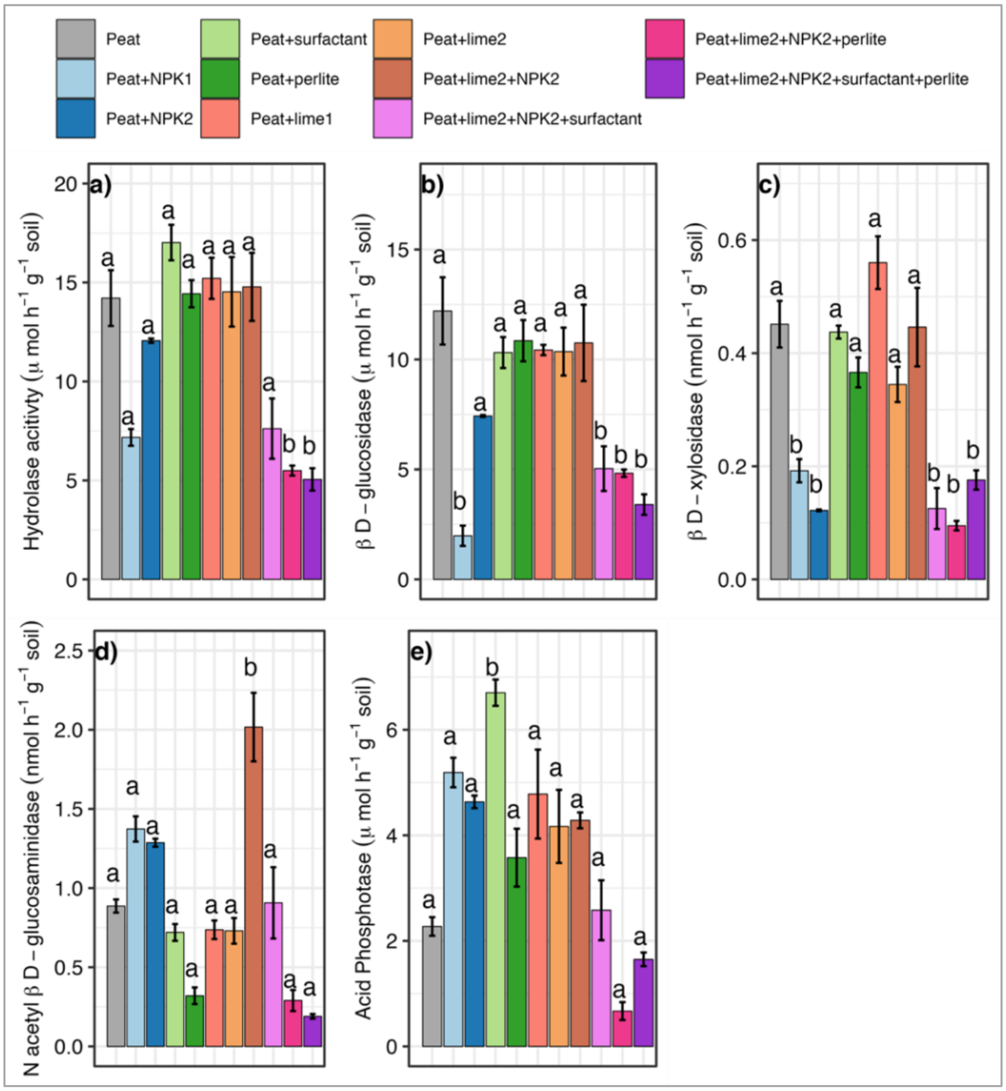

Figure 4. 5: Microbial extracellular enzyme activity across all treatments. Hydrolase enzyme activity is the sum of all the other enzyme activities.

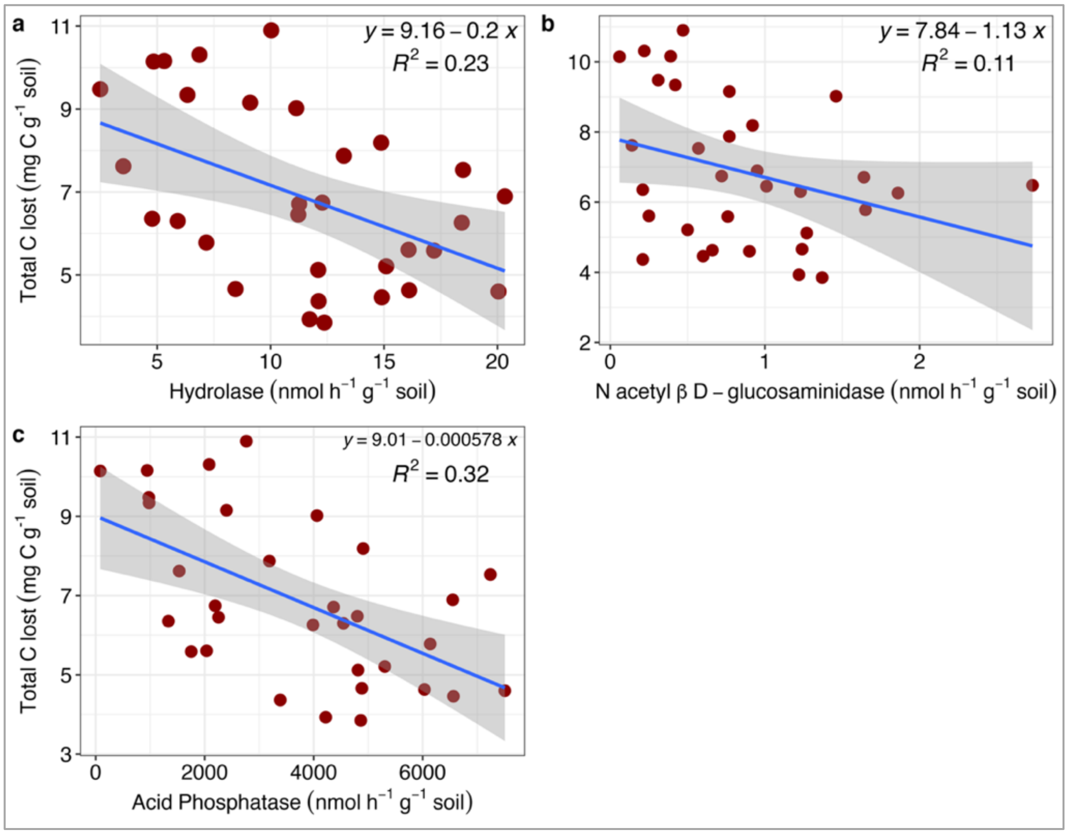

Figure 4. 6: Bi-variate relationship between enzyme activities and total C lost measured over the incubation period.

4.4.5 FT-MIR derived humification indices

The values of Hi_1, Hi_2, Hi_3, and Hi_4 for the raw peat before the start of the incubation were 0.46 ± 0.01, 0.27 ± 0.01, 0.58 ± 0.04 and 0.53± 0.04 respectively. For Hi_1 (1420/1090), Hi_2 (1510/1090) and Hi_3 (1630/1090), treatments with lime alone or lime together with minerals addition showed the highest increase in humification index. In contrast for Hi_4 (1720/1090), the opposite relationship was observed (Figure 4.6d). Across all four humification indices, the addition of perlite decreased the values. Linear relationships between Hi_s and total C lost showed that with higher total C lost, higher the humification index for Hi_1, Hi_2 and Hi_3 (r_s = 0.58, 0.59 and 0.63 respectively, all P <0.001) and higher the total C lost, the lower the Hi_4 (r_s= -0.55, P = 0.001). A similar direction of association between pH and humification indices also exists (Table 4.2). Meanwhile, with measured phenolic concentration, negative associations between Hi_1, Hi_2 and Hi_3 and no statistically significant association with Hi_4, were observed (Table 4.2).

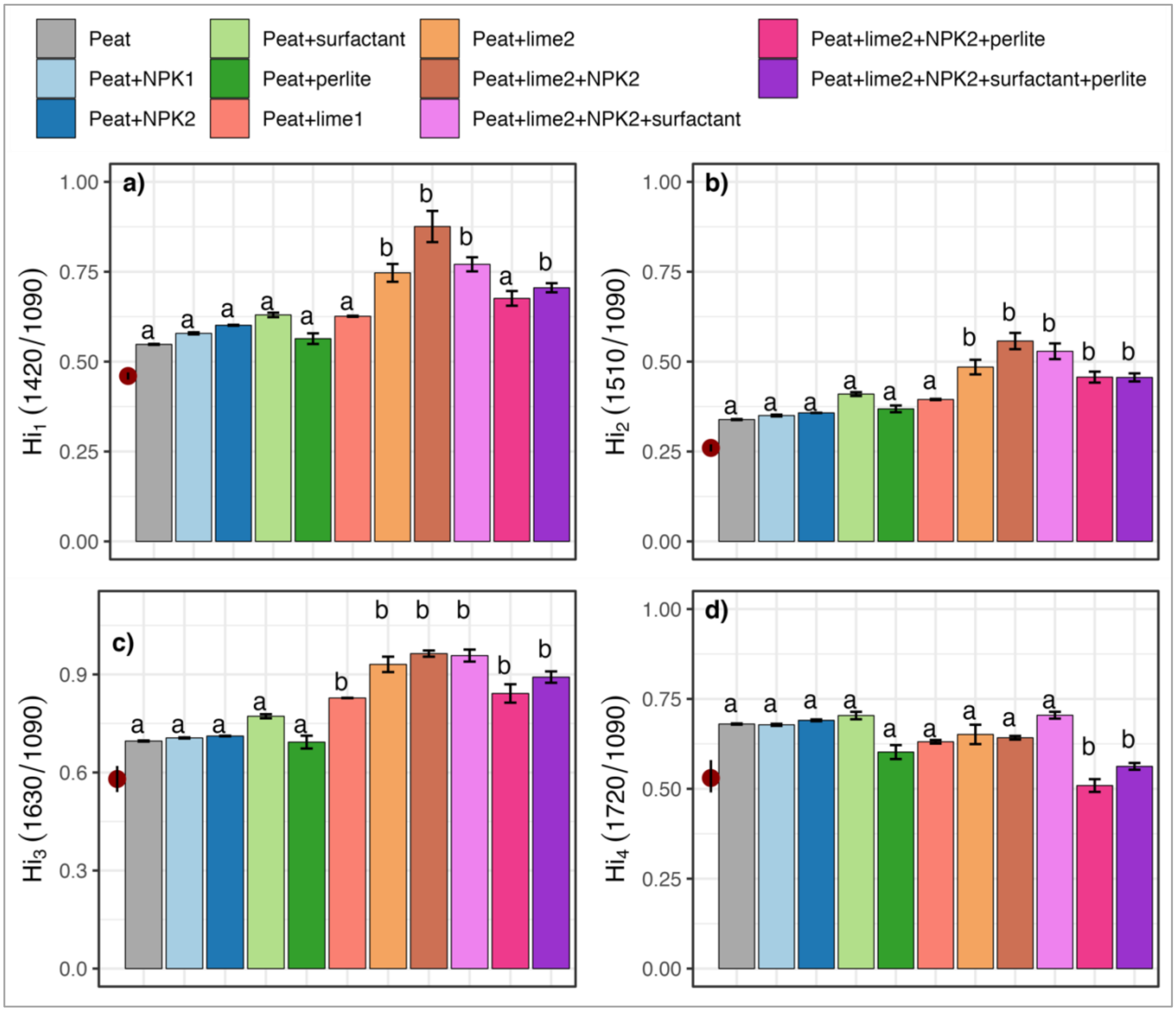

Figure 4. 7: FT-MIR derived humification indices across all treatments. The red dot and the error bar around it represent the mean and standard value for the control before the incubation started. Letters above the bar follow Dunnet test, where similar letter with control denotes no statistically difference with the control (Peat) and dissimilar letter signifies that the particular group is different from the control group.

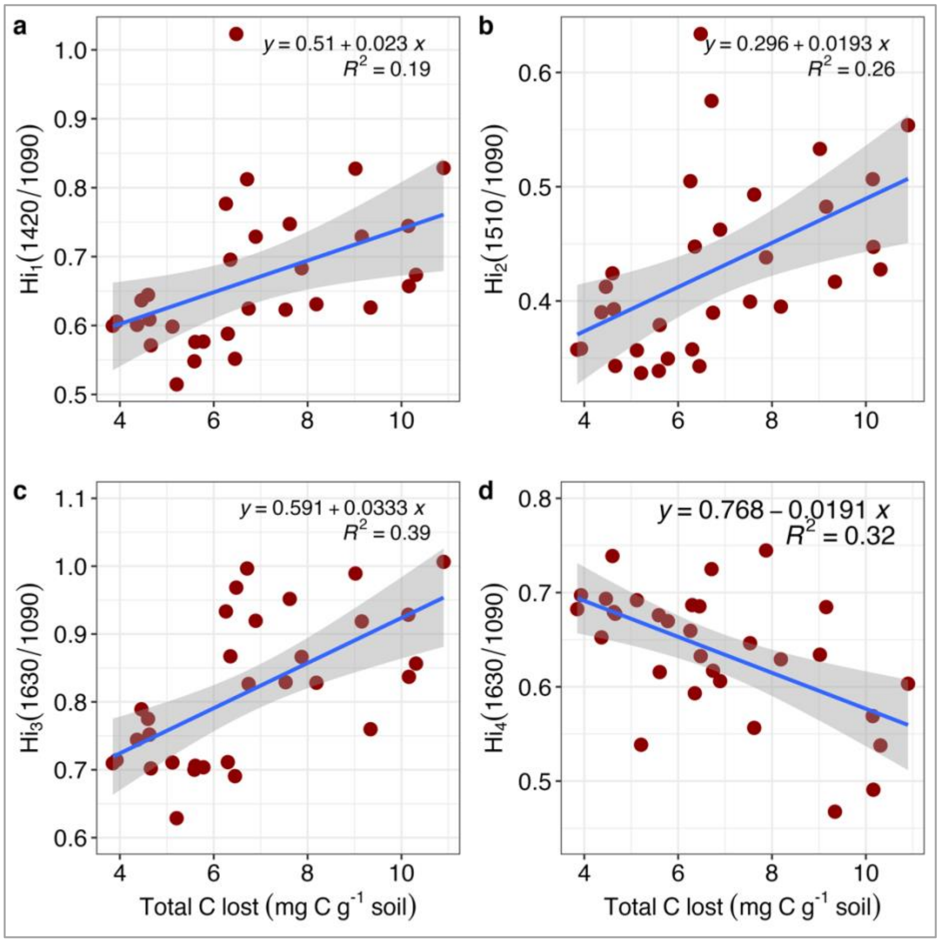

Figure 4. 8: Bi-variate relationship between humification indices and total C lost measured over incubation period.

4.5 Discussion

We investigated how different horticultural additives shift the decomposability of peat C and the effects on total CO_2 production across a 120-d incubation period. We hypothesized that the treatments with NPK, lime2, perlite and surfactants singly and in combination would generate larger total CO_2 production than the peat alone. We predicted that this could happen in two ways. First, total emissions that combine peat-C and carbonate-based CO_2 emissions would be higher than the control. Second, the indirect influence of horticultural additives that make peat-

C more decomposable and as a result peat-C based CO_2 emissions would increase in treatments with horticultural additives.

We found that the response to total CO_2 production differed between treatments; however, the effects of added lime on CO_2 production were the largest in both ways i.e. direct contribution from carbonates as well as increased CO_2 from peat-derived C. Nutrient, perlite, and surfactant additions in peat did not have as significant of an impact as expected. Potentially, as a result of accessibility and increased lability of phenolic compounds at higher pH, treatments with added lime tended to have less phenolic concentration at the end of the experiment. This trend of reduced phenolic concentration was complemented by cumulative peat-C CO_2 production values, as the higher the cumulative peat-CO_2 production, the lower the phenolic concentration measured.

4.5.1 Effect of horticultural additives on CO_2 production

From different horticulture additives, we demonstrate that liming has the most significant effect on cumulative peat-derived-CO_2 production. Building on the existing literature, we show that accounting for lime-borne emissions is important to not overestimate the biotic respiration from peat (Biasi et al., 2008). Through isotopic measurements of δ^{13}C- CO_2 over time, we highlight that the abiotic CO_2 contribution of lime-borne emissions is greatest initially and decreases over time (Figure 1). In contrast to abiotic, increased biotic CO_2 production in limed treatments may persist. For instance, on the 120th day of incubation, average peat-derived CO_2 production for treatments with lime1 and lime2 was 2.22 and 2.07 times higher than the treatments without lime. Other studies observed an increase (Andersson & Nilsson, 2001;

Andersson et al., 2000; Kunhikrishnan et al., 2016) , a decrease and no effect on soil respiration following liming (Kunhikrishnan et al., 2016).

In contrast to the influence of lime, the addition of NPK, had no significant effect on cumulative peat-CO_2 production compared to the control. The limed treatments with NPK, compared to limed-only treatments also did not differ significantly. Previous experiments have also shown that the NPK addition did not influence peat-CO_2 production even at different pH ranges (Li et al., 2022). An experiment at Mer Bleue after long-term fertilization reported slightly more decomposed peat in fertilized plots (increased humification indices based on FT-MIR) even though measurements on aerobic CO_2 production did not seem to be influenced by added fertilizers (Moore et al., 2019).

4.5.2 Biogeochemical properties following the incubation period

Measurements on DOC and phenolic concentration at the end of the incubation period indicates an increase in DOC as compared to the control (in all except NPK_2 treatment) and a decrease in phenolic concentration (across all treatments), potentially suggesting more lability that reduces phenolics suppression with horticulture additives. In line with the measurements of CO_2 production, there is a greater difference for treatments with lime than for nutrients, perlite and surfactant additions (Figure 4.3). Pinsonneault et al. (2016a) measured increased phenolic concentration following nutrient additions at Mer Bleue bog, but in contrast with our study, this increase was attributed to the replacement of moss layers with shrubs that are known to release large amounts of water-soluble phenolics. Lower phenolic compounds are measured with the degradation of peatlands (Yule et al., 2016) and with an increase in the degree of decomposition of sphagnum moss (Naumova et al., 2013). This is similar to our study, where we found that the horticultural additives, mainly lime, is likely to reduce the phenolic inhibition and increase the lability of peat compounds for decomposition. For example, samples with fewer phenolics showed higher DOC measurements, potentially indicating that removal of phenolic inhibition induces lability of peat C. Similarly, the higher the amount of phenolic concentration, a higher the enzyme activity was measured for all the hydrolase enzymes (Table 4.2). This contrasts to the previous findings that showed an increase in phenolics inhibition was associated with a decrease in hydrolase enzyme activity (Alshehri et al., 2020; Dunn & Freeman, 2018; Freeman et al., 2004).

4.5.3 Microbial biomass and microbial enzyme activity following incubation period

Though MBC and microbial enzyme activity varied between treatments, no discernible patterns were observed across the treatments. Correlation analysis showed that the increase in MBC was associated with increased hydrolase enzyme activity (true for all enzymes), though only the relationship with β-D-xylosidase was statistically significant (C. Wang et al., 2021) . Contrary to our expectation and although not statistically significant, all the hydrolase activity was negatively correlated with pH. In addition, N-acetyl-β-D-glucosaminidase did not correlated with increased N availability nor the increased MBN. However, the production of extracellular enzyme activity could be associated with contrasting mechanisms. First, it is unknown if the higher exo-cellular enzyme activity are produced with the availability of nutrients or in response to the scarcity of nutrients (Margenot & Wade, 2023). In addition to the substrate issue, enzyme production is also tightly coupled with pH of the soil (Puissant et al., 2019). We had anticipated that in treatments with horticultural additives would show higher activity, especially in treatments with higher nutrient availability and higher pH, but due to lack of measurements of enzyme activity at different time steps, our study failed to provide a mechanistic understanding of the what the hydrolase enzyme activity measured represents.

4.5.4 FT-MIR based humification indices

Humification indices derived from FT-MIR based spectra have been shown to be an important and sensitive measure to understand decomposition processes in peat with very low mineral interferences (Biester et al., 2014; Broder et al., 2012; Drollinger et al., 2020; Estop-Aragonés et al., 2022). In line with the results from CO_2 production in our study, we found that treatments with higher C loss over the incubation period demonstrated larger values for humification indices (Hi_1, Hi_2 and Hi_3). Theoretically, with a relative decrease in labile carbohydrate and a relative increase of carbonylic and carboxylic C = O, we anticipated increase in Hi_4 values, but our study showed a relative decrease in Hi_4 for most treatments. However, the addition of Ca^{2+} has been shown to decrease the absorption in FT-MIR band around 1720 cm^{-1}, thereby decrease the Hi_4 (1720/1090) value (Ellerbrock & Gerke, 2021). Though the increase in Hi_1, Hi_2 and Hi_3 appears plausible with increased CO_2 production, the potential influence of Ca^{2+} also in 1420 and 1630 cm^{-1} of the spectra cannot be ignored (Ellerbrock & Gerke, 2021). In this case, the confounding influence of increased humification and potential increase in also in absorption around the 1420, and 1630 cm^{-1} band due to Ca^{2+} addition limit our understanding of the decomposition process following the incubation period. However, Hi_1, Hi_2 and Hi_3 all show a positive correlation with total C lost.

4.6 Conclusion

By incubating peat with a combination of horticultural additives, we demonstrated that the additives impact biogeochemistry and C losses from peat. Treatments with increased pH following lime addition showed a decrease in phenolic inhibitors and a subsequent increase in C lability with higher DOC measured. This potentially translated into higher peat-C losses for the treatments with a higher pH. Using $\delta^{13}C$- CO_2 measurements, we demonstrated that the direct influence of limestone on CO_2 production can be considerable in limed soils and needs to be separated to avoid overestimation of soil respiration in limed soils. In contrast to lime, we found little evidence for the impact of inorganic NPK nutrients and perlite and surfactants in peat-CO_2 production. In contrast to our expectations, measurements on microbial biomass and hydrolase enzyme activity did not offer mechanistic understanding of nutrient cycling processes in horticultural peat. Similarly, the influence of Ca^{2+} in FT-MIR spectra could have masked the understanding of enhanced decomposition following incubation among the treatments. With the premise of rising demand of horticulture food production (Schmilewski, 2008) and environmental concerns that comes with peat extraction and use (Alvarez et al., 2018; Cleary et al., 2005), our results show that the some use of horticultural additives increase peat-C losses.

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4.8 Supplementary Information

Table S4. 1: Results of one-way ANOVA testing the effect of different treatments on measured variables. Hydrolase enzyme activity is the sum of four hydrolase enzyme.

Variables	**F** $_{(df1,\ df2)}$	**P-value**
Total C lost	6.80 $_{(10,21)}$	<0.001
Phenolic concentration	11.96 $_{(10,22)}$	<0.001
Dissolved Organic C	2.24 $_{(10,21)}$	0.05
Hydrolase enzyme activity	5.37 $_{(10,20)}$	<0.001
β-D-glucosidase	5.78 $_{(10,20)}$	<0.001
N-acetyl-β-D-		
glucosaminidase	8.42 $_{(10,22)}$	<0.001
Acid Phosphatase	5.42 $_{(10,22)}$	<0.001
β-D-xylosidase	7.81 $_{(10,22)}$	<0.001
Microbial biomass C	2.96 $_{(10,20)}$	0.02
Microbial biomass N	5.32 $_{(10,17)}$	<0.001
Microbial biomass C:N	3.88 $_{(10,17)}$	0.006
Hi_1 (1420/1090)	9.74 $_{(10,21)}$	<0.001
Hi_2 (1510/1090)	11.1 $_{(10,21)}$	<0.001
Hi_3 (1630/1090)	16.36 $_{(10,21)}$	<0.001

Hi_4 (1720/1090)	$7.57_{(10,21)}$	<0.001

Table S4. 2: Correlation table showing associations between variables measured. Significant relationships are shown by *, ** and *** representing significance at less 5, 1 and 0.1% respectively.

	MBC	MBN	MBC: MBN	DOC	TDN	DOC: TDN	Phenolic conc.	BG	PHOS	NAG	BX	Total C lost	Hi1	Hi2	Hi3	Hi4
MBN	.01	-														
MBC: MBN	.25	-.92***	-													
DOC	-.23	.14	-.06	-												
TDN	-.16	.74***	-.69***	.31	-											
DOC: TDN	.04	-.79***	.76***	-.08	-.95***	-										
Phenolic conc.	.25	-.28	.24	-.42*	-.37*	.25	-									
BG	.34	-.40*	.33	-0.1	-.56**	.48**	.44*	-								
Phos	.25	-.21	.23	-0.1	-.29	.23	.39*	.33	-							
NAG	.25	.2	-.19	-.12	.24	-.34	.17	.14	.55***	-						
BX	.49**	-.43*	.47*	-.24	-.66***	.57***	.50**	.72***	.48**	.19	-					
Total C lost	-.21	.16	-.17	.22	-.03	.08	-.63***	-.33	-.54**	-.33	-.24	-				
Hi1	.07	.36	-.29	.46**	.21	-.14	-.75***	-.16	-.16	-.01	-.11	.58***	-			
Hi2	.01	.35	-.29	.44*	.18	-.1	-.76***	-.16	-.2	-.08	-.12	.59***	.98***	-		
Hi3	.05	.29	-.22	.44*	.13	-.06	-.73***	-.14	-.17	-.06	-.1	.63***	.98***	.97***	-	
Hi4	.12	-.07	.05	-.09	.14	-.11	0.29	.2	.47**	.57***	.17	-.55**	-.2	-.24	-.23	
pH	-.24	.15	-.16	.50**	-0.01	.12	-.77***	-.18	-.33	-.28	-.17	.80***	.77***	.80***	.79***	-.72***

Chapter 5: Re-evaluation CO_2 emitted from peat use in horticulture supports the development of lower emission factor in Canada

Bridging statement to chapter 5

In Chapters 3 and 4, we established the decomposition rates of peat-based growing media. While this was important for understanding horticultural peat, its decomposition and mechanistic processes that drive the increased rate of decomposition, it leads to a bigger question of what this means at a larger scale and for future demand of peat.

Currently, IPCC Tier 1 provides 100% loss of extracted peat in a single year as EF for CO_2. This default value is used by Canada to report emissions related to peat extraction. Since the peat extracted in Canada is almost exclusively used in horticulture and peat decomposes slowly that extends over several years, current IPCC EF requires adjustment for the horticultural peat use. Using the results from previous experiments, we upscaled the peat extraction data at a national level to infer the emissions from horticultural peat decomposition. Using the peat extraction amount data available from Canada, we upscaled the emissions measured from growing media to show the historical, present, and future CO_2 emissions for Canada. I show that the peat decomposition is a significant and increasing source of CO_2 at a national scale. Development of It is valuable for Canada to have a Tier 2 EF which tracks residuals over time instead of one large emission in order to get an accurate picture of temporal trends in emissions, as these will have implications for policy and mitigation programs. For instance, implications for C taxation and cap and trade policy. In addition, decomposition of peat occurs at a longer-timescale which means that the emissions from horticultural peat will continue for a long time even if peat extraction were to reduce significantly or stop completely.

Note: The manuscript for the publication is currently under review in the journal of *Carbon management.*

5.1 Abstract

Peat extracted for horticulture is used for growing food, ornamental plants, and soil augmentation globally. In the absence of any other viable growing media available to use in horticulture, peat remains a key component. Peatlands are carbon (C) storehouses, and the disturbance and use of extracted peat in aerobic, off-site conditions have important implications on the accounting of CO_2 emissions for horticultural peat. The IPCC default emissions for use of peat assumes all extracted peat is mineralized to CO_2 in the year it was extracted. This can be applied to peat used for fuel but peat in horticultural use will take many years to decompose. This study aims to use historical and present peat extraction data to calculate a time-integrated emission based on a first-order decay rate peat since 1940; when horticultural peat extraction approximately started in Canada. Our data compilation shows that overall 36 Mt of peat C has been removed from peatlands in Canada with a current extraction increasing at the rate of 10.93Kt/year. Using a first-order decomposition model we calculate approximately 11.86 Mt C (95% CI= 10.69 to 12.71 Mt C) is released back into the atmosphere from the decomposition of the extracted peat between the years 1940-2022. Our estimation is 2.8 to 3.4 times lower than what the IPCC default would suggest for the same time period. Our findings have important implications for comparing peat-based growing media to other alternatives and to carbon taxes that potentially apply to horticultural peat users. Future research could focus on measuring the

decomposition rate of spent peat which could facilitate further constraining of the emission factors.

5.2 Introduction

Pristine peatlands are a small but consistent net carbon (C) sink and over thousands of years, peatlands store ~21% of the global soil organic carbon (SOC) (Yu et al., 2010). Approximately 12% of the global peatland area (381 to 463 M ha) has been degraded due to drainage and land-use change, including peat extraction (Fluet-Chouinard et al., 2023; IPCC, 2013; Joosten, 2010; Leifeld & Menichetti, 2018; United Nations Environment Programme, 2022; Xu et al., 2018). Degraded peatlands are responsible for 4-10% of global annual anthropogenic carbon dioxide (CO_2) emissions (IPCC, 2013). Canada has extensive peatlands cover, ~1.2×10^6 km^2 (United Nations Environment Programme, 2022) and current 380 km^2 of peatlands are drained for horticultural peat extraction (Environment & Climate Change Canada, 2023).

Peat extraction for horticulture involves lowering the water table, removing vegetation and harvesting peat which can last several decades before restoration or natural regeneration starts (Clark et al., 2023). With added nutrients and horticultural additives, peat is an economically accessible growing media (Barrett et al., 2016; Schmilewski, 2008). Currently, an average of 21Mt of horticulture peat is extracted annually in Europe and Russia (Hirschler & Osterburg, 2022). In Canada, from 2019-2021, 1.5Mt of peat is harvested annually (Natural Resource Canada, 2022). While growers and policymakers recognize there is a significant CO_2 emissions related to horticultural, there is still a lack of viable alternatives to replace peat (Hirschler & Thrän, 2023). With the growing extent of controlled environment horticulture and ornamental industry, Blok et al. (2021) estimate the demand for peat extraction is projected to increase by four-fold by 2050.

Emissions for horticultural peat extraction include direct emissions from the extracting field (Clark et al., 2023; He et al., 2023; He & Roulet, 2023), emissions from the equipment used for extraction (Cleary et al., 2005), and more importantly indirect emissions from the after-use of the extracted peat (He & Roulet, 2023) . Data from field measurements have been used for generating emission factors to estimate direct field emissions and are reported annually in the Canada's national greenhouse gas inventory report to the UNFCCC. Emissions from the equipment are also well quantified and reported under the scope emissions. However, there are very few data/estimates for the emissions from the peat after-use, despite the removal of peat C and its decomposition in the off-situ environment are previously reported to be the largest source of greenhouse gas (GHG) emissions for the Canadian peat industry (Cleary et al., 2005). Previous attempts to model the climate impact of peatland restoration on peat extraction sites excluded the C removed from the systems (Nugent et al., 2019). Therefore, knowing the amount of C released from off-site emissions is crucial for improving the understanding of the complete C footprint of horticulture and assessing the restoration success in terms of accounting for the C amount extracted.

Emissions from the peat extraction sector are reported annually in the national GHG reporting of Canada and off-site emissions from peat extraction are currently estimated to account for approximately 75% of the total GHG emissions for the horticultural peat extraction sector (Figure 6-7) (Environment & Climate Change Canada, 2023). According to IPCC, there are generally three approaches (Tiers) to estimate the amount of CO_2 during peat after use in horticulture. The IPCC default Tier 1 (Chapter 7, equation 7.5) which was initially developed for the peat extraction to be used for fuel, assumes 100% of the extracted peat lost in the same year of extraction (Eggleston et al., 2006). Current national reporting for GHG emissions from peat extraction in Canada follows the Tier 1 approach (Environment & Climate Change Canada, 2023). Alternatively, Cleary et al. (2005) used an assumed decomposition rate of 0.05 yr^{-1} to calculate CO_2 from peat use, but did not provide the time-integrated decomposition of peat remaining undecomposed from previous years. Hence, both approaches either largely overestimate or underestimate the C losses from peat in horticulture. More importantly both methods fail to capture the temporal trend of the emissions across the reporting period, which is important from a policy perspective - particularly for Canada in reaching its 2050 net zero climate goals and for capturing the true impacts of avoided conversion or restoration of peatlands in the context of extraction. Sharma et al. (2024) measured the rate of decomposition of horticultural peat with peat substrates from major commercial peat-growing companies in Canada. To the best of our knowledge, this is the first attempt at such measured data. Using the data from Sharma et al., (2024), our objective is to calculate the peat C emissions from peat use in horticulture and compare it with the current default Tier 1 emission factor that Canada uses. Using different future peat demand scenarios, we quantify what the contribution for peat C emissions from peat use in horticulture may look like until 2050.

5.3 Modelling approach

5.3.1 Historical Peat extraction data

The earliest record for peat extraction in Canada was for fuel purposes. From about 1940, the extraction focus shifted to horticultural peat extraction (Keys (1992); (Warner & Buteau, 2000).

However, national-level consolidated data for amount of annual peat extraction is available only from 1990 (Natural Resource Canada 2023). In their review, Warner and Buteau (2000) provide the data on the amount of horticultural peat extraction from 1940 and1945 and Keys (1992) provide additional data for 1985-1990. Based on these three sources, we linearly interpolated the horticultural peat extraction amount between 1945-1990 (Figure 5.2). For all the extracted amounts, similar to Cleary et al. (2005) we assumed extracted peat has 45% moisture content on wet basis and 50% of the peat is C.

5.3.2 Decomposition rate

For Tier 1 CO_2 emissions for peat used in horticulture, we used IPCC defaults of 100% loss in a single year for offsite emissions (Eggleston et al. 2006). We used newly available data for horticulture for peat decomposition rate. This was measured with representative samples from peat extraction companies in Canada over an incubation period of 48h (Sharma et al., 2024). The experiment yielded an average decomposition rate (k) value of 0.054 (95% CI= 0.04 to 0.06) yr^{-1} which we used in the exponential decay equation to calculate the mass remaining after t years of extraction using the formula:

$$M(t)= m_0\, e^{-kt.} \qquad (1)$$

Where,

m_0 is the peat mass extracted in the year

m_t is the peat mass amount that is remaining after t years of extraction.

The difference in mass remaining between two consecutive years would be the C that is emitted in that particular year. We calculated measurements for peat emissions from peat decomposition following the time-integration approach using the formula:

$$Current\ CO_2\ emission = (m_1*(1-k) + m_2*(1-k)^2 + ...m_{n-1}*(1-k)^{n-1})*k + m_n*k \qquad (2)$$

Where,

$m_{1,2,n}$= Dry peat C mass extracted for horticulture use from year 0 to the present year n.

k= decomposition rate

n= number of years since peat extraction

Using recently published data from horticultural peat and accounting for time-integrated decomposition(Figure 5.1), we calculate the off-site mass of horticultural extracted peat C that would be left over at each time step using equations 1 and 2. This includes emissions from the year of extraction as well as the emissions from the peat extracted in previous years. The peat C emissions amount and leftover peat amounts are presented with average and 95% CI around the average (Figure 5.2).

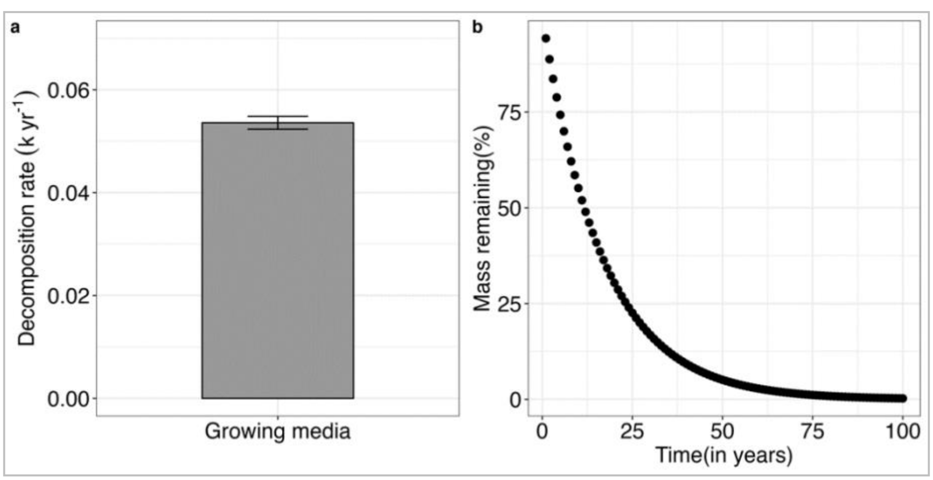

Figure 5. 1: a) Measured decomposition rate from peat based growing media and b) Illustration of decomposition of peat organic C following first order decomposition rate.

5.3.3 Modelling scenarios

To quantify what increased peat demand or policy changes could mean from horticultural peat extraction, we constructed three different scenarios until 2050, the year of Canadian net-zero commitments (Figure 5.3):

a. Four-time increase in peat extraction and use between 2017-2050 (Blok et al., 2021)

b. Business as usual, where peat extraction has increased at the same rate as historical extraction since 1940.

c. Reduction in peat use by 40%, where alternative growing media replace peat in part.

Previous modelling experiments use decomposition as a first-order process where the rate k declines linearly with mass loss. Using Frolking et al. (2001) as shown in equation 3, we applied decreasing k value as a function of initial k value and time.

$$k_t = k_0 / (1 + k_0 * t) \qquad (3)$$

Where,

k_t= decomposition rate after t years of extraction

k_0= initial decomposition rate

t= time of peat C extracted

5.4 Results

Our literature compilation shows that a cumulative total of 36 Mt of peat was extracted in Canada between 1940 to 2022 (Figure 5.2). Using the IPCC Tier 1 approach, current reporting estimates 36.05 Mt of peat C released back into the atmosphere to date. Using the most recent empirical data and considering time-integrated decomposition, we estimate the C release from peat decomposition for the same period to be on average, 11.86 Mt C with 95% CI between 10.69 to 12.71 Mt, the range caused due to the differences in the decomposition rate measured. The difference between Tier 1 and our time-integrated approach is by a factor between 2.8 and 3.4 for the period 1940-2022. It is very important to note that the legacy of CO_2 emissions from horticulturally extracted peat will continue due to the decomposition left over from previously extracted peat (Peat C remaining Fig 5.2 and 5.3 c), even if the extraction of horticultural peat ceases in the future. For instance, in 2022, 6.15 Mt (95% CI 5.3 to 7.32 Mt) of peat C is still left in the biosphere and is actively decomposing.

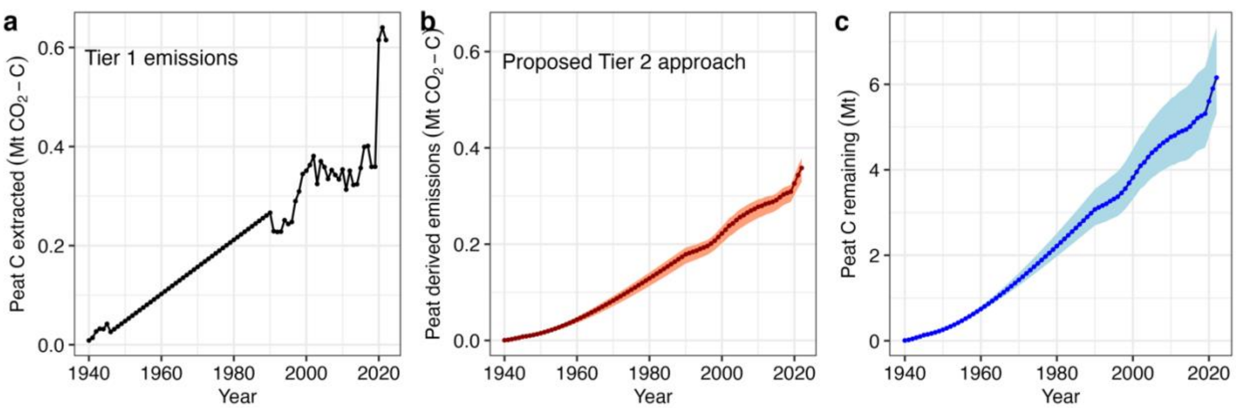

Figure 5. 2: a) Amount of peat C extracted in Canada for horticulture. Current IPCC Tier 1 default suggests all that is extracted is lost within the same year. (b); the amount of extracted peat C emitted back to the atmosphere over time as CO_2 using new decomposition rate and time-integrated method and c) extracted peat C that is left behind over time using the time-integrated method. The shaded region around the line represents 95% CI around the mean value.

CO_2 emissions from peat use are increasing due to the accumulating of peat remaining. In 2022, 0.35 Mt C was emitted during peat use. If the current increase of peat extraction were to continue until 2050, emissions would increase to 0.57 Mt C (95% CI= 0.53 to 0.59 Mt C) in 2050. The 95% CI exists because of the standard error around the average *k* value measured.

Given the premise that the peat demand is increasing rapidly (Blok et al., 2021), increased peat extraction will have significant future climatic repercussions (Figure 2). For instance, using the decay rates from this study above, if peat extraction were to grow as the increase in demand by four times, by 2050, annual emissions will increase by almost twice to 1.08 Mt (95% CI= 0.97 to 1.16 Mt) from horticultural peat decomposition. On the other hand, changes in horticultural practices that reduce the use of peat would be significant in reducing the ever-increasing footprint of peat use. Our analysis shows that an immediate reduction of peat in growing media by 40% means that by 2050, C emissions would decrease to about 0.37 Mt (95% CI 0.36 to 0.38 Mt).

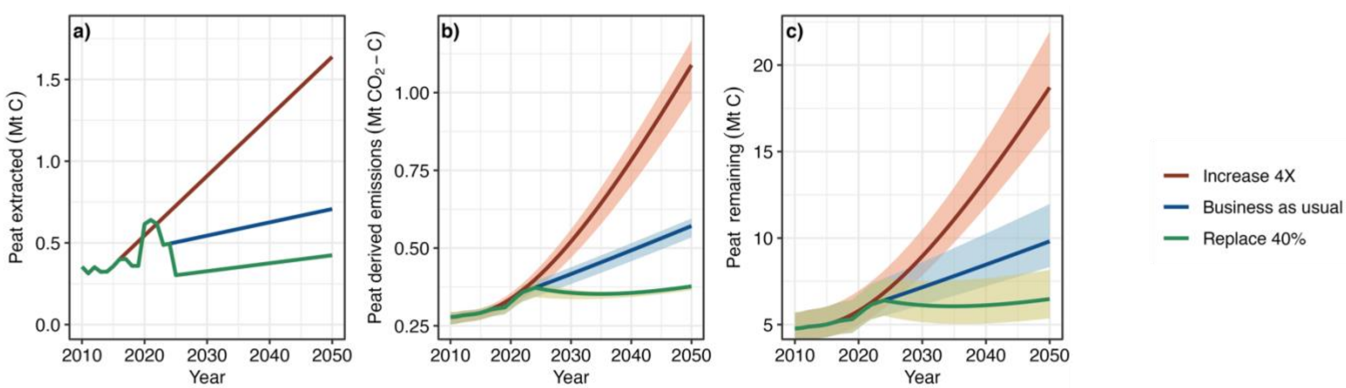

Figure 5. 3: Future peat extraction scenarios (a), C loss from peat decomposition (b) and peat left over in biosphere (c) up to 2050. Shaded areas around the line represent 95%CI caused by the decomposition rate values (0.054, 95% CI= 0.04 to 0.06). Scenario of *increase 4X* is increased demand in peat (Blok et al., 2021). Between 2017-2050, *Business as usual* is based on historical peat extraction and *Replace 40%* is a hypothetical scenario where peat is replaced by other growing media substrate by 40%.

An added scenario of declining decomposition rate with time is shown in Figure 5S.1. The results show that though the emission amount per year from the decreasing k does not change significantly, a larger portion of C is calculated to be left behind each year. In this simulation, in the year 2022, 0.46Mt is emitted whereas 14.7 Mt of peat C is left behind in the biosphere.

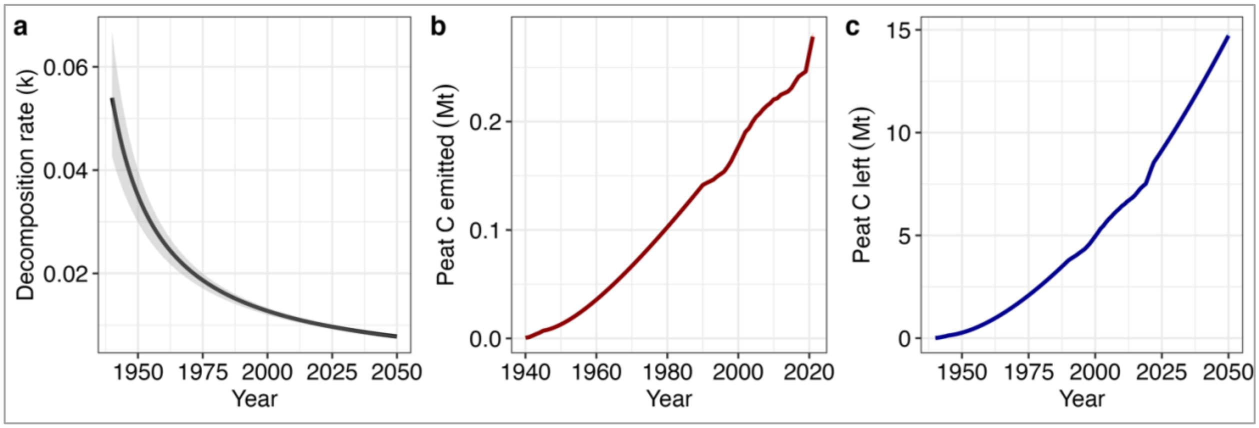

Figure 5. 4: Illustration of a declining k value (a); Peat C emitted using declining k value over time (b) and C left over when using declining k value (c).

5.6 Discussions and Conclusion

We demonstrate the current EF used for extracted peat for horticulture, is largely overestimated within the reporting timeframe because of the mistreatment of horticultural peat as fuel peat and improper accounting of the decomposing peat from previous years. Studies that account for emissions from the field during peat extraction have been important in determining the EFs for the extraction fields (Clark et al., 2023; He et al., 2023; He & Roulet, 2023; Hunter et al., 2024; Nugent et al., 2019). Recent suggestions for Tier 3 EF development for CO_2 emissions from extraction fields estimate 0.03 Mt C per year from 26,000 ha of peat extraction and unrestored sites in Canada (He & Roulet, 2023). The 0.36 Mt C emission per year that we estimate from peat use is an order of magnitude higher than what is attributed to the extraction fields, highlighting that the emission during use is a major source of C emissions for the peat extraction industry. Given the magnitude of C emission from peat products, the adjustments to the Tier of Efs would impact C taxation and cap and trade policy for peat use in horticulture immensely. For instance, the current C price of 65 CA$ per t of CO_2 emitted means that the current EF and the EF that we suggest would result in the difference of annual taxation amount by ~63 million CA$. Furthermore, having more accurate human signal trends is important for mitigation strategies and policy development towards Canada's 2050 net zero goals. While emissions from fields during extraction would be attributed to peat extraction companies in Canada (He & Roulet, 2023; Nugent et al., 2019), emissions from peat use would need to be accounted as downstream emissions- that extend beyond the Canadian national border.

Our analysis shows only in the case of a decrease in peat extraction by 40% and only for a decade, the annual CO_2 emission calculated using the time-integrated method would be higher than the estimated amount from IPCC Tier 1 calculations (Figures 5.3a and 5.3b). This difference occurs as a legacy of peat C accumulated before the hypothetical reduction in peat use. Once the contribution from the legacy peat tapers off, the time-integrated CO_2 emissions from the use of horticultural peat become lower than the amount estimated from the IPCC method.

The extracted peat is primarily used in soil-less cultivation by growers in professional and hobby markets (Schmilewski, 2008) as well as in ornamental horticulture (Alvarez et al., 2018). In addition, the use of peat can be circular (Vandecasteele et al., 2023), where another system could re-use the end substrate from a horticultural system. These multiple possibilities introduce uncertainties in determining the fate of extracted peat C and its emissions as the environmental conditions and the substrate biogeochemistry vary depending on the use and after-use conditions.

In addition, soil C mineralization is a complex measure, with a variety of different kinds of pools having differing decomposition rates, and further compounded by the environmental variables (Davidson & Janssens, 2006; Schmidt et al., 2011). Different measures of substrate quality exist for peat ranging from simple visual classification, C:N ratio, and ash content to spectroscopy-derived humification indices. Generally, lower substrate quality reduced the rate of decomposition (Glatzel et al., 2004; Moore & Basiliko, 2006; Moore & Dalva, 1997; Scanlon & Moore, 2000); however, in disturbed peatlands opposite relationship (Säurich et al., 2019) has also been reported. Since most peat extracted is older there is a narrow range of substrate quality and thus, the decomposition rate did not show dependence on substrate quality or von Post class (Sharma et al., 2024) in our previous study. In any case, in the long term decomposition rate will potentially decrease with decreased substrate availability (Frolking & Roulet, 2007) and our analysis with decreasing k value, did not show much difference in current emissions. However, the fact that leftover peat mass is quite high under this scenario means that the legacy of extracted peat will remain for a long time in the biosphere. Future research in measuring the decomposition rate over a longer period would be important in further constraining the C emissions from peat use in horticulture.

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Chapter 6: GHG emission and carbon balance for lettuce and petunia grown in a peat-based media.

Bridging statement to chapter 6

In the measurements of C losses in Chapters 3 and 4, only peat respiration was considered as the plants were not introduced. Since, peat extracted for horticulture is exclusively used for plant growth, what happens to peat respiration once plants are established in the growing media becomes an important question to answer since roots and exudates have been shown in the literature to affect soil decomposition.

By considering lettuce and petunia, representing food production and ornamental industry respectively, we measured the respiration dynamics over a period of four months in a growth chamber. Using radiocarbon signatures, we measured the role of plant roots in increasing peat respiration. In petunia, we measured an increase in peat respiration because of plant influence, whereas no statistical increase in peat respiration for lettuce was observed. Therefore, we conclude that the increase in heterotrophic respiration by influence of roots could be species dependent. Measured peat heterotrophic respiration rates (without plants) in growth chambers align well with previous measurements and show dependence in temperature and moisture conditions of the soil. In addition, we show that horticultural systems are a small source of N_2O, but CH_4 emissions measured was small and insignificant.

The manuscript for the publication is currently under preparation and we aim to submit it to *Frontiers in Plant Science*.

6.1 Abstract

Peat-based growing substrates are commonly used in plant production, such as within greenhouses and the decomposition of the peat releases old carbon to the atmosphere. The decomposition of peat and respiration dynamics of plants grown in peat mixtures is not well known. We grew lettuce and petunia, representing food and ornamental plant growth, in peat-based media and measured the exchange of carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). We use radiocarbon isotopes to partition ecosystem respiration (ER) into autotrophic respiration (AR) and heterotrophic respiration (HR) and estimate the priming effect of roots to enhance peat HR. Average (± standard deviation) N_2O emissions were 2.69 $\pm$ 3.47 mg N_2O m^{-2} d^{-1}. CH_4 emissions were variable and negligible with average of 0.55 ± 4.66 mg CH_4 m^{-2} d^{-1}. HR measured from peat alone is on average 0.28 ± 0.15 g CO_2-C m^{-2} d^{-1}. Average net ecosystem exchange (NEE) and ER measurements for pots containing lettuce were -1.45 and -0.56 g CO_2-C m^{-2} d^{-1} respectively and NEE and ER for pots containing petunia were 2.14 and 3.10 g CO_2-C m^{-2} $d^{-1,}$ respectively. Without considering the priming effect, HR contributed 9% and 13% to the total ER in lettuce and petunia, respectively. Radiocarbon partitioning of ER revealed that the HR contributes 10% and 18% for lettuce and petunia, showing a statistically significant positive priming effect in petunia but not in lettuce. Biomass C measurement at the end of the experiment showed that the plant assimilated six times more C than lost through HR. But rapid decomposition or consumption of this assimilated C means that horticultural plants are unlikely a sink for atmospheric C. Our measurements provide a basis for reporting of GHG emissions from horticultural plants grown in peat mixtures.

6.2 Introduction

Natural peatlands in the northern hemisphere are a sink of atmospheric CO_2 and have net cooling effect on Earth's climate since their initiation (Frolking & Roulet, 2007). Cold temperatures, water-logged soils and slow decomposition of Sphagnum moss lead to the accumulation of peat over centuries and millennium (Laiho, 2006). Peat is extracted from peatlands, following drainage and removal of vegetation (Waddington & Price, 2000). In Canada, extracted peat is used exclusively in horticulture as substrate for growing plants (Cleary et al., 2005) mostly in controlled environment agriculture (CEA), in greenhouses, and by the ornamental plant industry (Alvarez et al., 2018).

Technological advances in growing food products in controlled environments and increasing fluctuating weather patterns mean that the demand for horticultural practices in CEA is rising, and with it, the demand for horticultural peat (Blok et al., 2021; Schmilewski, 2008). In Canada, on average 0.6 Mt of C is removed from peatlands for horticultural use annually (Environment & Climate Change Canada, 2019). In 2022, CEA, mushroom and specialized greenhouse flower and plant producers in Canada that predominantly use peat as a growing substrate covered an area of 32 km^2 with a farm gate value of over 2.5 billion CAD (Agriculture and Agri-Food Canada, 2023a, 2023b). Significant research exists on the C footprint and mitigation strategies on conventional agriculture in mineral and increasingly in peat soils (Ma et al., 2021; Menegat et al., 2022; Säurich et al., 2019; Taft et al., 2017), and the numbers are well constrained in most of the national inventories. In contrast, research on greenhouse gas (GHG) emissions from CEA is not widely available, and in Canada, except for emissions from limestones and fertilizers, the emissions from the horticulture sector in general are not included in national GHG reporting (Environment & Climate Change Canada, 2023). Measurements of GHG exchanges in horticultural plant cultivation are few and do not address all the respiration components (Marble et al., 2011; Murphy et al., 2021). GHG Emissions Factors (EF) for organic agricultural soil, natural or disturbed peatlands or mineral soils are not likely to reflect emissions from the horticulture peat (due to differences in depth of peat used, nutrient conditions and management practices), there is a need to develop accurate EFs for the horticultural systems. This is reinforced by increasing demand for peat and its importance in food production in many countries (Blok et al., 2021).

When millennial old peat C is used in horticulture it is exposed to aerobic decomposition and released back to the atmosphere as CO_2 through heterotrophic respiration (HR). Once a plant is grown in peat-based media, the CO_2 exchange in full light conditions is the net value (Net Ecosystem Exchange - NEE) of of autotrophic respiration (AR) by plants, HR by soil, and the uptake of CO_2 by plants called gross primary productivity (GPP). During dark conditions, GPP ceases, and ecosystem respiration (ER) is measured which is a combination of HR by soil and AR by plants. In horticultural peat with added limestone or dolomites to increase the pH, the apparent HR measured from soil also includes limestone-derived CO_2 (Biasi et al., 2008; Kunhikrishnan et al., 2016). However, $\delta^{13}C$ tracers can be used to separate isotopically depleted biotic emission from enriched limestone emissions, the total CO_2 values can be portioned into their two sources (Fry, 2006).

Apparent HR can be measured in bare setups without introducing plants in the soil. Subtracting the HR value (measured in the bare setups) from the ER measurements with plants in dark chambers gives a reasonable estimate of AR from plants. However, this largely ignores the role that roots play in enhancing or suppressing the decomposition of soil. This effect is known as the priming effect (Blagodatskaya & Kuzyakov, 2008; Y. Kuzyakov et al., 2000), where root exudates stimulate microbial activity in the rhizosphere and cause an associated increase in the decomposition of the peat. Natural radiocarbon ^{14}C in emitted CO_2 can be used to provide information about the age of soil C and the age of respired CO_2. When used with two sources with differing age, ^{14}C in the emtted CO_2 can be used as a tracer to partition total respiration into two contributing fractions. In a horticulture setting, peat based substrate is old C, whereas fresh plant biomass is a modern C. with a contemporary radiocarbon signature (Torn et al., 2009). CO_2 from setups with plants is a mixture of the two sources, which makes it possible to separate AR and HR from the ER measured. By comparing the calculated HR using the radiocarbon method with the HR measured from bare setup, we can aim to understand the priming effect. Several studies have used isotope-based tracers to understand priming effect in laboratory and field studies to partition respiration sources (C Bader et al., 2018; Biasi et al., 2013; Hicks Pries et al., 2013). In thawing permafrost, Hicks Pries et al. (2013) measured that the AR ranged 40 to 70% of ER and its relative contribution depended on the growing season. Assuming no impact of priming effect in increasing or decreasing soil respiration, in an ombrotrophic bog (Rankin et al., 2023) measured that AR contribution to ER was ~75%.

The primary aim of this study was to quantify and compare emissions of CO_2, CH_4 and N_2O from horticultural systems that use peat-based growing media. Our specific aims were to:

1. Measure respiration components of peat and plants in a peat based horticultural system. To represent different horticultural systems, we selected lettuce, representing food production and petunia, representing ornamental industry.
2. Measure the potential increase in soil HR with the introduction of plants in the soil. We partition total CO_2 measurements into different respiration components and estimate impact of roots in increasing peat HR. We hypothesize that the introduction of horticultural plants in peat based substrate increases HR.

6.3 Methods

6.3.1 Experimental design

We sourced two different horticulture grade peats from Premiere Tech and an equal amount of 220g of oven dry equivalent peat was introduced to 40 experimental pots of 30.5 cm diameter and 20cm height. Peat received in bags had an initial moisture content of ~45% in gravimetric basis. HR was measured in pots containing peat alone (n = 12 for two types of peat). Lettuce and petunia seedlings were obtained from Jolly Farms, New Brunswick, Canada and planted in the experimental pots (n= 28, 7 replicates for two plant types grown in two different types of peat). The experiment was setup in chambers at a temperature of around 23°C, 75% relative humidity, diurnal light schedule of 16 h photosynthetic photon flux density (PPFD) of 300 µmol m^{-2} s^{-1}, and under ambient CO_2 conditions. The experimental period for lettuce was three months and that for petunia and bares was four months.

6.3.2 Chamber setup and CO_2 measurements

We conducted direct CO_2 measurements in the pots using manual chambers. Chambers of 20L volume were put directly on the water-filled plant saucers enclosing the pots, fitted with fan to allow for adequate mixing. Water-filled saucer ensured that the setup was air-tight.

Measurements on CO_2 exchange on the transparent chambers in a full light measurement represented NEE and dark measurements with covered chambers represented ER. Measurements using covered chambers without plants represented HR from the soil. For plant setups, we assumed that the AR= ER – HR.

In all cases, CO_2 concentrations in the chamber were measured every second over a period of approximately 5 min, using an SBA-5 CO_2 gas analyzer (PP Systems, USA). CO_2 flux rates were calculated from the rates of change in concentration within the headspace the volume and areal extent of the chamber and values are expressed in g CO_2-C m^{-2} d^{-1}. CO_2 measurements were carried out at least once every week for the experiment period.

Throughout the paper, a positive NEE value represents a net emission of C to the ecosystem and a negative value represents sequestration of C to the system.

6.3.3 $^{14}CO_2$ isotope gas collection and analysis

On the final day of sampling, we used closed chambers to collect the emitted CO_2 for $^{14}CO_2$ isotope analysis. An opaque 20L chamber was placed on the water-filled saucer and was allowed to accumulate CO_2 for 5 to 30h based on CO_2 emission rates, to obtain sufficient mass of C that allowed ^{14}C measurement. After the period, a pump with low flow rate was used to collect 1-2 L of gas. All the gas samples were sent to the AMS laboratory, University of Ottawa to be processed for ^{14}C analysis.

Radiocarbon analyses are performed on an Ionplus AG MICADAS (Mini Carbon Dating System). $^{12,13,14}C$+1 ions were measured at 200 kV terminal voltage with He stripping. Data is processed using the BATS data reduction software as described by Wacker et al. (2010). The fraction modern carbon, F ^{14}C, is calculated according to as the ratio of the sample $^{14}C/^{12}C$ to the standard $^{14}C/^{12}C$ (Ox-II) measured in the same data block. Both $^{14}C/^{12}C$ ratios were background-corrected and the result was corrected for spectrometer and sample preparation fractionation using the online AMS measured $^{13}C/^{12}C$ ratio and is normalized to $\delta\ ^{13}C$ (PDB). Radiocarbon ages are calculated as -8033 ln (F ^{14}C) and reported in per modern carbon (pMC) as described by Stuiver and Polach (1977).

To determine radiocarbon signature of the respired CO_2 and to partition it to old and new C, we first corrected for the background CO_2 concentration and background $F^{14}C$ signature following (Y. Wang et al., 2021) and used the following equation to calculate the $F^{14}C$ value of the respired $CO_{2.}$

$$F^{14}C_{samp} = \frac{CO_{2ms} \times\ F^{14}C_{ms} - CO_{2bac} \times\ F^{14}C_{bac}}{CO_{2ms-}\ CO_{2bac}}$$

Where, $CO_{2ms\ and}$ CO_{2bac} are the CO_2 concentration at the start and the end of the chamber closure. $F^{14}C_{ms}$ is the measured signature of the emitted $CO_{2.}$ $F^{14}C_{bac}$ is the signature of background CO_2. For the background signature, we used the mean value of -9‰ (pMC= 1.0017) for the year 2022 from Niwot Ridge station (Levin et al., 2023).

For setups with plants, using the isotope signature, we divided the total respiration into AR and HR using two-carbon source model. The measured $F^{14}C$-CO_2 from peat and $F^{14}C$ of background, representing the signature of the plants, were used to calculate the fraction of respiration from peat and from plant using the equal below (Y. Wang et al., 2021):

$$f_{plant} = \frac{F^{14}C_{samp} - F^{14}C_{peat}}{F^{14}C_{bac} - F^{14}C_{peat}}$$

$$f_{peat} = 1 - f_{plant}$$

Where, f_{plant} and f_{peat} are the relative contribution by plant and peat to total ecosystem respiration measured in the setups with plants.

6.3.4 Environmental variables and biomass measurement

We measured temperature and moisture at each pot after taking the CO_2 measurements. Temperature was measured at 15cm from the top. Soil moisture was measured using MP406 soil moisture sensor, ICT International, Australia. Pots were watered every week to volumetric water content to ~30% after taking the CO_2 measurements. In addition, we monitored the plant biomass by measuring height and width of the plant. We complemented dimension measurements with images of plants together with a reference of a known measurement. The number of pixels in the reference were then used to calculate the areal extent, and the biomass of plant using photoshop application. At the end of the experiment, we carried out destructive sampling washed the plant roots and measured the dry mass of overground and underground plant parts.

6.3.5 $\delta^{13}C - CO_2$, CH_4 and N_2O Measurements

On day 50 of the experiment, in the subsamples (n=3 each for peat, lettuce and petunia) we collected gas samples in a closed chamber to determine the δ^{13}C (V-PDB) signature of $CO_{2,}$ and CH_4 and N_2O emissions. 25 ml of sample was taken from the setup at 0, 10, 20, 30, 40 and 50 min. 5 ml of the sample was used to measure $CO_{2,}$ CH_4 and N_2O concentration on a Shimazdu GC-2014 gas chromatograph equipped with a methanizer and flame ionization detector, where N_2 was the carrier gas. The SRI column temperature was 70^oC and the flame ionization temperature detector (FID) was at 110 ^oC. Three to five standards of 5000 ppm, 5 ppm and 20 ppm of CO_2 , CH_4 and N_2O respectively were run through the GC before, during and after the sampling period.

CH_4 and N_2O emission rates emitted were calculated from the rates of change in concentration within the headspace expressed in mass per m^2 area.

For $\delta^{13}C$ determination, the remaining 20 ml of the sample was run through a G2201-i CRDS Isotopic Analyzer system (Picarro, Santa Clara, CA). During each sampling period, two replicate CO_2 standards of 850 ppm and -28.5‰ VPDB and an ambient air sample were run through the instrument. Measurements on the standards had a standard error of < 0.4‰ throughout the sampling period. The Picarro instrument was calibrated prior to the measurement period with two additional isotopic standards (100% CO_2) with $\delta^{13}C$ values of -15.6 and -43.2‰ VPDB (Stix et al., 2017). $\delta^{13}C$ of emitted CO_2 was calculated using Keeling plots, where intercepts were accepted only when the regression coefficient was >0.9 (Keeling, 1958; Pataki et al., 2003).

6.3.6 Statistical analyses

Gas fluxes are reported in mass^{-1}m^{-2}d^{-1}. Statistical analyses were performed using the R statistical software version 4.0.2 (R Development Core Team, 2021). We use linear models to understand the influence of environmental variables (biomass, temperature, moisture) in the fluxes measured. Fit of the models was checked using distribution of the residuals and p-values of the model. Comparison among the treatments was done using ANOVA or T-test. Mean and standard error are reported, else otherwise and significance level of 0.05 is used to establish statistical significance.

6.4 Results

6.4.1 CO_2 exchange

Loss of peat C through heterotrophic respiration (fluxes from bare peat) ranged from 0.05 to 0.55 g CO_2- C m^{-2} d^{-1} (Figure 6.1). HR did not differ between two peat types used in the experiment (t= 0.06, df = 108.65, p=0.94). Linear models indicated that the variations in temperature and moisture explained 14% of the variability observed in the flux measurements. Even in controlled conditions, HR generally increased with warmer measured soil temperature and drier conditions (Table 1). Temperature exerted more influence than moisture conditions (t= 3.35 and -1.94 respectively) in HR measurements.

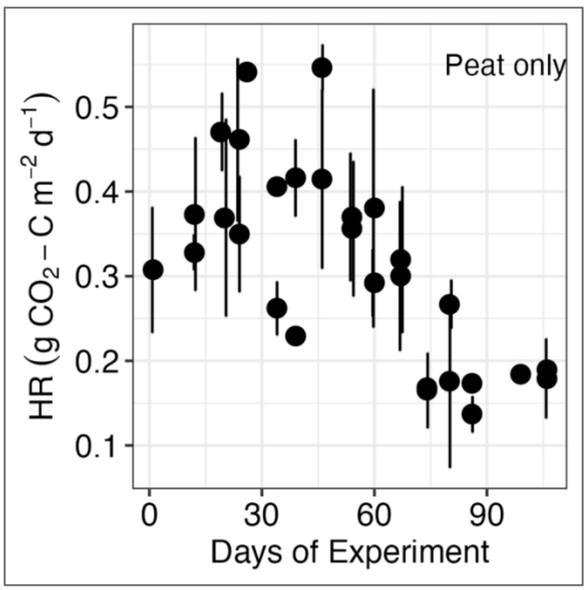


Figure 6. 1: Heterotrophic respiration in bare dark setups without plants. Dots represent mean values (n=12), and error bars represent standard deviation.

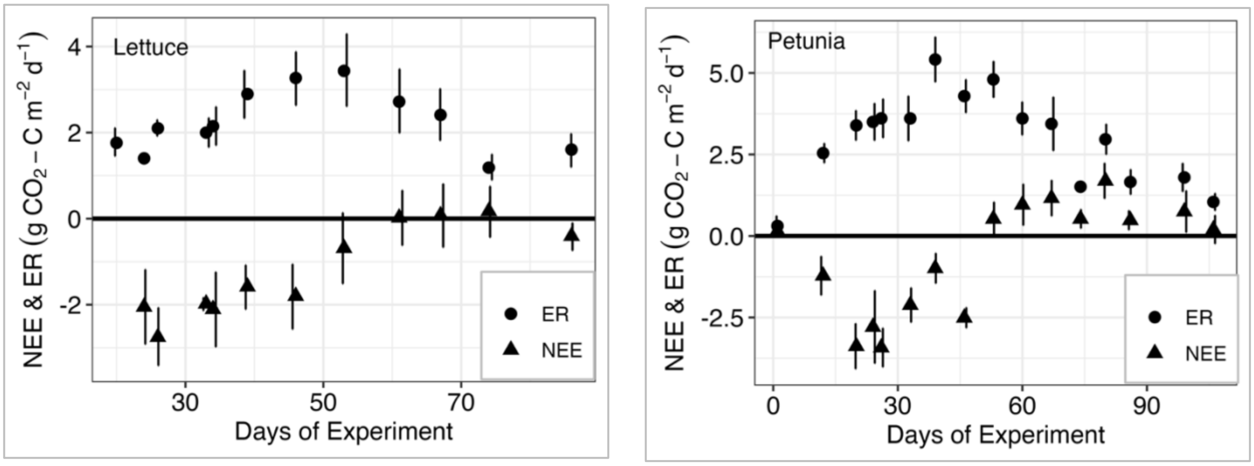
Table 6. 1: Regression results between respiration fluxes and environmental variables. Main and interactive effects between independent variables are denoted by + and * respectively. Interactive effects are shown whenever significant.

Variables	Df	F-value	P-value	R^2
HR-bare				

Moisture + Temperature	2, 84	8.21	<0.001	0.14
NEE-Petunia Biomass+ Temperature	2, 154	109	<0.001	0.58
NEE- Lettuce Biomass + Temperature* Moisture	4, 86	12.28	<0.001	0.33
ER- Petunia Biomass* Temperature +Moisture	4, 146	8.25	<0.001	0.16
ER- Lettuce				

NEE for lettuce and petunia ranged between -3.79 to 2.76 and -4.9 to 2.71 g CO_{2-} C m^{-2} d^{-1} respectively (Figure 2), following the pattern of the plant growth. In both cases, NEE was positive and the system was a net source of C to the atmosphere at the initial growth stage of the plant. As the plant gained biomass, NEE started to drop, and the system became a net C sink. However, as plants reached their full growth potential, NEE again increased above 0 and the system became a net CO_2 source. For Petunia biomass and temperature explained 58% of the variability observed in NEE measurements (Table 1). For Lettuce biomass, temperature, moisture, and the interaction term between temperature and moisture explained 33% of the variability observed in NEE measurements.

ER ranged between 0.84 and 4.81 and 0.08 and 7.25 g CO_{2-} C m^{-2} d^{-1} for lettuce and petunia, respectively (Fig. 2). Biomass, temperature, moisture and an interaction term between biomass and temperature explained 16% of the variability observed in ER measurements in petunia samples (Table 1). Order of importance of independent variables on ER measurements for petunia were the interaction term between biomass and temperature, biomass, temperature,



and moisture (t= 2.63, -2.73, -1.98 and 1.78, respectively). For lettuce, none of the environmental variables measured explained the variability in ER values.

Figure 6. 2: Net ecosystem exchange and Ecosystem Respiration for petunia and lettuce from left to right. Dots represent mean values (n=14) and error bars represent standard deviation around the mean.

Value of measured $\delta^{13}C - CO_2$ signature ranged from -22.08 and -28.21 ‰, with an average of -24.38‰ (Figure 6.3). Kruskal-Wallis test showed that the values did not statistically differ between peat, lettuce, and petunia (K= 1.80, df=2, P=0.4).

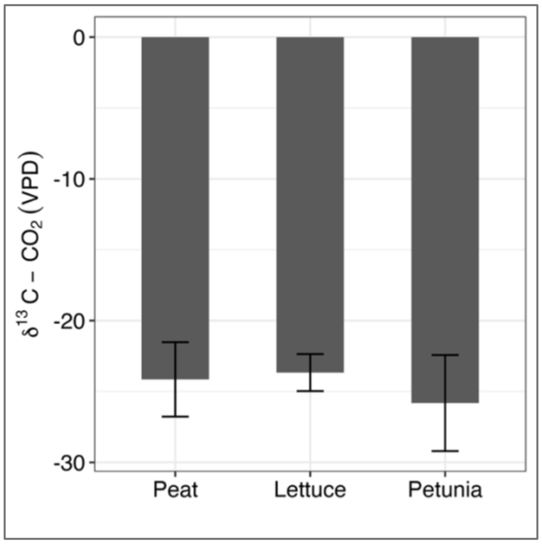


Figure 6. 3: δ^{13}C measurements for peat, lettuce and petunia respectively. n=4 for peat and lettuce and 3 for petunia. One-way ANOVA revealed no statistical significant difference among the three groups.

The radiocarbon pMC of peat was 0.81 ($\pm$ 0.03), and the CO_2 emitted from peat was 0.87± 0.05 The pMC of CO_2 emitted from peat was lower than that from lettuce (0.98 ± 0.003) and from petunia (0.97 ± 0.004) indicating a higher contribution of modern C to the overall CO_2 emissions in lettuce and petunia compared to peat-only setups (Figure 6.4a).

When calculated using a two-component mixing model, peat-derived C contributed an average of 10 ($\pm$3) % and 18 (± 3)% to ER in lettuce and petunia pots, respectively (Figure 6.4b). Peat-derived HR calculated in the lettuce setups was slightly larger but not statistically different than for peat (lettuce= 0.14 ± 0.02 and peat= 0.12 $\pm$ 0.07, P= 0.87), whereas peat-derived HR calculated in petunia was twice that of peat (petunia= 0.25$\pm$ 0.34, P= 0.007) (Figure 6.5).

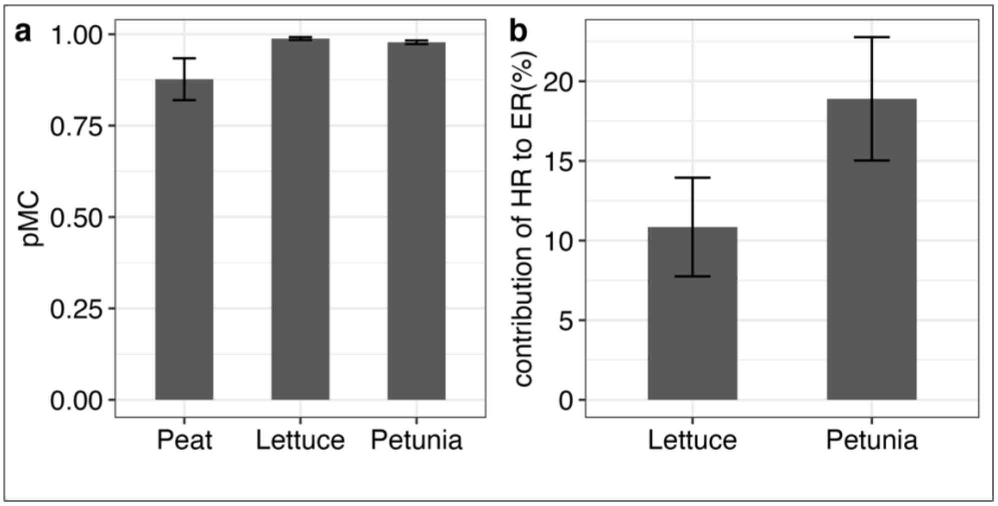


Figure 6. 4: Measured pMC- CO_2 values (a) and contribution of HR to ER for Lettuce and Petunia calculated using two-way mixing model (b) n=6 for each of the group. Errors represent standard deviation around the mean value measured.

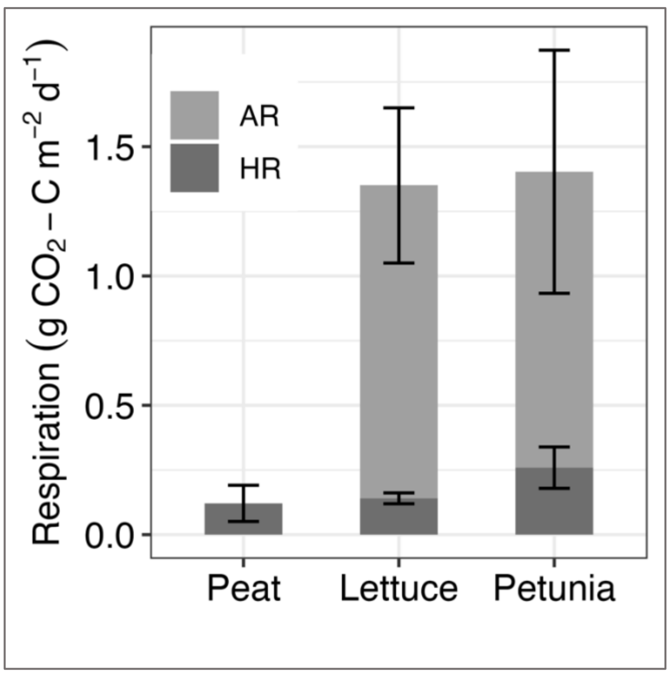


Figure 6. 5: HR measured in peat and calculated contribution of AR and HR to total respiration in lettuce and petunia samples. n=6 for each of the group. Calculations are made using radiocarbon signatures of peat, present day atmospheric signature and the emitted CO_2. Error values represent standard deviation around mean values calculated.

6.4.2 Biomass accumulation

In petunia, total oven-dried biomass accumulated over 120 days was 225 g C m^{-2}, comprising 212 g C m^{-2} in shoots and 13 g C m^{-2} in roots. In contrast, lettuce accumulated over 90 days, 168 g C m^{-2} comprising 153 g C m^{-2} in shoots and 14 g C m^{-2} in roots (Figure 6.7). These plant accumulations contrast with the 26 and 34 g CO_2-C m^{-2} lost from the peat alone, over 90 and 120 days.

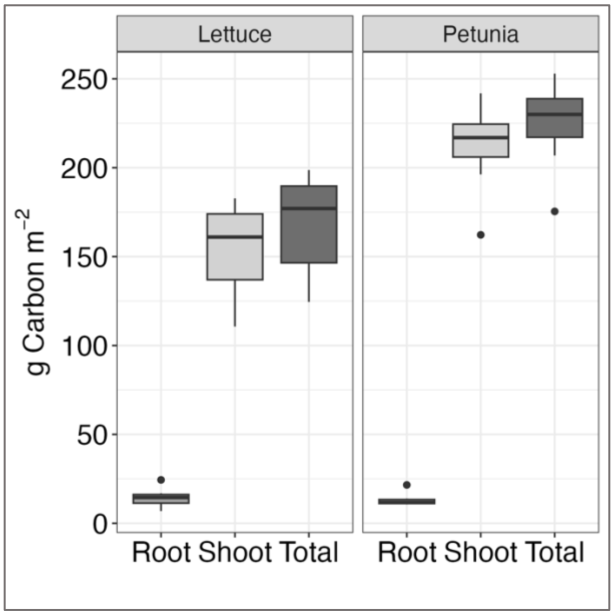


Figure 6. 6: Dry biomass measured at the end of the experiment period (n=4) for each. Carbon is assumed to be 50% of the dry biomass.

6.4.3 CH_4 and N_2O measurements

CH_4 and N_2O exchange measurements showed a large range extending from a source to a sink but did not differ by treatment. Average N_2O measurements for all setup was 2.6 ($\pm$ 3.47) mg m^{-2} d^{-1}, which did not differ significantly between the treatments (K= 2.8, df=2, P=0.2). CH_4 values were 0.55 ($\pm$ 4.66) mg m^{-2} d^{-1} and did not differ between the treatments (K= 1.37, df=2, P= 0.5).

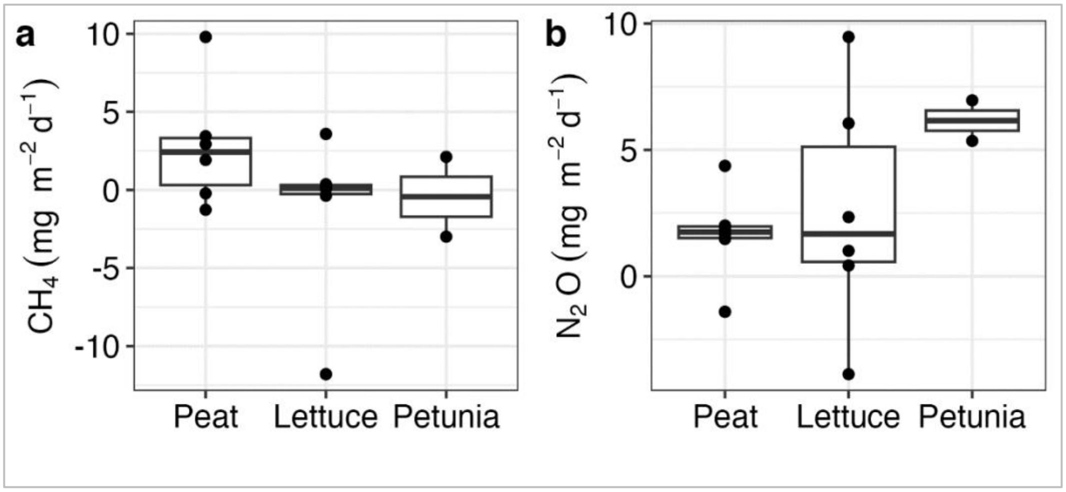


Figure 6. 7: CH_4 and N_20 measurements for different treatments. Measurements of CH_4 are made in mg CH_4 m^{-2}d^{-1} and for N_2O in mg N_2O m^{-2}d^{-} basis. Measurements were done on the day 50 of the experiment.

6.5 Discussion

We investigated the GHG emissions in horticulture plants when peat was used as a growing media by observing flux dynamics of CO_2, N_2O and CH_4 fluxes. We used radiocarbon measurements to separate ER into plant and soil respiration components. We also looked at the potential priming effect in increasing HR by horticultural plants. Finally, we measured the biomass of the plants grown as the fate of the biomass needs to be accounted for in an assessment of the total carbon losses as CO_2 to the atmosphere. Overall, NEE, ER, priming effect and biomass accumulated depended on plant types, whereas N_2O and CH_4 did not vary between the two plants studied.

6.5.1 CO_2 exchange

HR values measured in the peat only bare pots ranged between 0.05 to 0.7g CO_2-C m^{-2}d^{-1}. The measured CO_2 values from peat pots contains both biotic respiration as well as abiotic dissolution of limestone added to raise the pH of the substrate (Biasi et al., 2008). Our previous work in tracking the fate of added limestone over time has shown that the contribution to CO_2 from limestone is largest at the onset of addition and decreases over time. Potentially reflective of diminishing limestone contribution to CO_2 and removal of initial disturbance, CO_2 values from peat show decline after about 70th day. Our measurements on isotopic signature on day 86 for peat showed that the signature was -24.14 ‰, demonstrating a low contribution from carbonates (-0.03‰), and a high contribution to total CO_2 flux from the biotic peat source. Converting the area flux into mass flux, as known amount of peat (~110g C) was introduced in the pots, and assuming an average emission rate from the measured time period; we calculated that the measured decomposition rate for horticulture in one year amounts to 6.6 ± 3.1% of mass loss. The measured value in this study is very close to the earlier measurements of average extrapolated value of 5.4 ± 1.1% mass loss from lab incubations of horticultural peat (Sharma et al., 2024, under review). The slightly higher mass loss in this study could be because the limestone contribution has not been separated, as was done in the previous incubation study. For instance, considering that there is no limestone contribution after day 70 and taking the average value after day 70; the extrapolated yearly mass loss would be around 3.31 ± 1.62%. Previous numerous peat incubations have shown that the temperature and moisture conditions are key controllers in peat respiration (Blodau et al., 2004; Scanlon & Moore, 2000). Though our experiment was run in controlled environment at ~23^{o}C, minor fluctuations in temperature between the sampling plots and moisture explained 14% of the variability measured in HR values from samples. When extrapolating the HR values of average 0.28 ±0.15 g CO_2-C $m^{-2}d^{-1}$ to

32 km^2 of CEA, mushroom, and ornamental production in Canada, we estimate a 3.27 ±1.75 kt of CO_2 emission per year.

Average NEE values of -1.25 (±1.08) g CO_2-C m^{-2} d^{-1} for lettuce and-0.56 (± 1.76) g CO_2-C m^{-2} d^{-1} for petunia. Average ER values for lettuce and petunia are 2.14 (± 0.90) and 3.10 (± 1.33) g CO_2-C m^{-2} d^{-1}. In addition, we establish that the NEE and ER values, when measured with plants in them, differ by plant types as well as the growth status of the plants. During the initial phase of growth, as the plants were vigorously accumulating biomass, both ER and NEE exhibited their highest levels. However, these measurements gradually declined as the plants matured and established stable growth conditions. NEE and ER measurements were a combination of plant respiration depending on the plant growth stage (Van Iersel, 2003), soil respiration, and limestone-derived CO_2. The biomass measurements, temperature and moisture measurements could not always explain the large portion of the variability in the NEE and ER values.

In our study the $\delta^{13}C - CO_2$ signatures did not differ between the three groups, suggesting that by 50th day of the experiment, limestone contribution to total flux had largely diminished compared to what could have been in the initial experiment phase. However, in lack of continuous measurements of the $\delta^{13}C - CO_2$ signature, we failed to document the contribution of limestone-based emission through time.

The Radiocarbon age of peat was old (1737, pMC= 0.81), and so was the CO_2 respired from peat-only setups (pMC= 0.87). Even in peat-only setups, the value of decomposing CO_2 measured was always higher than that of the solid peat, indicating relatively young fraction of peat within the bulk peat was preferentially decomposed over older peat (C Bader et al., 2018; Biasi et al., 2013). The higher modern C fraction in setups with plants (pMC= 0.98) clearly shows that the respiration values are dominated by fresh plants (pMC = 1.0017) and, to a smaller degree, by old C in the peat substrate. While partitioning the total flux into their sources, we measured that plants' respiration fraction is different by plant species, as peat respiration contributed 10% and 18% to the total respiration in lettuce and petunia respectively. Previous studies have also pointed out that the relative contribution depends on plant functional type and abiotic factors (Rankin et al., 2022).

Rankin et al. (2023) and Hicks Pries et al. (2013) measured AR contribution to ER to be about 75% and between 40 to 70%, respectively. in natural peatlands. The larger proportions (82-90%) observed in our study is likely because our measurements were taken at the end of the growing season when plants were fully established, therefore AR contribution to ER would be at its highest (Hicks Pries et al., 2013). Measurements from early in the growth cycle likely could have smaller AR contributions. In addition, compared to Rankin et al. (2023) values from Mer Bleue, that cites a ratio of belowground aerobic peat C to aboveground plant biomass three times as high in this study, a small volume of peat that is contributing to the ER also explains the higher AR contribution to ER in our study.

We also demonstrate that the priming effect, caused by the roots, in increasing heterotrophic respiration was neutral or positive, depending on the plant type and potentially the physiochemical changes that the plants bring about in the soil. In peat studies, positive (C Bader et al., 2018; Basiliko et al., 2012) , negative as well as neutral (C Bader et al., 2018; Estop-Aragonés et al., 2022; Wild et al., 2023) priming effects have been shown previously. Other experiments in laboratory conditions mimicking root exudates have shown that the positive priming effect depends on compound added (Wild et al., 2023), soil type (C Bader et al., 2018;

Wild et al., 2023) among other factors. The differences in root exudates and structure could be the reason for the difference in the effect noted in our study. For instance, petunia roots are known to form a symbiotic association with arbuscular mycorrhizal fungi (Druege & Franken, 2019; Reddy et al., 2009). These fungi form intracellular structures by penetrating the individual cells in the root cortex and form an important role in supplying nutrients to host plants (Reddy et al., 2009). At the same time, arbuscular mycorrhizal fungi are also known to be substantial contributors to total ecosystem flux that rapidly return plant-derived C to the atmosphere (Nottingham et al., 2010). It is important to note that we collected the CO_2 samples for radiocarbon measurements towards the end of the experiment because of the large cost of the isotope analysis. Monitoring the extent of the priming effect through the experimental period could have provided a better understanding of the priming effect in horticultural crop production.

6.5.2 Biomass accumulated

In the experiment period, plant assimilated six times more C than it was lost through soil HR. Larger amount of C accumulation in horticultural plants than that is lost through peat respiration may seem as though horticultural use of peat as a carbon sink. While this may be true in short term, most of the horticulture plants are used for food production or as ornamental plants and their biomass is readily consumed as food or decomposed at the end of the season.

6.5.3 CH_4 and N_2O measurements

Methane emissions from our study (0.55 ± 4.66 mg CH_4 m^{-2} d^{-1}) were low and uptake was also recorded. In cropped peat soils, methane emissions are well documented to be low (Taft et al.,

2017) as soils are well-mixed and not completely saturated creating the conditions needed to support the methanotrophic activity (Mer & Roger, 2001). In addition, the lower and even negative methane that we observed are similar to results from container horticulture CH_4 measurements reported (Marble et al., 2012a; Marble et al., 2012b; Murphy et al., 2019; Murphy et al., 2021).

Except for two measurements, all the treatments were a significant source of N_2O. Values of N_2O emissions in our study (2.69 $\pm$ 3.47 mg N_2O m^{-2} d^{-1} are lower than previously reported for vegetable crops in organic soils in Ohio, average ranging from 40 to 133 mg N_2O m^{-2} d^{-1} (Elder & Lal, 2008), in peat soil in Finland, an average of 14.24 mg N_2O m^{-2} d^{-1} (Regina et al., 2004) and arable peat soil in summer months in the UK, ranging from 58.58 to 132 mg N_2O m^{-2} d^{-1} (Taft et al., 2017). Nevertheless, when comparing our values to horticultural plants grown in containers, the results we report are in general agreement with previously reported values of an average 0.83 mg N_2O m^{-2} d^{-1} in peat-based substrate in annual horticulture species (Murphy et al., 2021) and with an average of 2.23 mg N_2O m^{-2} d^{-1} from pine bark and sand based media (Marble et al., 2012b). We recognize that to track a complete picture of N_2O emission, a larger seasonal or cropping pattern should be accounted for as N_2O peaks have been reported following irrigation (Lloyd et al., 2019), cultivation or management interventions (Elder & Lal, 2008; Regina et al., 2004). Nonetheless, we think these findings are important to further constrain the understanding of overall GHG impact from horticulture, values for which are rarely compared to conventional agriculture. Using the global warming potential of emitted N_2O as 270, the average CO_2 equivalent for our study is 0.73g CO_2- eq m^{-2} d^{-1}. Although the results that we present comes from limited number of samples in limited timeframe, an initial extrapolation to horticulture sector in Canada amounts emissions to 2.33 Kt of CO_2-eq per year.

6.6 Conclusion

We measured the respiration dynamics of two horticultural plants representing food production and ornamental horticulture by measuring ER, NEE, and biomass accumulated. Radiocarbon measurements made at the end of the experiment showed that the HR contributes 10% and 18% to the ER in lettuce and petunia, respectively. The introduction of plants in the peat increased HR in soil, showing a positive priming effect in petunia, but no such effect with lettuce. We anticipate that the measurements on GHG emissions that we report provide a basis for upscaling and reporting emissions from horticulture plants for controlled environment agriculture and ornamental plants.

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Chapter 7: Synthesis, conclusion, and future directions

In less than 3% of the world land area, peatlands store up to one-third of the global soil organic carbon. When peat is extracted for use in horticulture, addition of horticultural additives and exposure to aerobic conditions means that the peat C could be rapidly mineralized. Natural peatlands when undisturbed, on the other hand, are potential nature-climate change solutions as they have net cooling effect in the atmosphere and reduce large potential emissions when avoided conversions. Given that the demand of peat for its use in horticulture is increasing and no viable alternative to completely replace peat is available, quantifying CO_2 emissions from horticultural decomposition of peat is a current necessity. This thesis analyzed the peat-based growing media properties, its decomposition rate, and the emission factors (EFs) from decomposition horticultural peat in Canada. In addition, it quantified the respiratory components once horticultural plants are introduced in the peat. Peat end-use is the largest emission from horticultural peat extraction means that our ability to track anthropogenic impacts on emissions and their trend over time allows to make informed decisions on policy or climate mitigation measures related to peat extraction.

7.1 Chapter syntheses

In Chapter 3, I measured biogeochemical properties and decomposition rate of raw peat and growing media, which is the peat that has been amended with several horticultural additives (for example: limestones, nutrients, surfactants, perlite) to make it optimal for plant growth. Using laboratory measurements and incubations of raw peat and peat-based growing media, I demonstrated that the biogeochemical properties and decomposition rates differ significantly between peat and growing media. Using $\delta^{13}C$- CO_2 as a tracer, I show that the limestone, a horticulture additive, contributes on average 22% to the total CO_2 production measured. After accounting for limestone-based emissions, growing media produces on average twice as much short-term CO_2 emissions as compared to raw peat. The analysis shows that the total dissolved nitrogen (TDN) and pH status that are changed in growing media potentially cause the increased C loss through increased microbial activity. In both raw peat and growing media, there was no evidence that CO_2 production depended on von Post scale of the peat. Our estimates using the findings suggest that of the yearly average 0.45 Mt of C extracted from Canada, around 0.024 Mt C (95% CI 0.019 to 0.030 Mt) is released back to the atmosphere in the first year of extracted peat use. Quantification of the decomposition rate of peat-based growing media will be important in allowing comparisons with alternative growing media that might replace peat fully or partially in future.

To understand which horticultural additives (or combination of additives) play a role in increasing CO_2 emissions in growing media, I conducted a controlled factorial experiment, as described in Chapter 4. In the experiment, using ranges of potential and most used additives (limestones to raise pH, nutrients, surfactants, and perlite); I constructed 10 different combinations of treatments and a control group. Like in the first experiment, I used $\delta^{13}C$- CO_2 as a tracer to tease out the direct contribution of carbonate dissolution to total CO_2 production. I show that the contribution of carbonates to total CO_2 produced is maximum in the first days of mixing and gradually declines over time. In 120 days of measuring decomposition rate, treatments with added lime showed the largest loss of peat C, whereas any effect of other horticultural additives were minimal. In addition, the limed treatment with largest peat C losses were also associated with having lowest phenolic concentration measured, suggesting that the reduction in phenolic concentration by liming could have increased the peat C loss. I anticipate that the methodologies used and the direct and indirect contribution of liming in increasing CO_2 brings new knowledge that could be extended to limed agricultural soils in the future.

In Chapter 5, I extrapolated the findings from Chapters 3 and 4 to simulate the CO_2 emissions for Canada. In doing so, I used historical and present Canadian peat extraction data and calculated a time-integrated emission based on first-order decay rate for Canadian horticultural peat extraction that began around 1940. For instance, decomposition of historical and present-day horticultural peat means that in year 2022, 0.35 Mt C [95% CI= 0.33 to 0.38] emitted could be attributed to peat use. With a prediction of a four times increase in horticultural peat demand by 2050 (Blok et al., 2021), emission amounts would increase to 1.08 Mt C [95% CI = 0.97 to 1.16]. I show that the C emissions from peat use reported are eight times higher than the on-site emissions reported from peat extraction fields. While there are uncertainties in my calculations that arise from variability in decomposition rate depending in the environmental conditions and peat decomposability, I anticipate that these findings will be crucial in devising Tier 2 IPCC reporting defaults for horticultural peat use. Accurate tracking of peat-based emissions over time will assist in devising future policy and mitigation strategies.

While I established peat respiration rates in previous Chapters, peat use in horticulture means that it is imperative to understand the role of introduced plants in peat decomposition. This is what I did in Chapter 6 where I introduced lettuce and petunia, representing food production and ornamental industry respectively in peat-based growing media. In growth chambers, I measured peat heterotrophic respiration (HR) in bare setups (peat only) and measured ecosystem respiration (ER) and average net ecosystem exchange (NEE) in setups with plants. I measured the respiration dynamics over a period of four months in a growth chamber. At the end of the experiment, I measured the role of plant roots in increasing peat respiration using ^{14}C radiocarbon signature. Measurements on heterotrophic respiration in peat only setups aligned well with the decomposition rate measured from lab incubations. In petunia, I measured an increase in peat respiration because of plant influence, in lettuce peat was not different from that of the bare setups. Therefore, I concluded that the increase in heterotrophic respiration by influence of roots could be species dependent. Establishing C dynamics in horticultural plants using radiocarbon measurements; I anticipate it setups up a baseline in future to investigate impact in increasing HR from other horticultural plants.

7.2 Directions for future research

Peat extraction and its use in horticulture is an important part of ongoing debates on peatland degradation, climate change, food production and the importance of ornamental horticulture. While the where and how peat is extracted might change, unless a suitable alternative that replaces peat is available, it remains certain that peat extraction will continue. This thesis quantifies the C footprint that remains with continued use of peat. Thus, I anticipate that the findings from the thesis will have global relevance as the scientific, political, and environmental debates goes on around the future of peat use in horticulture.

While this thesis was an important step in understanding and quantifying emissions related to peat use, there are several future avenues that my research opens. First, in this thesis the measurements come from recently extracted peat and considers emissions within first 120 days. However, decomposition rate is known to depend on interactive effects of substrate availability, environmental conditions and so on. Therefore, to measure how the decomposition rate of used peat could change over time and in different environmental conditions to which after-use peat (or spent peat) is subjected would be an important avenue to explore. This finding would be useful in further constraining the developed EFs.

Second, peat use in horticulture is a cyclic process. Although the combinations of how spent-peat is reused could be many, it is probably reasonable to assume that most used and reused peat ends up being mixed with mineral soils for gardening or landscaping. The peat use phase is comparatively small as compared to the timescale where the peat is mixed with mineral soils, therefore what happens to the peat C once in contact with mineral soil would be an important research topic to explore further.

Lastly, research on existing and new alternative media that can completely or partially reduce the demand of peat for growing media is urgent. Indeed, as we show in Chapter 5, partial or complete halt to peat extraction would be the only way to reduce future CO_2 emissions from peat use in horticulture.

Chapter 8: Master Reference List

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