Influence of fire on peat organic matter from Indonesian tropical peatlands.

Thesis submitted for the degree of Doctor of Philosophy at the University of Leicester

by

Leanne Elizabeth Milner BSc.

Department of Geography

University of Leicester

September 2013

Leanne Elizabeth Milner

Influence of fire on peat organic matter biogeochemistry from Indonesian tropical peatlands.

ABSTRACT

Effects of fire on peatlands globally are reasonably well documented, however studies of fire effects on tropical peatlands are limited. Specifically, the influence of fire on the biogeochemistry of tropical peat organic matter (OM) is not well understood and this study is the first to investigate this topic. Peat samples from undrained and degraded (drained and burnt) peatland in Central Kalimantan, Indonesia were analysed using novel chemical techniques. Short-term (one month post-fire) effects on peat OM composition were determined using Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS), allowing for detailed molecular investigation. Results revealed significant compositional differences between burnt and unburnt peat pyrolysates including, dominance of recalcitrant aromatic- and aliphatic-derived compounds in pyrolysates from burnt peat, while those from unburnt/undrained peat contained greater contributions of labile compounds including derivatives of lignin and polysaccharides. At one month-post fire, pyrolysates from the upper 5 cm of peat showed that almost all polysaccharides (0.1±0.1%) and lignin-derived compounds (0.8±1.2%) were depleted, although these compound classes were relatively concentrated in subsurface peat (5-50 cm). Charcoal was a significant fraction of the upper 5 cm up to one month post-fire, but none was detected in significant quantities deeper in the peat column (5–50 cm). One-month post-fire, the burnt peat was hydrophilic in the upper 5 cm but retained its inherent hydrophobic character at greater depth.

Similar to fire, peat drainage also reduced OM diversity i.e. the number of identified pyrolysis products. Peat pyrolysates from a drained unburnt site were dominated by aliphatic components (41.5-70.8% in the upper 50 cm). Thus both fire and drainage result in alteration of peat OM composition. The effects of fire were, however, short-lived (persisting up to 1.5 years post-fire), implying that peat OM composition can exhibit some recovery over a relatively short time period. Fire frequency had no significant influence on peat OM composition; thermal alteration occurred during the initial fire with no further modification during subsequent fires. The implications of these results for peatland carbon cycling and post-fire ecosystem recovery are discussed.

Acknowledgements

There are a number of people that have given me support in conducting this research and in writing this thesis. Firstly, I wish to pass on my deepest gratitude to my primary supervisor, Professor Sue Page who has supported me in my studies for many years now, tirelessly proof-reading my work and providing invaluable guidance for this project. I will be forever grateful to Sue for introducing me to the fascinating peatlands of Indonesia, I feel privileged to have worked in such a beautiful yet delicate ecosystem. My research would not have been possible without the patience and expertise of my supervisor, Dr. Arnoud Boom. Thank you for being so generous with your time, I appreciate the many hours spent in the laboratory discussing organic geochemistry which has helped me climb the steep learning curve since the commencement of this PhD.

I extend my thanks to Dr. Suwido Limin of CIMTROP, University of Palangka Raya. Thank you for your provision of field assistants and your kind hospitality in your home without this it would not have been possible to conduct vital sampling needed for the research. Thank you to Kitso Kusin who was always willing to help me with organising my field teams and gave me invaluable advice on shipping my samples back to Leicester. Thank you also to Dr. Sam Moore and Alex Cumming for joining me in the field – I do appreciate the sweat, mosquito bites and endless games of cards that were endured whilst we were in and around the peat swamps.

Lastly, thank you to my friends who have encouraged and supported over the last few years; thanks to you all. Thank you to my Mum, and grandparents for motivating me by giving me a firm but encouraging push on more than one occasion. Thank you to my partner Lee, I simply couldn’t have done this without you. You have always believed in me and your patience during those difficult times has been incredible.

This thesis has been funded by a joint studentship the University of Year 08/09 and REDD-Alert (James Hutton Institute, directed by Dr.Robin Matthews).

Contents

1 Chapter 1 – Introduction

2 Chapter 2 – Literature Review

3 Chapter 3 – Materials and Methods

4 Chapter 4 – Effects of fire on the organic matter composition of tropical peat

5 Chapter 5 – Effects of fire regime on the organic matter composition of tropical peat

Chapter 6- Fire modified peat OM: Implications for charcoal content and water repellence.

Chapter 7

List of Figures

south of the city of Palangkaraya, the provincial capital of Central Kalimantan. Source: modified from Google Maps (1/11/2011).

Fig.8: Location Map of sampling areas (1, 2& 3). Site 1: Intact peat swamp forest. Site 2: Drained peat swamp forest. This area has been selectively logged and the peat drained but this area has not been burnt. Site 3: Burnt and degraded area.

Fig.9: Left; Mixed Swamp Forest (MSF) during wet season (March 2011), Right; Tall Interior Forest 12km from edge of peat dome (March 2011).

Fig.10: Site 2: Drained secondary peat swamp forest, Block 'C' of the former MRP.

Fig.11: Examples of the range of vegetation types and conditions in Block 'C' of the former MRP. Recently burnt (2009) secondary forest (upper left). A recovering area of peatland that was burnt during the 1997 fires; the fern Stenochlacena palustris *occupies the foreground (upper right). An area of peatland adjacent to a canal which had burnt on four different occasions (lower left). An example of recolonisation by non-woody vegetation in an area of Block 'C' that burnt during the fires in 1997 and 2006 (lower right).*

Fig.12: Burnt area of Block C of the former MRP area from the following years a) 1997, b) 2002, c) 2006 and d) 2009. Burn scar data were derived by using a series of pre and post-fire satellite images (Landsat MSS, TM and ETM+) of the area and calculating the Normalized Burn Ratio (dbnr) to derive the burnt area for each year. Source adapted from, Hoscilo, (2009.) and Yunos, (2010).

Fig.13: Map of fire frequency in Block 'C' of the former MRP area. Burnt area data were combined for fires during 1997, 2002, 2006 and 2009 to determine the fire frequency regime. Data used from Yunos, (2010).

Fig.14. Map of pre-exsiting transects in the intact peat swamp forest area (Site 1). Samples taken at the site was conducted 5 m parallel to transect 0.4 km. Source (*http://www.orangutantrop.com/MapofLAHG.pdf (02/05/2010)*

Fig. 27: Plot of compounds, loadings based on factors 1 and 2 which explain 46.92% of the total variance (Factor 1, 30.86 %; Factor 2, 15.91 %).

Fig. 28: Plot of cases in factor space. Pyrolysates from Sites 1 (N), 2 (1) and 3 (F) plotted on factors 1 (30.36 %) and 2 (15.04 %).

Fig. 29: Plot of compounds in factor space. Pyrolysates from Sites 1 (N), 2 (1) and 3 (F) plotted in factors 1 (30.36 %) and 2 (15.04 %).

Fig. 30: Total aliphatic content in peat pyrolysates along a pre-fire (drainage only) and post-fire chronosequence (1997- 2011). Sample pyrolysates from the upper 5 cm and at the 30- 50 cm depth intervals are presented. Negative years on the horizontal axis represent time between initiation of drainage and collection of the sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29 – 35.

Fig. 31: Relative phenol content in peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29 – 35.

Fig. 32: Total PAH content in peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29– 35.

Fig.33: Relative content of nitrogen-containing compounds of peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29 – 35.

Fig. 47: Plot of mean recovered material (n=3) (%) against 'Time Since last burn'. '0' years represents peat from the intact PSF site (Site 1) that has not been burnt. Surface data represent the 0-5 cm depth interval. Subsurface data represent the 15-30 cm depth interval. Error bars represent 1 standard deviation. Please note vertical axis is a logarithmic scale.

Fig. 48: Pyrograms of peat OM before (a) and after (b) treatment with nitric acid and hydrogen peroxide. This sample experienced burning 1.5 years prior to collection and had been burnt on four separate occasions.

Fig. 49: Results of MED test of intact (Site 1) and recently burnt (Site 3) peat from the upper 50 cm of peat.

Fig. 50: Results of MED test from a range of samples collected in intact, drained and burnt sites.

Fig. 51: The temperatures of peat layers during a fire event from 21st to 26th August 2002 in Kalampangan, Central Kalimantan, Indonesia. Data shows temperatures at the ground surface and 10cm depth on 22nd August 2002. Source: Usup et al., (2004).

Fig. 52: Schematic diagram of a peat dome illustrating the changes in the degree of water repellence following drainage and fire in Site 3.

List of Tables

List of Equations

List of Acronyms

Al – Aliphatics

ANOVA – Analysis of Variance

Ar – Aromatics

BAER – Burned Area Emergency Response assessment

BD – Bulk Density

C – Carbon

CC - Carbon Consumed

CIMTROP – Centre for International Coperation in Sustainable Management of Tropical Peatland, University of Palangka Raya

C/N: Carbon to Nitrogen ratio

dbnr – Normalised burn ratio

DOC – Dissolved Organic Carbon

ENSO - El Niño-Southern Oscillation

ETM+ - Landsat Enhanced Thematic Mapper

FTIR – Fourier Transform Infrared Spectroscopy

GBC – Graphitic Black Carbon

GC – Gas Chromatograph

GC/MS – Gas Chromatography Mass Spectroscopy

GHG – Greenhouse Gases

Lg – Lignins

LOI – Loss On Ignition

MS – Mass Spectrometer

MED –Molarity of an Ethanol Drop test

MRP – Mega Rice Project

MSF – Mixed Swamp Forest

MSS – Landsat Multispectral Scanner

N- Containing – Nitrogen-containing

NDVI – Normalised Difference Vegetation Index

NIST – National Institute for Standards and Technology

PAH - Polyaromatic Hydrocarbon

PCA – Principal Components Analysis

POC – Particulate Organic Carbon

Ps - Polysaccharides

PSF – Peat Swamp Forest

PVC – Poly-vinyl chloride

Py-GC/MS – Pyrolysis Gas Chromatography Mass Spectroscopy

PyOM – Pyrogenic Organic Matter

OM – Organic Matter

R.T. – Retention Time

TM – Landsat Thematic Mapper

TOC – Total Organic Carbon

^{13}C NMR – ^{13}C Nuclear Magnetic Resonance Spectroscopy

Chapter 1- Introduction

1.1 Significance of the tropical peatland carbon pool

Peat is defined as ‘sedentarily accumulated material consisting of at least 30 % (dry mass) of dead organic material’ (Joosten & Clarke, 2002, p. 24). Other, contrasting definitions exist, however, including ‘a surface layer of soil, consisting mostly of partially decomposed vegetation with an organic content of at least 65 % and a minimum thickness of 30 cm’ (Andreisse, 1988; Rieley & Page, 2005; Page *et al.*, 2011. p. 799). Tropical peats are defined as ‘all organic soils in the wetlands of the tropics and subtropics lying within latitudes 35 degrees North and South including those at high altitudes’ (Andriesse, 1988, Section 1.2).

The majority of the world’s peatlands are located in the boreal and temperate zones formed under high precipitation, low temperature regimes in low relief areas (Gorham, 1991; Charman, 2002). The peatlands in the tropics, however, have formed due to the regional topography (extensive, low-lying, poorly-drained coastal and sub-coastal plains) which has allowed peat to accumulate under high precipitation, high temperature regimes (Rieley & Page, 1997). Peat is rich in organic carbon (C) and peat C contents from Southeast Asian peatlands range from 41.6 % (Sajarwan *et al.*, 2002) to 62.0 % (Page *et al.*, 2004). This C rich substrate accumulates over time due to net primary production exceeding decomposition (Vitt, 1990; Sorenson, 1993). The most recent best estimate of global tropical peatland area is 441,025 km^2 (~ 11 % of global peatland area), spanning areas of Southeast Asia, Africa, the Caribbean, Central and South America. Of this area, 247,778 km^2 (57 %) occurs within Southeast Asia with the majority, 206,950 km^2 (84 %) within Indonesia (Page *et al.*, 2011).

Tropical peatlands, including those in Indonesia, provide many ecosystem services and they support a wide range of flora and fauna including endangered species such as the orangutan and Sumatran tiger (Page, 1997). Tropical peat swamp forests are a habitat for many tree species, including several valuable timber species (Anderson, 1976; Page and Rieley, 1998) and provide a range of non-timber forest products for use by local communities, including latex, gums, fruits, rattan and medicinal plants (Page and Rieley, 1998). Tropical peatlands are also critical for the regional water balance by retaining water in the acrotelm (upper) peat layer during the wet season (October-May) and discharging water into adjacent waterways during the dry season (June-September) (Wösten *et al.*, 2006). More recently, however, there has been an increased interest in tropical peatlands due to their importance as C stores and their role in the global C cycle (Jauhiainen *et al.*, 2005; Hooijer *et al.*, 2006; Hirano *et al.*, 2007). The disproportionally large (relative to the surface area) pool of terrestrial C is primarily stored in the peat substrate (Gorham 1991, Immirzi & Maltby 1992), rather than in the aboveground biomass. Deposits of peat up to 20 m thick contribute to an estimated global tropical peatland C stock of 88.6 Gt (~15-19 % of the global peatland C stock), of which 57.4 Gt is located in Indonesian peatlands (Page *et al.*, 2011).

1.2 Disturbance of peatlands by fire

Fire disturbs peatlands on a global scale with wildfires burning in boreal, temperate, and tropical regions. An estimated 90 % of the world's peatlands occur at high-latitudes (Yu *et al.*, 2010) and these areas are particularly vulnerable to fires. Historically, fires have rarely taken place in boreal peatlands, but since the 1960/70's burning on North American peatlands has become more frequent (Turetsky *et al.*, 2010). Fires have regularly occurred across large areas of peatland in Canada, Alaska (Kasischke *et al.*, 2006) and also Russia (Conard *et al.*, 2002). Warming of the Earth's climate systems and lowering of natural water table levels is believed to be responsible for the increasing frequency of peatland fires (Turetsky *et al.*, 2010). Currently, an average of 1,850 km^2 of peatland burns annually in western Canada, however, with future climate change this is expected to increase by 200 - 300 % in the next 50-100 years (Turetsky *et al.*, 2010). Despite boreal regions hosting the largest area of peatlands, fires in tropical peatlands have also been frequent in recent decades, particularly in disturbed peatlands in Indonesia (Page *et al.*, 2002, 2009). Fires cause disturbance to peatland ecosystems by burning the aboveground biomass and belowground peat, releasing C in the form of greenhouse gases (GHG's) including CO_2, CO and CH_4 to the atmosphere, thus contributing to climate change.

Southeast Asian tropical peatlands are currently undergoing rapid rates of deforestation (Langner *et al.*, 2007; Langner & Siegert, 2009) caused by government resettlement programmes in addition to demands for agricultural produce such as oil palm and pulp wood as well as timber (Goldammer, 2007; Page *et al.*, 2009). Fire is one of the principal drivers of such deforestation and is the source of considerable C emissions to the atmosphere (Page *et al.*, 2002; Hooijer *et al.*, 2006, 2010). Fire is having an increasingly devastating impact on tropical peatlands in the study area chosen for this thesis (the former Mega Rice Project area in Central Kalimantan, Indonesian Borneo). A previous study of land cover change in part of this area revealed an increasing trend in deforestation (2.2 % yr^{-1} forest loss rate, 1973-1996; 7.5 % yr^{-1}, 1997-2005) and identified fire as the principal cause of this loss (Hoscilo, 2009).

Disturbance of tropical peatlands is a consequence of both deforestation and fire combined with and exacerbated by land drainage. This disturbance results in the release of C from the belowground peat C store to the atmosphere. Drainage leads to aeration of the upper peat layers which increases oxidative microbial decomposition and hence the release of C in the form of CO_2 to the atmosphere (Hooijer *et al.*, 2006, 2010 & 2012; Jauhiainen *et al.*, 2012), while fire results in emissions of a range of C gases (CO_2, CO, CH_4 and others) from direct peat combustion (Page *et al.*, 2002, 2009; Hirano *et al.*, 2007).

Average annual emissions from fires on peatlands in Southeast Asia are estimated to be at least 1400 Mt y^{-1} for 1997- 2006 (Hooijer *et al.*, 2006). Fire in Indonesia is predominately caused by land use change such as development of timber concessions; however, fire is also aggravated by the occurrence of El Niño conditions (Langner & Siegert, 2009). The 1997 fire event in Southeast Asia caused the release of between 0.81 and 2.57 Gt of C to the atmosphere which is the equivalent of 13-40 % of the mean annual global C emissions from fossil fuels (Page *et al.*, 2002). In 2006, severe peatland fires resulted in the release of a further 0.049 ± 0.027 Gt of C from burning of just 13 % of the total Indonesian peatland area. This estimate was equivalent to 10–33 % of all C emissions from transport for the European Community during that year (Ballhorn *et al.*, 2009). Such substantial C emissions from peatland burning highlight the significance of fires on tropical peatlands for atmospheric greenhouse gas concentrations.

To date there is limited research that has considered the role of fire and its implications for the biogeochemical composition of tropical peat and there are no studies that have investigated how fire regimes affect the organic matter composition of tropical peat. In peatland ecosystems, the preservation of the below-ground peat substrate is important in order to sustain ecosystem functions, i.e. post-disturbance recovery of ecosystem functions such as C storage, nutrient cycling and vegetation support, are directly linked to the peat's physical, chemical, and biological functions. With a predicted increase in fire frequency under future climate change scenarios in the Southeast Asian region (Page *et al*., 2009), it is critical to understand the biogeochemical response of tropical peat to fire as this could influence post fire nutrient cycling, vegetation recovery and ultimately C cycling. 'Black Carbon', is combustion-produced black particulate carbon that has a graphitic microstructure, (Novakov, 1984). This material which includes charcoal, is not often considered when modelling the C cycle in tropical peatlands. In other ecosystems, however, black carbon derived from biomass burning contributes a considerable long term store of recalcitrant C in the terrestrial system (Baldock & Smernik., 2002; Masiello *et al*., 2004; Bell and Worrall, 2011). Disregarding the black carbon pool in fire-affected tropical peats could result in overestimation of post-fire soil respiration and therefore of oxidative CO_2 emissions (Lehmann *et al*., 2008).

Heating of soil caused by fire leads to the development of water repellency in some environments (DeBano, 2000a; Doerr *et al*., 2000). Water repellent soils have been widely identified across the globe, including environments in Southern California, USA, Portugal, Spain, South Africa and Chile (DeBano, 2000a). Chemical alteration of soil organic matter as it is heated is thought to explain this development of soil water repellency. Despite peatland scientists being aware that peat can be difficult to rewet when it becomes dry (Andriesse, 1988) it is not currently known if fire leads to the development of water repellency. If below-ground heating during a fire leads to the formation of water repellent peat there could be a variety of implications for peatland ecosystem processes including; soil erosion, reduced infiltration, and preferential flows in hydrophilic areas of soil leading to leaching of nutrients (Certini, 2005).

The aim of this study is to reveal some of the biogeochemical changes that occur as a result of fire on peatland in Central Kalimantan, Indonesia. At present there is very little known about the biogeochemistry of tropical peats despite the importance of peat soils in the wider field of global biogeochemical cycling and the earth's climate system. Biogeochemical changes as a result of fire are reasonably well documented for mineral soils (Tomkins *et al*., 1991, Romanya *et al*., 1994, Neary *et al*., 1999, Ketterings & Bingham, 2000, González-Pérez *et al*., 2004, Certini 2005, Knicker *et al*., 2007, De La Rosa *et al*., 2008) but there is a research gap when considering peat soils and in particular tropical peats. Peat is a highly concentrated store of C (Sorenson, 2003) but the increasing frequency of fires on tropical peatlands, particularly in Indonesia, adds urgency to obtaining an improved understanding of the biogeochemical response of peat to environmental degradation.

1.3 Introduction to the study area

The chosen study area was in an area of tropical peatland in the lowlands of Central Kalimantan, Indonesia. Two peatland areas, south of the city of Palangkaraya, were chosen, firstly an area of relatively intact peatland that supports peat swamp forest vegetation, and secondly, an area of degraded peatland namely the former Mega-Rice Project area. This area of degraded peatland is a site of over one million hectares that was deforested and drained in 1995 for the purposes of agricultural development. The Mega-Rice Project area has since become a fire-prone area due large areas of drained open peatland that provide conditions conducive for burning. Comparisons are made throughout the data chapters and discussion in order to meet the research aims and objectives outlined in section 1.4. More substantial detail regarding the study sites is provided in in Chapter 3 (Section 3.1).

1.4 Research Aims and Objectives

The overall aim of this research is to assess the effects of fire on the organic matter (OM) composition of tropical peat through geochemical analysis. This thesis provides data that meet the following research objectives:

1) **To provide evidence of the change in OM composition after a single fire event in the chosen study area (Chapter 4).**
2) **To determine if the fire regime variables namely, 'time since last burn' and 'fire frequency', influence the chemical composition of peat OM (Chapter 5).**
3) **To quantify the mass of charcoal in peat affected by a range of fire regimes (Chapter 6).**
4) **To determine if fire affects the degree of water repellency of tropical peat (Chapter 6).**

1.4 Thesis Structure

The rest of this thesis is composed of 6 chapters which include the following;

<u>Chapter 2</u> (Literature Review) – This chapter contains a review of relevant literature and is divided into two parts. Part 1 explores the current wider knowledge on tropical peatland C dynamics including forms of disturbance in tropical peat swamp forest with a particular focus on the impacts of fire in Southeast Asian peatlands. Part 2 presents the wide range of literature from the field of organic geochemistry and reviews results from analytical methods used to assess the organic matter composition of burnt soils. Gaps in current scientific knowledge are highlighted, particularly those regarding the methodologies used to assess OM composition.

<u>Chapter 3</u> (Methods) - Presents full details of the general methods applicable to all data chapters including, explanation of the study sites and sampling strategies. Specific methods are described in individual data chapters (Chapters 4-6). Background information about Py-GC/MS including its application to environmental research is provided in detail.

<u>Chapter 4</u> (Data Chapter One) – This chapter includes the rationale, specific methods, data and discussion of experiments conducted to address research objective 1; **To**

assess the short term effects of fire on the organic composition of tropical peat. Py-GC/MS data are presented to provide evidence for OM alteration observed in peat samples collected one month post-fire. Specific methodologies used solely to generate data used in this chapter are included.

Chapter 5 (Data Chapter Two) - This chapter contains further data from Py-GC/MS analysis and conveys an assessment of the effects of a range of fire regimes on peat OM in order to address research objective 2; **To determine if the fire regime variables namely, 'Time since last burn' and 'Fire frequency', influenced the chemical composition of peat OM through analysis of peat pyrolysates.** This includes an analysis of the medium and long term effects of fire (18 months and up to 14.5 years post-fire) and the impact of repeated burning.

Chapter 6 (Data Chapter Three) - This chapter presents two sets of data; the results of a charcoal analysis and of a water repellence analysis in order to address research objectives 3; '**To quantify the mass of charcoal in peat affected by a range of fire regimes'** and 4; '**To determine if fire affects the degree of water repellence of tropical peat'.** Specific methodologies related to the two sets of data (charcoal content and water repellence) are described within this chapter.

Chapter 7 (Discussion) - The final chapter in this thesis synthesises the data from the previous three results chapters in order to embed the findings in the context of the current literature. It begins by examining the specific findings in relation to other similar studies in the field of organic geochemistry before examining their implications for the tropical peatland C cycle and the global C cycle.

Chapter Two – Literature Review

2.0 Introduction

The purpose of this chapter is firstly, to discuss the impact of fire on the biogeochemistry of soils from different climatic regions and secondly, to present a review of the current literature on the effects of fire on peat soils. A range of laboratory techniques are used to investigate organic materials, therefore the literature reviewed in this chapter will consider the key findings of studies using techniques that are particularly relevant to the research objectives and methodologies of this thesis.

This chapter is structured into four sections. Section 2.1 discusses background literature relevant to the occurrence of fire in the tropics and specifically Indonesian peatlands. The results of this thesis are likely to be relevant to a wide range of future research in tropical peatland environments and peatland fire science, therefore it is important to place the work in the context of the wider literature. The first section and sub-section focus on these topics.

The further three sections are linked more closely to the four research objectives. Section 2.2 and its sub-sections focus on the effects of burning on OM composition and nutrient status in a range of environments. The impact of fire regime is considered and the results from studies that have utilised a range of laboratory techniques are taken into account. This section is relevant to research objectives 1 and 2.

Section 2.3 addresses the significance of black carbon stocks in soils and the uncertainties involved in quantifying these stocks. The environmental implications of the storage of black carbon are also reviewed, with relevance for research objective 3.

The final section (2.4) links to the last research objective by reviewing the literature concerned with fire-induced water repellency in soils and the methods that have been used to assess this phenomenon.

2.1 Tropical Peatlands

There has been increasing scientific interest in tropical peatlands in the last two decades due to their various ecosystem functions but particularly due to their globally important store of terrestrial carbon (C). Terrestrial C is primarily located belowground within the peat substrate (Immirzi & Maltby 1992; Page *et al.*, 2011). Tropical peatland disturbance, brought about by deforestation, land use change, drainage and fire, is, however, causing C from the peat store to be emitted to the atmosphere, principally in the form of CO_2, but also CO and CH_4, and, to a lesser extent, into waterways as dissolved organic carbon (DOC) (Moore *et al.*, 2011, 2013). Land use change in tropical peatlands, which often takes place for the development of industrial-scale plantations of oil palm and pulpwood trees, typically involves drainage. This results in aerobic conditions in the surface peat, increased microbial activity, accelerated aerobic decomposition of organic materials and thus emission of soil C to the atmosphere (Hooijer *et al.*, 2006, & 2010, 2012; Jauhiainen *et al.,* 2012) and an enhanced loss of DOC into rivers and other waterways (Moore *et al.*, 2013). In addition, fires on tropical peatlands, which have increased as a result of forest degradation, peatland drainage and increased human access, have also resulted in C emissions to the atmosphere through combustion of above ground biomass and, more importantly in terms of the scale of emissions, the surface peat (Page *et al.*, 2002, 2009).

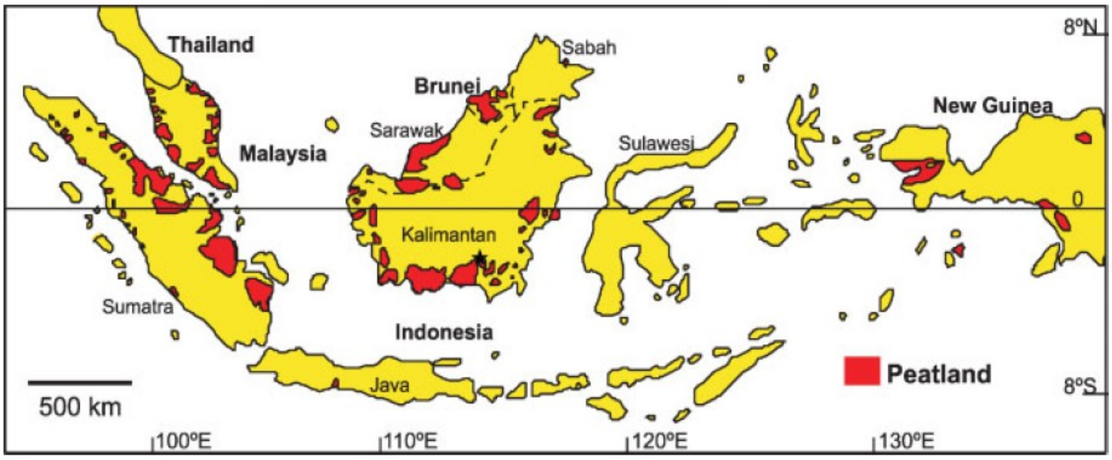


Fig. 1: Distribution of tropical peatlands in Southeast Asia and location of the study area (*). The map illustrates that most of the peatlands are on the islands of Borneo and Sumatra. (Source: Page et al., 2004).

2.1.1 Characteristics of Indonesian Peatlands

Indonesian peatlands have long been of scientific interest due to their unique and dynamic nature. They are unbalanced systems in their natural undisturbed state; the rate of production of organic material exceeds the rate of decomposition, leading to an overall accumulation of peat. In Central Kalimantan, Indonesia, peat has been accumulating for ~22,120 ^{14}C yr (Weiss *et al.*, 2002; Page *et al.*, 2004), while in coastal areas of Sarawak and Sumatra, peat accumulation commenced later during the Holocene (e.g. 7,000 to 5,000 yr BP; Page *et al.*, 2010). In Central Kalimantan, ideal conditions for peatland development are presented by permanent water logging in coastal and sub coastal lowland areas. The peatlands of this region experience a wet tropical climate with annual rainfall between 2300 and 3000 mm yr^{-1} and temperatures ranging between 25-27 °C (Shimada, 2001). Most precipitation is experienced during the 'wet' season between the months of October and April and less during the 'dry' season of May to September. Inter-annual climate variation occurs in response to changes in the El Niño-Southern Oscillation (ENSO). During the warmer phase of the ENSO cycle (El Niño) rainfall is reduced due to suppression of the tropical monsoon, resulting in an extended dry season across western Indonesia (including Kalimantan). During the colder phase (La Niña), monsoon rainfall commences earlier than in an average year (Li *et al.*, 2007), thus the length of the dry season is reduced. Temperature variation also occurs between El Niño and La Niña events with recorded increases in temperature during El Niño years (Kiladis & Diaz, 1989).

Peatlands in Indonesia are typically either ombrotrophic (peat swamps), which are rain-fed, or topogeneous (freshwater swamps), which are under the influence of both rain and ground water. The former ombrotrophic swamps are far more widespread than the freshwater swamps which are restricted to river flood plains. Ombrotrophic peat swamps derive all of their water and nutrients entirely from aerial deposition (Page *et al.*, 1999; 2006). They typically form large, shallow domes with a convex surface, with the thickest peat deposits in the centre (up to 10 metres or more) and shallower peats (1-2 metres) at the dome margins (Page *et al.*, 1999). The water table is at (usually within 40 cm) or above the peat surface all year round with some variation in depth both above and below the peat surface between the wet and dry seasons (Page *et al.*, 1999). Permanently waterlogged conditions inhibit microbial decomposition which reduces the availability of nutrients from the breakdown of litter (Yule & Gomez, 2008). The low nutrient and ash contents of both peat and pore waters provide further evidence these peatlands are ombrotrophic (Shotyk 1989; Page *et al.*, 1999), i.e. they receive no additional inputs of nutrients from groundwater sources.

The characteristic vegetation of ombrotrophic tropical peatlands in Southeast Asia is 'peat swamp forest', a type of tropical rainforest. Typical tree species include *Gonystylus bancanus*, *Shorea spp.*, *Cratoxylon glaucum* and *Combretocarpus rotundatus* among several hundred other species (Morrogh-Bernard *et al.*, 2003). Many of the tree species are adapted to the waterlogged conditions, displaying buttress or stilt roots that provide improved stability and breathing roots (pneumatophores) that protrude above the peat surface (Page *et al.*, 2006). Variations in peat depth, hydrology and nutrient status are linked with variation in aboveground vegetation species composition and structure, such that there is a zonation of different forest communities from the edge to the centre on any peat dome (Page *et al.*, 1999, 2009).

Four different forest types have been identified in the Sungai (River) Sebangau catchment in Central Kalimantan namely, Riverine, Mixed Swamp Forest, Low Pole Forest and Tall Pole Forest. These different vegetation types form approximate concentric rings from the margin to the centre of the peat dome (Page *et al.*, 1999). The 'Riverine Forest' is located on the edge of the peat dome and is subject to frequent inundation by river water flooding. Approximately 2 km from the river the riverine forest grades into 'Mixed Swamp Forest' which in the upper canopy layers hosts trees that are up to 35 metres tall (Morrogh-Bernard *et al.*, 2003). Mixed Swamp Forest grades into 'Low Pole Forest' about 6 km onto the peat dome and has a more stunted and open tree canopy and a dense ground vegetation dominated by *Pandanus* and *Freycinetia spp*. (pandans) (Page *et al.*, 1999). At the centre of the peat dome are the tallest trees with emergents up to 45 metres tall (Morrogh-Bernard *et al.*, 2003) aptly called 'Tall Pole Forest'. The above ground vegetation contributes to the accumulating organic material at and below (in the case of roots) the peat surface that continually allows for the formation of fresh peat. In the absence of human intervention Indonesian tropical peatlands are accumulating peat or are in steady state (Brady, 1997).

Fig.2: Intact peat swamp forest, Sebangau National Park, Central Kalimantan, Indonesia, July 2008. Peat is permanently waterlogged allowing for accumulation of organic material and continuing development of peat. (Photo: L. Milner).

The peat swamp forests of Central Kalimantan are ecologically diverse and are classed as biodiversity hotspots (Page *et al.*, 1999). There are many endemic and endangered flora and fauna species found in these environments, including the orangutan *(Pongo pygmaeus)* (Morrogh-Bernard *et al.*, 2003; Meijaard, 2005) and up to 927 species of plants have been recorded in the peat swamp forests of Borneo (Anderson, 1961, 1963 & 1964).

2.1.2 Tropical peatlands and the C cycle

In their natural state tropical peat swamp forests are a significant store of C in both the aboveground vegetation and the belowground peat (Jauhiainen *et al.*, 2005; Page *et* *al.*, 2011). Tropical peatlands account for up to 25% of the global peat volume and therefore are highly significant in terms of the global C cycle (Immirzi & Maltby, 1992). The tropical peatland C store has been estimated at 88.5 Gt which accounts for between 17 % and 19 % of the global peatland C pool, with Indonesian peatlands alone containing 57.4 Gt of C and accounting for 65 % of the tropical peatland C pool (Page *et al.*, 2011).

In tropical peatlands, decomposition of organic matter (OM) is inhibited when the peat is waterlogged, due to the anoxic conditions which suppress microbial respiration, thereby allowing for the accumulation of partially decomposed OM in the form of peat. Since the C content of tropical peat is around 56% (Page *et al.*, 2011), tropical peatlands are a large terrestrial C sink (Qualls & Haines, 1990; Gorham, 1991). This sink function is, however, only maintained if the hydrology of the peat dome remains intact and disturbance can rapidly convert the peat C pool to a C source. There are many examples where disturbance of the natural peatland ecosystem has led to a net efflux of C from the peat surface, thereby reducing the C storage capacity. For example, drainage of peatlands and subsequent alteration, (i.e. lowering) of the water table, leads to aeration of the surface peat, and enhanced microbial oxidation (Hooijer *et al.*, 2006 & 2010; Wösten *et al.*, 2008). Estimates of C losses arising from degradation and specifically drainage of peatlands in Southeast Asia are between 97 M t C yr^{-1} and 238 M t C yr^{-1} (Hooijer *et al.*, 2006; 2010) (N.B. these estimates exclude emissions from fires which would significantly increase these estimates (Page *et al.*, 2002)). Conversion of peat swamp forests in Southeast Asia has led to rapid land-use change to industrial plantations and has involved deforestation, drainage and burning. This land management practice is unsustainable because peatlands which were previously C sinks are becoming sources of C (Hooijer *et al.*, 2010) and it is likely that Southeast Asian peatlands will become an ever greater source of C as demand for products such as oil palm and timber continues and there is further expansion of industrial plantations.

Land-use changes through deforestation and drainage have placed Indonesian peatlands at particular risk from wildfires. Fires in tropical peatlands influence the global C cycle through C emissions from burning of the aboveground vegetation and the belowground peat (Page *et al.*, 2009). C emissions from peatland fires are generally greater than fires in forests on mineral soil due to partial combustion of the belowground C stocks and not just the above-ground vegetation. The fires that affected large areas of Indonesian peatlands during the 1997 ENSO event were the most devastating peatland fires to date with an estimated release of between 0.81 and 2.57 Gt of C to the atmosphere (Page *et al.*, 2002). It is likely that emissions from this fire event made a significant contribution to the high atmospheric CO_2 concentrations detected in 1998 (IPCC, 2001). Other major fire events on Indonesian peatlands since 1997 have occurred in 2002, 2006 and most recently in 2009. Over the period 1997 to 2007 it is estimated that the total C emissions from peatland fires in Southeast Asia have been of the order of 2 to 3 Gt or equal to 4% to 6% of the region's peatland C store (Page *et al.*, 2009).

C is also being lost from Indonesia's peatlands in the form of dissolved organic carbon (DOC) via rivers and canals (Baum *et al.*, 2007; Moore *et al.*, 2011, 2013). A study of DOC concentrations from the Siak River, Sumatra estimated Indonesia's total DOC export to be 21 Tg yr^{-1} which represents ~10% of the global riverine DOC input into the ocean. The TOC (Total Organic Carbon) flux from the Sebangau river basin in Central Kalimantan to the Java Sea is estimated at 0.46 Tg yr^{-1}, comprising of 93 % (0.43 Tg) DOC and 7 % (0.03 Tg) POC. TOC flux was significantly higher in disturbed (105 – 131 g C m^{-2} y^{-1}) compared with intact (63 g C m^{-2} y^{-1}) peatland areas (Moore, 2011). In addition, ^{14}C dating has revealed that DOC from disturbed areas within the Sebangau catchment (i.e. within the former Mega Rice Project area) is much older (centuries to millennia) than DOC from intact sites (recent primary production from plant growth) (Moore *et al.*, 2013). DOC export from peatlands is influenced by a drop in the water table brought about by land use change (Worrall *et al.*, 2003). Disturbance to the peat by drainage destabilises the peat column at depth leading to a collapse of the C store and losses of older C from deep peat layers (Moore *et al.*, 2013). In addition to land cover change and drainage, fire has also been shown to lead to an immediate post-fire enhancement of DOC losses from tropical peatlands (Moore *et al.*, unpublished data).

2.1.3 Tropical peatland disturbance

Southeast Asian tropical peatlands are subject to disturbance due to deforestation (Joosten & Clarke, 2002; Sodhi *et al.*, 2004), drainage (Hooijer *et al.*, 2006, 2010), fire (Page *et al.*, 2002, 2009) and conversion for agriculture (Melling *et al.*, 2005; Koh *et al.*, 2011). Peat swamp forests are under particular pressure from the demand for timber and the development of oil palm and pulpwood plantations for food, fuel and paper production (Hooijer *et al.*, 2006; Pearce, 2007). The inherent low fertility and high acidity of tropical peats mean that they are typically unsuitable for agriculture, although oil palm and *Acacia* (grown for pulpwood) are reasonably suitable when the peat is heavily drained and, in the case of oil palm, heavily fertilised (Tan *et al.*, 2009). Plantation development, however, results in considerable emissions of C from the peat as it oxidises following drainage (Murdiharyso *et al.*, 2010). Driven by the demand for biofuels, industrial plantations are expanding and approximately 3.1 Mha, equivalent to 20 % of the total peatland area of Peninsula Malaysia, Sumatra and Borneo, is now occupied by plantations of mainly oil palm or *Acacia* (Miettinen *et al.*, 2012).

Rates of deforestation in peatlands vary between different parts of Southeast Asia; for example during the period 2000 to 2010, there was an estimated 2.2 % average annual reduction of peat swamp forest across insular Southeast Asia (Miettinen *et al.*, 2011). Kalimantan's rainforest area, of which significant proportions were located on peatland, was reduced by an estimated 56 % between 1985 and 2001 (Curran *et al* 2004). Projections for future forest cover have been calculated based on data from land cover change models, for example, for the period 2005-2020 it is projected a further 45.1 % of peat swamp forest in Central Kalimantan will be deforested (Fuller *et al.*, 2011). Peat swamp forests have been heavily affected by land use change across the entirety of Indonesia, particularly in Sumatra where by the early 1990's over 90% of the peat swamp forests had been affected by human interventions (Giesen, 2004). Forest cover on the peatlands of Peninsular Malaysia, Sumatra and Borneo was monitored over two decades (1990-2010) and the proportion of forest cover reduced from 77% to 36%; much of this reduction was linked to the incidence of fire. It is predicted that at current deforestation rates all peat swamp forests in Southeast Asia will have been cleared by the year 2030 (Miettinen *et al.*, 2011).

In the past, large agricultural projects have proven to be of varying success when established on tropical peat. The Mega Rice Project (MRP) was initiated in 1995 across 1.46 Mha of tropical peatland in Central Kalimantan; an area equal to approximately 7 % of the total peatland extent in Indonesia (Ludang *et al.*, 2007). This was an example of a government-led land use project that ultimately resulted in severe tropical peatland disturbance and degradation, considered by many to have been an environmental disaster (Page *et al.*, 2002, Wösten *et al.*, 2008; Jaya *et al.*, 2009). In 1996, after extensive forest clearance, canals were constructed in order to drain the substantial (up to 10 m deep) peat deposits (Boehm, 2001, Page *et al.*, 2002). It was these canals (4,600 km in total length) that caused a considerable drop in the peat water table and, combined with poor hydrological planning, ultimately led to a lack of water needed for irrigation of crops. In addition, the nutrient poor peat substrate was not suitable for the development of rice paddies. The failed project was terminated by Presidential Decree in 1999 (Page *et al.*, 2009), but the abandoned peatland became a significant source of C emissions, as the aerated peat surface provided favourable conditions for microbial decomposition, as well as greatly increasing the risk of wildfires.

A study by Hoscilo (2009) based on data from Block 'C', the western part of the former MRP, revealed that fires had increased in frequency and severity, particularly during the decade from 1996 to 2005 which coincided with the period immediately after the peat swamp forest was cleared and drained for the MRP. Between 1997 and 2005, 55 %) of Block 'C' had been affected by burning and in 2005 just 22 % of the area was occupied by forest vegetation and just 12 % by peat swamp forest. This was in contrast to the period before the implementation of the MRP, when in 1993, just 7 % of the area of Block 'C' had been recently burnt and forest cover still accounted for 57 % of the total area (44 % peat swamp forest). It is clear from this analysis that the incidence of fire is linked to land-use change and human activity (land clearance for plantations, logging and transmigration projects). It is thought that drainage increases the likelihood of fire explaining why the heavily drained MRP area was subject to extensive fires. It is likely that future climate change will further increase the incidence of fire across tropical peatlands, particularly in the former MRP area and other areas that are deforested or degraded (Li *et al.*, 2007). With a predicted increase in future global temperatures, climate models predict that rainfall will decrease over Southeast Asia (Li *et al.*, 2007). It is believed this could lead to a particular problem in peatlands because the water table level could be reduced and surface dryness enhanced during the dry season. This reduction in rainfall would therefore increase the degree of peat decomposition and the incidence of wildfires.

2.2.0 Fire in the tropics

Fire affects atmospheric chemistry, biogeochemical cycling and the global C cycle; it is estimated that 3.9 Gt C are released annually to the atmosphere by biomass burning (Andreae, 2001). The incidence of fire is sensitive to climatic conditions and it is anticipated that future climatic change may increase fire frequency (IPCC, 1996). Fire is also an increasingly regular phenomenon in the tropics, even in the humid tropics, with the largest fires in recent decades occurring in tropical ecosystems (Goldammer and Seibert, 1990, Goldammer, 1993; Cochrane, 2003). This observed increase in the frequency and intensity of fires in tropical regions is largely due to increased human disturbance i.e. from deforestation and logging which lead to conditions that are conducive for fire in previously fire-resistant ecosystems (Page *et al.*, 2009). Fires have serious economic, social and environmental impacts and can be beneficial or detrimental depending on the ecosystem type (Glover, 2006; Schweithelm, 1999). Fire is an integral disturbance factor in some tropical ecosystems such as savannas in northern Australia (Gill and Stephens, 2009) where fire has shaped the vegetation dynamics over thousands of years. Fires, however, can have devastating consequences in other tropical environments, particularly in humid tropical forest environments including tropical peat swamp forests (Page *et al.*, 2009; Baker & Bunyavejchewin, 2005). Fires in these latter environments have only become a regular occurrence in the last 20 years due to anthropogenic disturbance. With increasing pressure of human land use change as well as continuing climatic change, fire is likely to become an ever increasing agent of tropical ecosystem dynamics.

2.2.1 Fire history in Southeast Asian peatlands

Fires have only occurred occasionally in Indonesian peatlands over the last two millennia (Kershaw & Bohte, 1997; Goldammer and Hoffmann, 2002) but more recently they have become a regular occurrence (Langner *et al.*, 2007). During the last 10 to 20 years land clearance and the incidence of ENSO events have caused an increase in frequency and severity of fire (Hoscilo, 2009). The 1982-1983 Great Fire of Borneo was followed by subsequent fire events in 1987, 1991, 1994, and 1997 all of which are described as 'mega fire events' (Tacconi *et al.*, 2007). The 1982-1983 fire affected 0.55 Mha of peat swamp forest although a notably larger area (2.4 Mha) was affected by the 1997 fires (Page *et al.*, 2002). There were also large fire events during 2002, 2006 and most recently in 2009, although none were as extensive as the 1997 fires. During 1997-1998, fires burned across eight million hectares of Indonesia as a whole.

Many areas of tropical peatlands are being successively burnt with ever shorter fire return intervals which prevents the successful regeneration of the original forest vegetation (Hoscilo, 2009). Langner and Siegert (2009) analysed fire events in Borneo between 1997 and 2006 and their results showed that 21 % of the land surface had burnt once, while 6.1 % burned more than once. This same study also highlighted the problem of an increasing incidence of fire in peatland areas. Although only 23 % of Borneo's forest is in peatland areas, the fires of 2002 burnt 73 % of this peatland area and 81% of the fire hotspots for 2002 occurred in peat swamp forest. These figures highlight that Indonesia's peat swamp forests are at high risk of fire, particularly when they have previously been burnt.

The El Niño Southern Oscillation (ENSO) is defined as the anomalous warming of ocean temperatures on a timescale of two to seven years, with the eastern equatorial Pacific climate varying between anomalously cold (La Niña) and warm (El Niño) conditions (Collins *et al.*, 2010). These changes in temperature are often associated with variations in rainfall patterns in many parts of the world including Southeast Asia. El Niño and La Niña events control rainfall variation over Southeast Asia and during an El Niño year the onset of the Asian summer monsoon is suppressed (Hamada *et al.*, 2002) reducing rainfall in Indonesia. El Niño events are also associated with increased temperatures throughout Southeast Asia (Kiladis & Diaz, 1989) and extended periods of drought particularly in the peatland areas of southern Sumatra and Kalimantan (Page *et al.*, 2009). The El Niño phase of the ENSO cycle has been associated with the most severe fires in tropical peatlands (Page *et al.*, 2009). Fires have been associated with El Niño as early as 1914 in East Kalimantan although these were very small scale (Goldammer *et al.*, 1996). There is much evidence to suggest El Niño conditions increase the likelihood of fire especially in degraded and drained peatlands such as those in the MRP area in Central Kalimantan (Hoscilo *et al.*, 2011) where low peat water tables during an extended dry season can expose more than 1.0 m or more of dry surface peat to the risk of fire. Recent findings suggest that fire occurrence almost tripled across Peninsular Malaysia, Sumatra, Borneo and Java from a wet La Niña year (2008) to a dry El Niño year (2009) (Miettinen *et al.*, 2011).

Although the onset of El Niño may bring about conditions that exacerbate fire, the principal driver of tropical peatland fires is not climate but land use change (Boehm *et al.*, 2001; Aldhous, 2004; Page *et al.*, 2009). Both deforestation and drainage have been linked with the increased occurrence of fire on peatlands (Van de Werf *et al.*, 2008). There has been a lack of government enforcement to prevent and monitor illegal logging, leading to forest degradation (Tacconi *et al.*, 2003) and pressure from logging and clearance for agriculture have left forested areas fragmented and at high risk of fire (Langner, 2007). Siegert *et al.* (2001) revealed that there is a relationship between recently logged forests and the incidence of fire. Fire fragments the peat swamp forest canopy leading to enhanced solar radiation at the ground which increases surface peat temperatures, thus drying out the litter layer and increasing the risk of subsequent fires (Cochrane, 2001). In peatland areas in Indonesia the removal of the forest canopy and forest degradation also alter the microclimate leading to an enhanced albedo effect, increasing temperatures and reducing relative humidity (Takahashi and Yonetani, 1997). Data collected from a variety of locations in the former MRP area revealed that temperatures are significantly higher in deforested areas (+27.62 ± 1.38 ^{o}C) than in areas covered by forest vegetation (+25.72 ± 0.72 ^{o}C) (Ludang *et al.*, 2007).

In the past, peat soils have been used for small scale agriculture by smallholder farms for growing fruit and vegetable crops (Page *et al.*, 2009), but more recently there has been rapid and widespread peat swamp forest clearance for the development of commercial oil palm and pulpwood plantations (Siegert & Hoffmann, 2000; Suyanto, 2004). Demand for biofuel, vegetable oil and paper has resulted in large areas of land being cleared and drained. Fire is often used as a tool for large scale land clearance by industrial plantation companies as well as by farmers to clear land and burn agricultural waste (Schweithelm, 1998). Following the 1997-98 fires, the Government of Indonesia largely blamed the fires on commercial companies that had been clearing land for oil palm and pulpwood (Page *et al.*, 2009), but in addition transmigration settlements had placed a further pressure on Indonesia's peatlands, (Fearnside, 1997). By 2006, Government initiatives had involved relocating 6.2 million people from areas of high population density such as Java to "under populated" islands including Borneo by offering incentives such as jobs and land ownership. A relationship between increasing migrant numbers and the occurrence of fire on peatlands has been demonstrated (Anderson & Bowen, 2000).

The former MRP area in Central Kalimantan is an example of how land use change has caused extensive degradation to forest vegetation and belowground peat as a result of extensive fires. This over-drained and now fire prone landscape, which was once covered with peat swamp forest, is now largely dominated by a secondary vegetation of ferns and sedges, with a greatly reduced forest cover (Hoscilo *et al.*, 2013) (Fig. 3). The implementation and subsequent failure of the MRP has had serious implications for the environment in terms of high C emissions from regular fires and also for human health as a consequence of the high levels of air pollution associated with smoke plumes (Heil and Goldammer, 2001). The spatio-temporal analysis conducted for Block 'C' of the former MRP reveals the extent and severity of fires (Hoscilo 2009). Forest cover was shown to have decreased dramatically since the implementation of the MRP in 1996 and up to the end of the study period (2005); this was largely due to successive fires. The fires of 1997 were particularly devastating as 33.5% of the total land area of Block 'C' of the MRP area was affected. In total around 80% of the land area of Block 'C' has been affected by fires since 1973 with the majority of the area affected since

1997 (Fig. 4). Although much of the forest cover, and hence fuel load, has now been destroyed, fires still return almost every dry season (i.e. May-November), mostly concentrated in the heavily burnt and degraded areas, which are now colonised by herbaceous vegetation.

*Fig.3: Fire affected, degraded peatland in the former MRP, Central Kalimantan, Indonesia. An area once occupied by peat swamp forest is now dominated by ferns (*Stenochlacena palustris and Blechnum indicum*) sedges, grasses and shrubs that rapidly colonize after a fire. Several years after a fire a limited number of pioneer tree species will grow. (Photo taken: March 2011).*

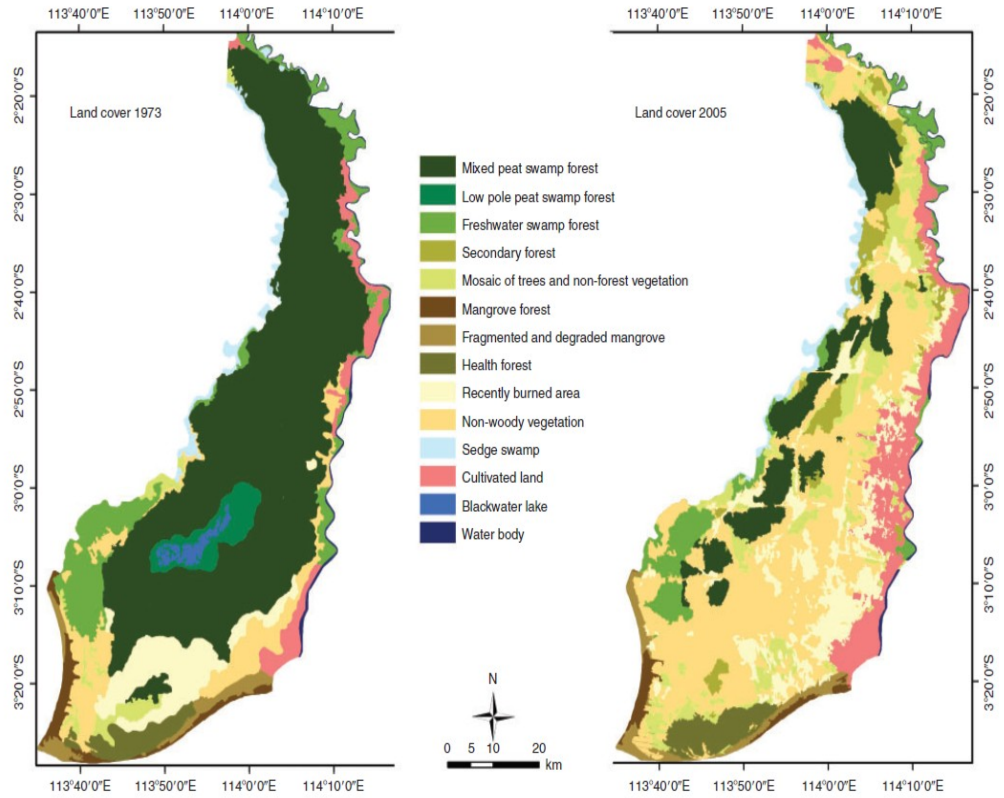


Fig.4: Land cover change in Block 'C' of the former Mega Rice Project area in Central Kalimantan, Indonesia from 1973 (left) to 2005 (right). Fire is indentified as the principal factor in influencing vegetation succession. Figure taken from Hoscilo et al., (2011).

2.2.2 Fire dynamics in Indonesian tropical peatlands

Fire is an exothermic reaction that requires a source of fuel and oxygen that allows combustion to take place, as a result of which, during complete combustion, CO_2 and water are released (Cochrane & Ryan, 2009). Combustion may volatize fuels and create a mass of incandescent gas, a process known as flaming combustion. At lower temperatures, with low oxygen availability and without the presence of flames, smouldering combustion is likely to occur (Rein *et al.*, 2008 & 2009). Much of what is understood regarding the thermodynamics of tropical peatland fires has been gathered from research based on fires in temperate (Lavoie & Perillerin, 2007) and boreal regions (Hogg *et al.*, 1992; Kuhry, 1994; Robinson & Moore, 2000; Camill *et al.*, 2004). Currently there are only a small number of studies that have investigated the thermodynamics of tropical peatland fires (Usup *et al.*, 2004; Hamada *et al.*, 2012) and, as a result, our understanding of fire characteristics in tropical peatlands is very limited.

Peatland fires can be referred to as either 'surface' or 'deep peat' fires (Usup *et al.*, 2004) during which, respectively, either flaming or smouldering combustion will occur. Surface, flaming fires involve exothermic combustion processes, while smouldering, sub-surface fires are usually endothermic (Rein *et al.*, 2009). Peat fires consume fuel, in the form of peat OM, and release CO_2 during complete or flaming combustion (Borghi & Destriau, 1995). During incomplete or smouldering combustion a pyrolysis reaction takes place (Palmer, 1957; Drysdale, 1998; Rein *et al.*, 2008). Pyrolysis is the thermochemical decomposition of organic material in the absence of oxygen (Uden, 1993). Pyrolysis is typically the first reaction to take place during combustion and cause organic material to break down into pyrolysis products that are characteristic of their source (Wampler, 2006). Pyrolysis reactions likely cause charring (Hadden *et al.*, 2013) and increase the C content of the remaining OM. Smouldering fires also emit higher yields of particulates than flaming fires (Rein *et al.*, 2009). Due to the occurrence of these smouldering fires and associated oxygen limited conditions, when pyrolysis reactions take place within the peat substrate, CO and CH_4 are released in addition to CO_2 to the atmosphere (Worden *et al.*, 2013). Surface fires in tropical peatlands typically burn between 0-20 cm of the peat profile, while deep peat fires can have burn depths of between 20-50 cm (Page *et al.*, 2002; Usup *et al.*, 2004; Ballhorn *et al.*, 2009). In an experimental burn in a 3 m by 4 m plot in a degraded area of peatland in the former MRP area a mean burn depth of 7.5 ± 6.2 cm was recorded (Hamada *et al.*, 2013). All flaming combustion had ceased after 2-3 hours but smouldering combustion continued for a week after ignition. In Central Kalimantan surface fires are most evident in areas where the vegetation has been deforested or cleared, however deep peat fires have also been noted to occur predominantly in areas that have not been deforested (Usup *et al.*, 2004). Rapid rates of fire spread in deforested areas do not allow burning to extend into deeper peat layers, however where the vegetation remains intact there is increased duration of burning owing to the higher fire fuel load, allowing the fire to penetrate deeper into the peat surface (Usup *et al*., 2004).

Fig.5 illustrates the development of a smouldering fire in a tropical peatland system. Initially a fire will ignite at the surface and depending on environmental conditions, such as water table depth, peat moisture content and available fuel in the peat matrix, the fire will propagate into deeper peat layers (Usup *et al*., 2004). Smouldering fires in deeper peat layers are common in Central Kalimantan (Page *et al*., 2002 & 2009; Usup *et al*., 2004), particularly in areas of drained peatland where there is a high fuel load of dry peat above the water table. A combination of complete and incomplete combustion will occur, depending on whether the fire penetrates the peat surface. These fires will have consequences for the physical, chemical and biological properties of peat, but there have been no studies to date of these fire-driven changes.

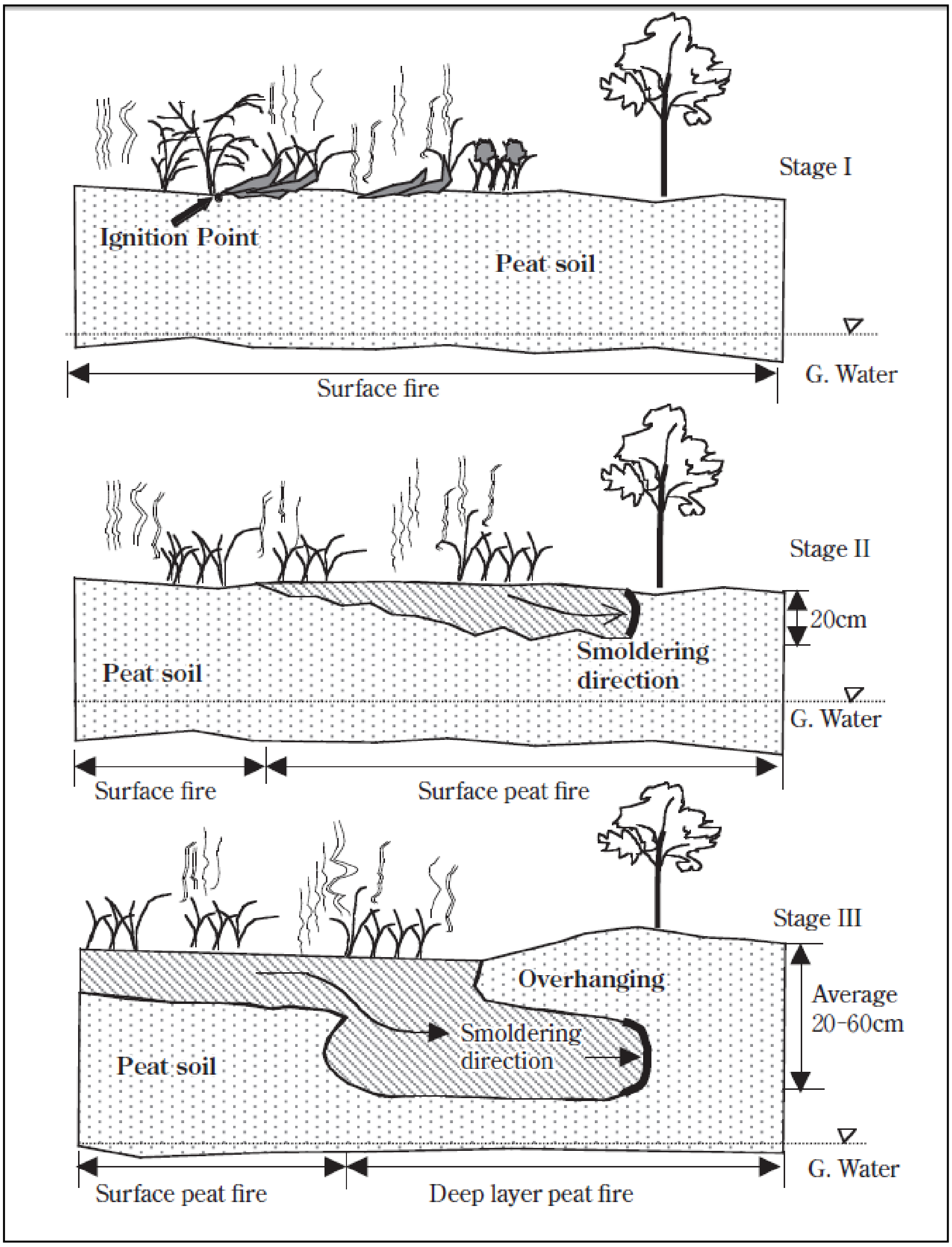


Fig.5: Cross-sectional diagram of peat fire development in a tropical peatland of Central Kalimantan. Stage I: a spot of peat surface is ignited during the surface fire event. Stage II: surface peat fire burns at <20cm depth, Stage III: deep peat fire burns at >20cm depth. (Source: Usup et al 2004).

2.2.3 Fire Regimes

'Fire regime' is a term used to describe the characteristics of a particular fire event, including fire extent, frequency, intensity and severity (Cochrane & Ryan, 2009). There is considerable variability in the behaviour of a fire in a particular ecosystem, however broad-based fire regimes have been used to classify fire events (Whelan, 1995). Fire regimes are dynamic and are likely to change with predicted future climatic changes (Bowman *et al.*, 2009). It is anticipated that in tropical peatlands future climate change will increase the frequency and intensity of fires, (Hoscilo, 2009) unless degraded and drained areas are re-wetted and restored (Dommain *et al.*, 2010). The effects of fire will vary depending on the fire regime in any particular location (Neary *et al.*, 1999; Williams *et al.*, 1999). When reporting the biogeochemical impacts of fire it is beneficial to determine the fire regime that brought about those impacts because the chemical composition of soil will be altered at specific temperatures and duration of burning (Neary *et al.*, 1999).

The following terms are used in this chapter and throughout the thesis:

Fire Extent is measured by the average area of a given fire (Cochrane & Ryan, 2009). The area affected by fire will have varying consequences for the biogeochemistry of soils and peats.

Fire Frequency refers to the number of fires over a particular period of time or in a given ecosystem. *Fire Return Interval* is a term used to determine the interval between different fire events at a particular site and is often used alongside *Fire Frequency* to reveal information about the prevalence of fires.

Fire Severity is a broad term used to describe the ecological impacts of a particular fire (Ryan, 2002). The term is used in different ways by different scientific groups, for example the remote sensing community commonly measure fire severity using correlations between the Normalized Difference Vegetation Index (NDVI) and biomass loss (Chafer *et al.*, 2004; Hoscilo, 2009). However, other studies have made use of a variety of different indices (Ryan & Noste, 1985; Turner *et al.*, 2004; Ryan, 2002) that classify fire severity by assessing the effects of fire on the ecosystem particularly those effects on the OM and vegetation. The Burned Area Emergency Response assessment (BAER) is a measure used by some USA state governmental agencies and specifically measures fire-driven soil modification to assess fire severity (Lewis *et al.*, 2006).

Fire Intensity and ***Fire Severity*** are closely related terms, however their meanings are slightly different. Fire Intensity is measured by the physical energy release created by the combustion process (Keeley, 2009). The term is often confused with and used to describe the impacts of fire and there is current debate in the literature as to whether there should be changes made to the current terminology (Parsons, 2003; Lentile *et al.*, 2006).

Fire regimes, including frequency, intensity and severity, can influence biogeochemical cycling and the chemical composition of soils in a range of ecosystems (Tomkins *et al.*, 1991; Badia and Marti, 2003; Choromanska and DeLuca, 2002; Czimczik *et al.*, 2005) therefore by gaining an understanding of the impact specific fire regimes have on the chemical composition of tropical peat could be particularly important in order to predict the ecosystem response to fire which is critical for post-fire ecosystem management.

2.3.0 Biogeochemical response to fire

Soil OM contains a C pool that is twice as large as the C pool present in the atmosphere (760 Pg) and is about two or three times larger than that stored within all living matter, (Prentice *et al.*, 2001). When soil OM is burnt during a fire, as occurs during the majority of tropical peatland fires, this large C pool can be diminished as a result of OM oxidation (Houghton, 2005). Above and below- ground biomass burning is a significant source of C to the atmosphere in the form of greenhouse gases such as CO_2 and methane (CH_4). However, the combustion of biomass is often incomplete and results in the formation of thermally altered C forms (Cofer *et al.*, 1998). During this alteration, recalcitrant products, namely black carbon (BC), are formed “de novo” (Schulze *et al.*, 2000; Maisello, 2006). It is known that burning can also influence the nutrient status of soils and peats (DeBano *et al.*, 1978; Neary *et al.*, 1999; Certini., 2005; Neff *et al.*, 2005), but the biogeochemical response is highly dependent on the fire regime (Neary *et al*, 1999; Capogna *et al.*, 2009). A fire may be beneficial or detrimental to an entire ecosystem depending on the fire regime and whether the ecosystem is ‘fire-adapted’ (Cochrane, 2009). Research is required to understand how fires alter soil chemistry; this knowledge will assist in planning for post-fire rehabilitation as well as providing more accurate information for soil C models.

2.3.1 Effects of fire on the nutrient status of soils and peats

It is well documented that fire alters the nutrient status of mineral soils (DeBano *et al.*, 1978 & 1991; Kauffman *et al.*, 1993; Kutiel and Shaviv., 1993; Neary *et al.*, 1999). Studies have shown that fire may temporarily increase soil water pH and electrical conductivity, owing to denaturation of organic acids and release of inorganic ions and bases from combusted OM (Certini, 2005). In some cases, however, a decrease in pH is observed (Hamman *et al.,* 2007). Under low intensity fire regimes, plant nutrient availability often increases (Van de Vijver *et al.*, 1999); under high intensity fire regimes, however, soil nutrients are usually depleted (Kauffman *et al.*, 1994).

Nitrogen (N) limits primary productivity in ecosystems, therefore many studies have focussed on how fire alters soil total N content (Christensen, 1987; Fenn *et al.*, 1998). Fire alters soil total N stocks to differing degrees depending on the ecosystem type. Many forest soils experience a decline in total N content post-fire (Kauffman *et al.*, 1995; Bormann *et al.*, 2008) while others experience significant increases in soil total N (Covington *et al.*, 1991; Fenn *et al.*, 1993; Johnson *et al.*, 2001). Loss of N is temperature dependent, with volatilisation commencing at 200 °C (Neary *et al.*, 1999). The quantities of N lost during a fire can be high if the fire reaches temperatures greater than 200 °C and can be correlated to the degree of OM combustion (Geir, 1975). Studies also indicate short term increases in soil N content followed by a longer term decline (Romanya *et al.*, 2001; Wan *et al.*, 2001). Some soil organic N may be lost through volatilisation but in moderate to high intensity fires a large proportion is converted to inorganic forms (Hamman *et al* 2007). Changes in soil N contents have implications for soil fertility and subsequent recovery of an ecosystem, with the rehabilitation of fire damaged forests often limited by N availability (Stegmoller & Chappell, 1990.).

Higher temperatures are required to combust inorganic Potassium (> 760°C) and Calcium (> 1240°C) (Weast, 1988; Certini, 2005). These nutrients may be lost from the soil system by a variety of pathways including; volatilisation, mineralisation, erosion, leaching and ash convection (Christensen, 1994; Certini, 2005). Although nutrient rich ash is a product of biomass burning, it is often lost rapidly from the system by surface runoff or wind transport (Cook, 1994; Thomas *et al.*, 1999). Ash losses are highly dependent on post-fire climatic conditions with large nutrient losses reported in areas with high intensity rainfall which leads to erosion and surface runoff (Gimeno-Garcia *et al.*, 2000).

Quantification of post-fire soil C content has become increasingly important for improved understanding of the global C cycle. After burning, soil C contents are variable, depending on the fire regime and type of environment. In particular differences have been observed between prescribed fires and wildfires. C contents have been shown to increase after wildfires in a range of environments (Johnson & Curtis, 2001) and this is thought to be due to the accumulation of charcoal fragments as well as the transport of hydrophobic organic matter from surface horizons and stabilization with cations. Soil C contents have, however, also been shown to decrease after burning (Page-Dumroese *et al.*, 2006), particularly during prescribed (lower temperature compared to wildfire) burning (Johnson & Curtis, 2001). Immediately (one month) after a prescribed fire in a pine forest in the Galicia region of Spain the soil C contents had been significantly reduced but four months after the fire, C contents were greater than control samples that had not been burnt (Johnson and Curtis, 2001). This result is attributed to an initial decrease in mineral soil C later followed by gains in C through addition of unburnt residues (e.g. charcoal) and N-fixing vegetation (Wells, 1971). Following a fire in artificially drained peat at Lake Gavur in Turkey, the soil C contents significantly declined by 76 % and 91 % at both surface and subsurface sampling depths (Dikici and Yilmaz, 2006). Peat fires in the Florida Everglades also resulted in initial declines in peat C contents. The surface layer of peat was most affected by the fire leading to a pronounced vertical gradient between upper and sub-surface peat layers with regard to concentrations of a range of nutrients, including C and N (Smith *et al.*, 2001). In the Everglades, peat nutrient transformations lead to growth of the invasive species *Typha domingensis* (southern narrow leaved cattail). Soil C contents may, however, also remain unaltered by fire (Hatten & Zabowski, 2010).

The effects of fires on nutrients in mineral soils are well documented (DeBano & Conrad, 1978; Raison *et al*., 1979; Klopatek *et al*., 1990, 1991; Romanya *et al*., 1994; Ketterings & Bingham, 2000) but there are very few studies that focus on the impact on peat soils (Smith *et al*., 2001) with fewer studies still that have investigated fire impacts on tropical peats. Preliminary field data from Indonesia (Wust & Page, unpublished data) indicate that fire alters the chemical properties of peats and the availability of plant nutrients, which will have an immediate influence on post-fire vegetation and ecosystem recovery. These changes in peat nutrient status will likely affect the community structure of the post-fire vegetation with, in turn, implications for peatland C budgets.

2.3.2 Effects of fire on soil OM composition

Following a wildfire, soil OM may be altered and often includes thermally altered C forms that suggest presence of black carbon (Cofer *et al*., 1997). As well as GHG's being emitted from the soil directly from combustion, if heat is transferred to the soil (Alexis *et al*., 2012) it can lead to alteration of the OM composition (De La Rosa *et al*., 2012).

Revealing the composition of soil OM is important for an improved understanding of how fire alters soil OM composition, quality and, as a result, overall ecosystem functioning. The cycling of C is thought to be profoundly altered by the fire induced modification of soil OM composition in many environments including, temperate scrub-oak ecosystems (Alexis *et al*., 2012), Mediterranean leptosols in Portugal, (De La Rosa *et al*., 2012) and soils from a pine forest in Northern Alberta, Canada (Otto *et al*., 2006). The thermolabile (less resistant) C fraction is often depleted as a result of fire (Harden *et al*., 2000; Neff *et al*., 2005), whilst an accumulation of recalcitrant (more resistant) forms may provide a store of C in the slow cycling geological C reservoir (Kulhbusch & Crutzen 1995; Knicker *et al*., 2005). Studies of fire-affected soils have reported a loss of both carbohydrates and of organic compounds with oxygen-containing functional groups (González-Pérez *et al.*, 2004; Certini, 2005). Post-fire C cycling in soil systems is modified as a result of enhanced oxidation of OM (Hogg *et al.*, 1992; Kasischke *et al* 1995). In general, in addition to the depletion of oxygen-containing functional groups (Gonzláez-Pérez *et al* 2004), a reduction in the chain length of aliphatic homologues such as alkanes and alkenes (Kaal and Rumpel, 2009), along with the formation of heterocyclic N compounds and aromatisation of sugars (Certini, 2005). Generally a reduction in o-alkyl structures occurs alongside an accumulation of alkyl and aryl structures (Alexis *et al.*, 2010).

The effects of fire on soil OM are highly variable and depend on a number of factors, including fire regime. Soil OM may be almost totally destroyed (Chandler *et al.*, 1983; Haslam *et al.*, 1998) but moderate or prescribed fire usually results in an increase in soil OM (Knicker *et al.*, 2005a), due to increased input from slightly charred plant material and through the addition of charcoal and recalcitrant forms of OM.

The effects of fire on OM in all soil types including peats, is highly dependent on duration and temperature of the burn (González-Pérez *et al.*, 2004; DeBano *et al.*, 1990). Mineral soil forest fires do not typically burn significant quantities of soil OM, although any chemical changes that do occur as a result of burning depend on the temperatures reached at different depths and the specific temperature that different chemical components can withstand before degrading (Gonzláez -Vila, 2004). In a study of Australian mineral soils, wildfire conditions caused just the upper 1 mm of soil to reach a maximum temperature of 200 ^{o}C (Humpreys & Craig, 1981). Changes are also time dependent (i.e. burning at 1000 ^{o}C for 10 seconds is not directly comparable to 350 ^{o}C for 1 minute) as well as temperature dependent. It is well understood that different components of OM will undergo structural changes at different temperatures (Certini, 2005). Above 150 ^{o}C, dehydration occurs leading to an increase in C and N contents and a decrease in hydrogen and oxygen contents (Baldock and Smernick, 2002). Loss of organic C begins at slightly higher temperatures (between 100 and 200 ^{o}C) and lignins and hemicelluloses will begin to degrade between 130 ^{o}C and 190 ^{o}C (Chandler *et al.*, 1983). Above 350 ^{o}C, polyaromatic compounds are formed (Paris *et al.*, 2005). Tropical peatland fires are reported to typically smoulder belowground, heating the belowground peat substrate. Once these smouldering fires ignite they are difficult to extinguish and have been known to burn for weeks, often until doused by rain (Page *et al.*, 2002). The temperatures that are obtained at different depths depend on the type of fire; 'surface fires' burn the surface fuels only, 'surface peat fires' burn at depths of between 0 and 20 cm, while 'deep peat fires' burn at depths greater than 20 cm and up to 50 cm below the peat surface (Usup *et al.*, 2004). 'Surface peat fires' and 'deep peat fires' are dominated by smouldering combustion and generally burn at lower temperatures than flaming fires (surface fires) (Rein, 2008), although they are likely to be more damaging for the peat system due to long residence times and increased depth of heating. The thermal severity of peatland fires is generally higher than in mineral soil environments due to this difference between smouldering and flaming fire types (Certini, 2005). Smouldering fires heat the subsurface peat (Rein, 2008) and therefore they are more likely to cause modification to the OM composition. To summarise, characteristic variables such as temperature, duration and depth of burn can all influence the degree and nature of the chemical changes in peat OM following a fire.

The intensity (the physical energy release created by the combustion process (Keeley, 2009)) of the burning process is important to consider when analysing changes in soil OM. High intensity fires have long lasting effects on forest soils (Knicker *et al.*, 2005), causing increased contributions of aromatic and heterocyclic N forms to soil OM. Aromatisation of many soil compounds is caused by dehydration (the loss of water from a reacting molecule) followed by cyclisation (formation of cyclic structures) of carbohydrates, lipids and peptides (Almendros *et al.*, 2003). Heterocyclic N formed during burning could fragment into pyrolysis products such as pyridine, pyrroles and indole (Almendros *et al.*, 2003). Addition of ash may increase the alkalinity and increase C loss by leaching or microbial degradation (Knicker *et al.*, 2007). Although not a direct effect of fire, fire frequency can also be significant when assessing the post-fire chemical composition of soils. Short fire return intervals do not allow recovery of the vegetation thereby increasing the post-fire temperature of the soil surface; therefore, the nature of chemical change in soils could vary (González-Pérez *et al.*, 2004). For example, microbial activity will subsequently be enhanced, leading to increased rates of mineralization of the remaining soil OM (Mills & Fey, 2004).

In this study, it is hypothesized that surface and sub-surface fires in tropical peatlands will lead to thermal alteration of the non-combusted OM. Estimated average burn depths during fires in the former MRP area range from 7.5 ± 6.2 cm during week long experimental burns (Hamada *et al.*, 2012), to 33 ± 18 cm during the 2006 wildfires (Ballhorn *et al.*, 2009) and up to 51 ± 4.0 cm during the 1997 wildfires (Page *et al.*, 2002). It is not known how vertical transport of heat below, as well as within, the partially combusted surface peat layer may cause alteration of the OM composition, but any modification that does occur is likely to have wide ranging impacts on long term ecosystem dynamics, including the potential for vegetation re-growth and overall ecosystem recovery, and on the peatland C cycle.

2.4.0 Formation of 'Black Carbon' by fire

During the burning of OM, incomplete combustion typically occurs due to low oxygen availability, resulting in the formation of pyrogenic organic matter (PyOM), also known as 'Black Carbon' (Hammes, 2007; Knicker *et al.*, 2008). Black carbon is defined as a chemically heterogeneous and biologically refractory form of organic matter (ROM) remaining as a residue from incomplete combustion processes (Rosa Arranz, 2009). C contents of black carbon materials are typically > 60 % (Goldberg, 1985). During biomass burning in mineral soil fires most of the black carbon formed will remain on the ground surface (80 %) with the rest being emitted as aerosol particulates in smoke (Kulhbusch & Crutzen, 1995).

Black carbon is a heterogeneous mixture of combustion products, from char to ash and charcoal (Marseillo, 2006). It is often described as a continuum since it contains a wide range of structures (Preston & Schmidt, 2006). This combustion continuum, as presented by Hedges (1999), can be used to identify the different types of black carbon. All of the combustion products in the continuum have a high C content and are based on aromatic structures (Fig.6.) The aromaticity of black carbon increases with the maximum temperature that is attained during burning (Marseillo, 2006). In addition, the size of individual black carbon particles decreases and the chemical reactivity increases with an increase in the temperature of formation (Masiello, 2002). Baldock & Smernik (2002) used ^{13}C NMR to assess the effects of charring on pine wood and demonstrated that as temperatures increased there was a loss of carbohydrate structures and an increase in aromatic ring structures. A common defining characteristic of fire altered biomass is the presence of aromatic structures that indicate the presence of charcoal in soils (Preston and Schmidt, 2006). The presence of charcoal-derived (black carbon) organic compounds such as benzene, pyridine and toluene, have previously been detected in analytical pyrolysis products of samples from burnt soils (Campo *et al.*, 2011).

There has been increased scientific interest in black carbon for two reasons; firstly it has an effect on the Earth's radiative heat balance. Black carbon aerosols, commonly referred to as soot, have a high solar absorption of near-infrared and ultra-violet wavelengths which are reflected by the earth's surface, thus reducing the Earth's albedo (Ramananthan and Carmichael, 2008). Surface albedo can also be reduced when black carbon is deposited on the Earth's surface, particularly when black carbon is deposited on snow or ice (Flanner *et al.*, 2007). Secondly, black carbon is relatively resistant to thermal or chemical degradation, therefore it represents a potential C sink (Kulhbusch, 1998; Glaser, 2000). Original work by Goldberg (1985) first presented the idea that black carbon produced from biomass burning is highly stable in the soil system and may potentially contribute to the Earth's slow-cycling carbon pools. The ^{14}C ages for black carbon in soils are between 1,160 to 5,040 years (Pessenda *et al.*, 2001) which is greater than most non-black carbon organic fractions (Schmidt *et al.*, 2002). Black carbon is widespread across terrestrial systems and its high stability suggests importance for the global C budget (Forbes *et al.*, 2006), although it is important to note that only a fraction of the highly resistant C produced from biomass burning is likely to be sequestered in long term geological cycling (Bird *et al.*, 1999). Some authors have presented evidence to suggest that black carbon is not as resistant to microbial breakdown as initially thought (Knicker, 2007; Zimmerman *et al.*, 2012) and that often the microbial mineralisation rate for black carbon can be as high as for non-combusted OM (Hilscher *et al*., 2009). A debate continues regarding the stability of black carbon. In some soils black carbon has been shown to have old radiocarbon ages; in particular, '*terra preta*' soils (dark fertile soils which have a high charcoal and OM content that were created by human activities and often contain indigenous artefacts such as ceramics from previous settlements (Eden *et al*., 1984)). *Terra preta* soils are predominately found in Amazonia (Glaser *et al*., 2001) and are cited as evidence that black carbon is preserved in some environments (Cheng *et al*., 2008). In other environments, however, black carbon can be decomposed rapidly, for example Bird *et al*. (1999) found black carbon degradation in tropical savannah soils occurred over the order of decades. Environmental conditions, such as temperature, may influence the preservation of black carbon (Cheng *et al*., 2008), with higher temperatures likely to favour mineralization of black carbon. Black carbon may also be degraded in areas subject to repeated and high intensity fires. If an area is subject to multiple fires the fires may not increase the quantity of black carbon as the residues formed after the initial fire will be consumed by subsequent fires (Preston & Schmidt, 2006). Indeed, high intensity fires may completely combust soil OM, thereby resulting in low quantities or the complete absence of black carbon (Czmickik *et al*., 2005).

	Slightly Charred Biomass	Char	Charcoal	Soot	GBC*
Formation (T)	Low ⟶	⟶	⟶	⟶	High
Size	●——	Mm & larger ——●	Mm-submicron		Submicron
Plant structures	Abundant	Significant presence	Few		none
Reactivity	High ⟶	⟶	⟶	⟶	Low
Initial Reservoir	●——	Soils ——● ●——	—— Soils &	Atmosphere ——	——●
Paleotracer range	Short (Meters)		Short (m to km)		Long (1000s km)

*Fig.6: Black carbon combustion continuum: Initially presented by Hedges, (1999). *GBC – Graphitic Black Carbon. (T) – Temperature. Adapted from Maisello (2004).*

Currently, there is increasing interest in black carbon stocks across many different environments. This is in part driven by the belief that this knowledge will contribute to improved understanding of climate systems and long term C storage in soils and ocean sediments (Maisello, 2004). Very little is known about the stabilization of organic C in soil systems (Preston & Schmidt, 2006) and there is certainly a gap in knowledge with respect to organic C stabilization in tropical peatlands. The fire induced sequestration of C in fire-affected ecosystems could represent a significant sink of C resulting in implications for climate models (Maiseillo, 2004; Lehmann, 2008). If black carbon were found to represent a significant portion of the recalcitrant soil organic C pool, soil C models would need to be adjusted, since neglecting or underestimating the global BC pool would significantly inflate the projected CO_2 emissions from soil OM.

Various studies have attempted to quantify black carbon stocks in different environments (Rovira *et al.*, 2009; Lorenz *et al.*, 2010; Caria *et al.*, 2011). Many of these studies are based on experimental burns. In a study of the effect of changing fire regimes on black carbon stocks in boreal forests on mineral soils, Czimczik *et al*. (2005) found maximum concentrations of 72 g m^{-2} in the organic layer,. In the same study, low intensity fires resulted in greater quantities of black carbon (> 5 g m^{-2}) compared with high intensity fires (0.1 g m^{-2}) (based on the black carbon remaining in the upper 25 cm of the soil). A study following a forest fire in Yellowstone National Park found that 640 g m^{-2} of char material was produced (Tinker & Knight, 2000), while between 114 and 454 g m^{-2} of char were produced during studies of fires in Amazonia (Fearnside *et al*., 1993, 2001; Garcia *et al*., 1999).

No studies to date have attempted to identify the presence or quantify the amount of black carbon produced during fires in tropical peatlands.

2.4.1 Techniques to quantify black carbon in soils

There are a wide variety of techniques employed for quantifying black carbon in soils. Each of these techniques have their own limitations when attempting to identify and quantify black carbon stocks due to the wide variety of black carbon sub-types (Schmidt & Noack, 2000) and there have been various reviews on the different methods used to detect and quantify black carbon stocks (Preston & Schmidt, 2006; Maseillo, 2004; Hammes *et al*., 2007; Knicker, 2007). There is no one accepted method for the quantification of black carbon; this is mainly due to each method having an analytical window that only allows quantification of one part of the continuum of different black carbon substances (Hammes, 2006). Black carbon quantification methods generally fall into one of six categories; microscopic, optical, thermal, chemical, spectroscopic, or molecular marker (Masiello, 2004). These analytical techniques attempt to analyse the different forms of C present in the OM of soils and sediments including the thermally unaltered organic C (such as humic substances and plant material) and pyrogenic C. Once these different forms have been separated, chemical methods, e.g. elemental analysis, are often used to determine the black carbon content (Simpson & Hatcher, 2004a).

The cut off point that identifies black carbon from the remaining OM may differ from one method to another, therefore black carbon quantification may vary considerably depending on the type of analysis used. Schmidt *et al*. (2001) used a range of different detection methods to quantify black carbon in a number of soils and sediments; their results showed variation of up to two orders of magnitude.

Molecular marker methods use markers such as benzenecarboxylic acids (BCPA's) (Dai *et al*., 2005; Glaser *et al*., 1998; Czmizcik *et al*., 2003). Dai *et al*. (2005) attempted to quantify black carbon stocks in temperate savannah soils in the southern Great Plains, USA. Black carbon concentrations increased with depth and correlated with the incidence of fire events, although results of repeated burning did not significantly increase concentrations. Chemical methods can be problematic because of interference from mineral impurities that can appear and act like black carbon (Glaser *et al*., 1998) causing overestimation of black carbon stocks if these are included in the analysis.

Pyrolysis-GC/MS has not typically been used as a method to detect BC stocks in soils. For example, a methodological review by Hammes *et al*. (2007) does not mention this approach, although more recently there has been increasing use of this method for black carbon characterization (González- Vila *et al*., 2001; De La Rosa *et al*., 2008; Kaal *et al*., 2009b).

Pyrolysis GC/MS was used to detect black carbon in soils and characterise black carbon compounds in charcoal from a colluvial soil in North West Spain (Kaal *et al*., 2009b). Identification of black carbon markers was not without its difficulties. The method of Py-GC/MS includes a pyrolysis step that can lead to a rearrangement of organic molecules that may interfere with the rearrangements caused by natural burning. Therefore, a Py-GC/MS method, optimised for BC identification was used. Initally the authors, experimented with varying pyrolysis temperature (up to 1200 ^{o}C) and after intital pyrolysis of the sample the non-pyrolysable residues were re-analysed at 1000 ^{o}C. By pyrolysing at higher temperatures markers of BC were more readily observed in the pyrolysates. The optimum temperature for pyrolysis of charcoal-BC was 700 ^{o}C and higher. 750 ^{o}C was used to pyrolyse BC-containing soil samples as this resulted in a good balance between good quality chromatographs, with BC markers readily identifiable with limited structural rearrangement of other molcules including lignins. Results showed a suite of aromatic compounds, indicative of black carbon such as benzene, toluene and PAHs (naphthalene, biphenyl, fluorene and phenanthrene). Some aliphatic material had also survived the fire which formed part of the black carbon. There were no differences in BC markers between different plants thus Py-GC/MS does not distinguish between different vegetation species (Kaal *et al.*, 2009b).

Quantification of black carbon stocks in tropical peatlands and other C-dense ecosystems may go some way towards explaining the 'missing C' in the global C budget (Kuhlbusch, 1998a) but there are currently no studies of black carbon or charcoal in tropical peatland environments. A study of charcoal in temperate upland peats in the UK Pennines reported values of 4.3 % black carbon/CC (CC= C consumed) or 6.35 g cm^2 (Clay and Worrall, 2011) (equivalent to 635 kg C ha^{-1}) (N.B. this result is expressed as a percentage of the total CC during a fire (black carbon/CC, a method first proposed by Forbes *et al.* (2006)). Between 0.9 % and 1.1 % black carbon/CC has been reported in South African savannas fires, 0.1 % and 0.5 % in tropical Australian grasslands, and 2.9 % and 7.8 % in Amazonian rainforest fires (Forbes *et al.*, 2006). The method used in this latter study involved determining the charcoal added to the surface during a fire and did not consider any black carbon that may have been formed through burning of the soil. The results of black carbon analyses presented in this thesis will be some of the first to attempt to quantify the black carbon produced as a result of a fire in an area of tropical peatland in Indonesia, however the method used in this study will only reveal the black carbon content contained within the peat itself.

2.5 Fire induced water repellence

It is widely documented that fire can enhance the water repellence status of soils (DeBano, 2000a, Doerr *et al*, 2000; Macdonald *et al.*, 2004). Water repellent soils can have significant implications for local hydrology, soil erosion and plant growth (Doerr *et al.*, 2000). Water repellent soils have also been observed to cause reduced infiltration and preferential flows in hydrophilic areas of soil leading to leaching of soil nutrients (Andrieu *et al.*, 1996, Certini, 2005). In overall terms, water repellence may lead to reduced availability of both water and nutrients required for plant growth; therefore if water repellence is shown to be enhanced by fire on tropical peatland it could impede regeneration of forest vegetation. In most cases water repellence is a short-lived phenomenon, as heavy rainfall will penetrate even the most hydrophobic of soils (Wondzell & King, 2003) causing the water repellency effect to be masked. In degraded peatland areas, however, when the peat becomes very dry and the water table is low, e.g. shortly after a fire, it is hypothesised that water repellence may increase peat erosion and subsequent fluvial loss of C stocks into waterways.

Fire can cause hydrophilic soils to become hydrophobic and can enhance or reduce hydrophobicity in soils that are already hydrophobic (Savage, 1974). Heating of soils causes volatilisation of hydrophobic organic substances such as cuticular waxes in the litter and topsoil which move down the soil profile, following the temperature gradient until the soil becomes cooler; the hydrophobic substances then condense forming a water repellent layer (DeBano, 2000; Doerr *et al.*, 2000). Hydrophobic compounds in soils may be bonded more strongly to soil particles if they are subjected to heating during a fire (Giovanni, 1994). The amount of OM is also thought to be linked to water repellence of a soil (Doerr *et al.*, 2000) and typically water repellence is linked to OM content (Täumer *et al.*, 2005). Soils with high OM contents (such as peat soils) will generally be more water repellent (Benito *et al.*, 2003). There are, however, some studies that present results that are not consistent with these findings (DeBano, 1991). Thus the type rather than the quantity of OM may influence the water repellence (Dekker and Ritsema*,* 2000), for example humic and fulvic acids are possible sources of water repellent substances in both burnt (Almendros *et al.*, 1990) and unburnt soils (Wallis and Horne, 1992).

Fire induced water repellence is temperature dependent (Doerr *et al.*, 2000). In mineral soils, water repellence does not increase at temperatures <175 °C, however between 175 °C and 200 °C it increases dramatically (Doerr *et al.*, 2000). Above 280 °C, water repellence is often destroyed in many soils (Savage, 1974; Doerr *et al.*, 2000). Many authors have reported a variety of temperature thresholds for the degree of water repellence in different types of soils (DeBano *et al.*, 2000; Doerr *et al.*, 2004, 2005; Zavala *et al.*, 2010), however all report water repellence is destroyed at temperatures typically between 280 °C and 300 °C.

There are many studies of peats that report on the difficulty of re-wetting peat once it becomes dry (Andriesse, 1988, Robichaud & Hungerford, 2000). Irreversible-drying is a term used to describe a peat that does not become wetted easily after intense drying. Irreversible drying occurs when a layer of peat at the surface becomes extremely dry and therefore highly susceptible to fire (Hooijer *et al.*, 2006). It is likely that this process of irreversible drying is due to an enhanced water repellence effect when peat water content drops below a certain threshold. It is not currently understood, however, if peat soil that is already water repellent is further altered by burning. It is therefore hypothesised that dry peat, i.e. peat in drained areas particularly during the dry season, will become water repellent and that water repellence will be further altered by fire, although this is likely to be dependent on temperatures reached at different depths within the peat (i.e. a high temperature fire could reduce the water repellence but a lower temperature fire could enhance peat water repellence).

2.6 Summary – Current Research Gaps

This literature review has highlighted the following gaps in knowledge relating to fire effects on the OM composition of tropical peatlands:

- A lack of understanding of the composition of the peat OM in tropical peatland subject to differing land management (intact, drained and burnt) which is likely to be of significance when trying to establish methods to rehabilitate the vegetation of degraded peatlands.

- A lack of information on how ‘surface fires’ and ‘sub-surface peat fires’ and their associated temperature differences at depth cause thermal alteration of the peat OM. Although it is known that peat fires frequently burn to depths of up to 30 cm or more into the surface peat it is not know if sufficient heat is transferred to chemically alter the peat OM below this depth.

- Knowledge of the short and longer term effects of fire on the biogeochemistry of tropical peat including OM composition and nutrient content is lacking.

- Understanding of how single and multiple fires affect the biogeochemistry of tropical peat including the OM composition and nutrient content is lacking.

- There is a lack of quantification of fire derived BC from tropical peat fires. There is also a lack of a reliable method to detect charcoal that may be formed when peat smoulders belowground.

- There is a lack of knowledge of how fire may affect peat by enhancing or destroying water repellence and whether this is a sustained or short-lived post-fire phenomenon.

More generally, this review has indicated that there is very little known about the biogeochemistry of tropical peat despite its importance in the wider field of global biogeochemical cycling and the earth's climate system. Biogeochemical changes as a result of fire are reasonably well documented for mineral soils (Tomkins *et al*., 1991, Romanya *et al*., 1994, Neary *et al*., 1999, Ketterings & Bingham, 2000, González-Pérez 2004, Certini 2005, Knicker *et al*., 2007, De La Rosa *et al*., 2008) but there is a research gap when considering peat soils and, in particular, tropical peats. Given that firstly, peat is a highly concentrated store of C (Sorenson, 1993) and, secondly, that there is an increasing frequency of fires on tropical peatlands, particularly in Indonesia (Hoscilo, 2009 & 2011), it is important to understand the biogeochemical response of peat to such environmental disturbance. This knowledge will be of particular relevance to resource managers involved in the rehabilitation of fire-degraded peat landscapes as well as to modellers who require an improved knowledge of the scale and nature of fire-driven changes in soil C pools.

Chapter Three -Materials and Methods

3.0 Introduction

This chapter describes the general materials and methods that are used throughout the subsequent three results chapters presented in this thesis. It is divided into three main sections as follows: Section 3.1 is the description of the field sites including their fire history. Section 3.2 describes the method of plot selection and sample collection. Section 3.3 incorporates background information regarding sample analyses, in particular the application of Pyrolysis–Gas Chromatography-Mass Spectroscopy (Py-GC/MS) in analysing peat samples. More specific laboratory methods applied to investigate the individual research questions will be described in their corresponding data chapters (Chapters 4-6). Section 3.4 details the statistical methods that have been used to analyse the data.

3.1 Study Sites: General Overview

The study area is located in the Indonesian province of Central Kalimantan, south of the provincial capital, Palangkaraya (2^{o}12’36’’S 133^{o}55’12’’E). The climate in Central Kalimantan is classified as humid tropical; mean annual temperatures range from 25-27 °C and average rainfall varies between 2,300 and 3,000 mm yr^{-1}; the average humidity ranges between 85 to 90 % (Shimada, 2001). The annual pattern of rainfall is determined by two monsoon systems: the southeast dry monsoon and a northeast wet monsoon; there is a long wet season (September – April) and a shorter dry season (May – August). Extensive ombrotrophic (rain-fed) peatlands have developed in the coastal and sub-coastal lowlands of Central Kalimantan due to favourable waterlogged conditions and substrate acidification.

During the mid-1990s, more than one million hectares of tropical forest, the majority of which were forest covered peat lowlands, were allocated for agricultural development. The ‘Mega Rice Project’ (MRP) was a result of the 1995 Presidential Decree ‘Development of 1 million Hectares of Peatland for Food and Crop Production in the Province of Central Kalimantan, Peat Reclamation' (Notohadiprawiro, 1998). The overall aim of this was to ensure Indonesia's self sufficiency in rice production. The project began in 1995 and involved clearing one million hectares of tropical forest followed by drainage of the peat through construction of 4,600 km of drainage canals across each of five project blocks (A-E) (Notohadiprawiro, 1998; Jaya *et al.*, 2010). A few years after the implementation of the project it was clear, however, that it would be unsuccessful. Unsuitable growing conditions for rice due to the acidic peat substrate and difficulties in controlling water levels (Sulisiyanto, 2004) resulted in the project being abandoned in 1999. What remains is a vast area of degraded peatland, largely deforested and heavily drained, that is susceptible to frequent fires during the dry season. To the west of the MRP is an area of relatively intact peat swamp forest (PSF) known as the Sebangau Forest. This area has a history of small-scale selective logging activity, but it remains relatively undisturbed in comparison with the MRP area (Page *et al.*, 1999). Sampling locations were selected in Block C of the MRP and in the nearby Sebangau Forest. Importantly, the sampling location in the Sebangau Forest not only had an intact vegetation cover (i.e. PSF) but it had also not been affected by either fire or large-scale drainage.

Three areas were selected as sampling sites. Site 1 (Sebangau Forest) was chosen as a control site (forested, undrained, unburnt peatland). Site 2 (drained forest, Block C, MRP) was chosen in order to elucidate the effects of peat drainage on soil OM composition in the absence of fire. This was necessary since all fire-affected peatlands in Southeast Asia have to a lesser or greater extent been influenced by drainage. Site 3 (fire-affected, drained peatland, Block C, MRP) was representative of peatland that had been subject to both drainage and a range of different fire frequencies (Fig.7 and 8). By comparing the results of various chemical analyses of samples from the three different sites deductions were able to be made about some of the biogeochemical effects of fire. In addition to the effects of fire, results also revealed some of the effects of drainage on peat biogeochemistry.

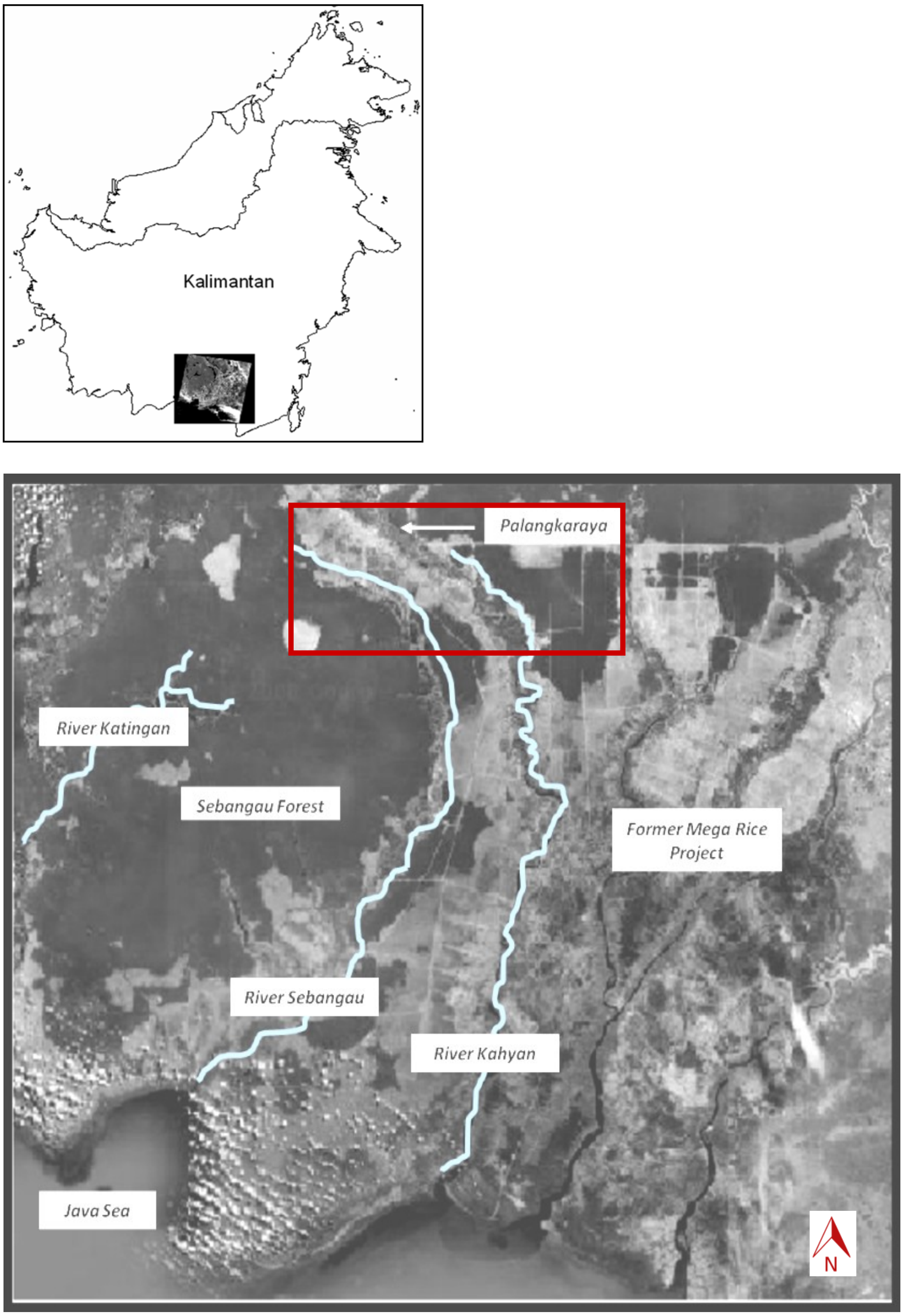


Fig.7: Map of general study area. Upper: Map of study area in relation to the island of Borneo. General study area in southern Kalimantan, Borneo is represented by the image tile shown in lower map. Lower: Map of general study (whole of the former MRP area) and the specific study area also show in detail in Fig. 8 (highlighted by red

box) Sebangau Forest (between the Rivers Katingan and Sebangau) and Block C of the former MRP area (to the west of the River Sebangau). The study area is located due south of the city of Palangkaraya, the provincial capital of Central Kalimantan. Source: modified from Google Maps (1/11/2011).

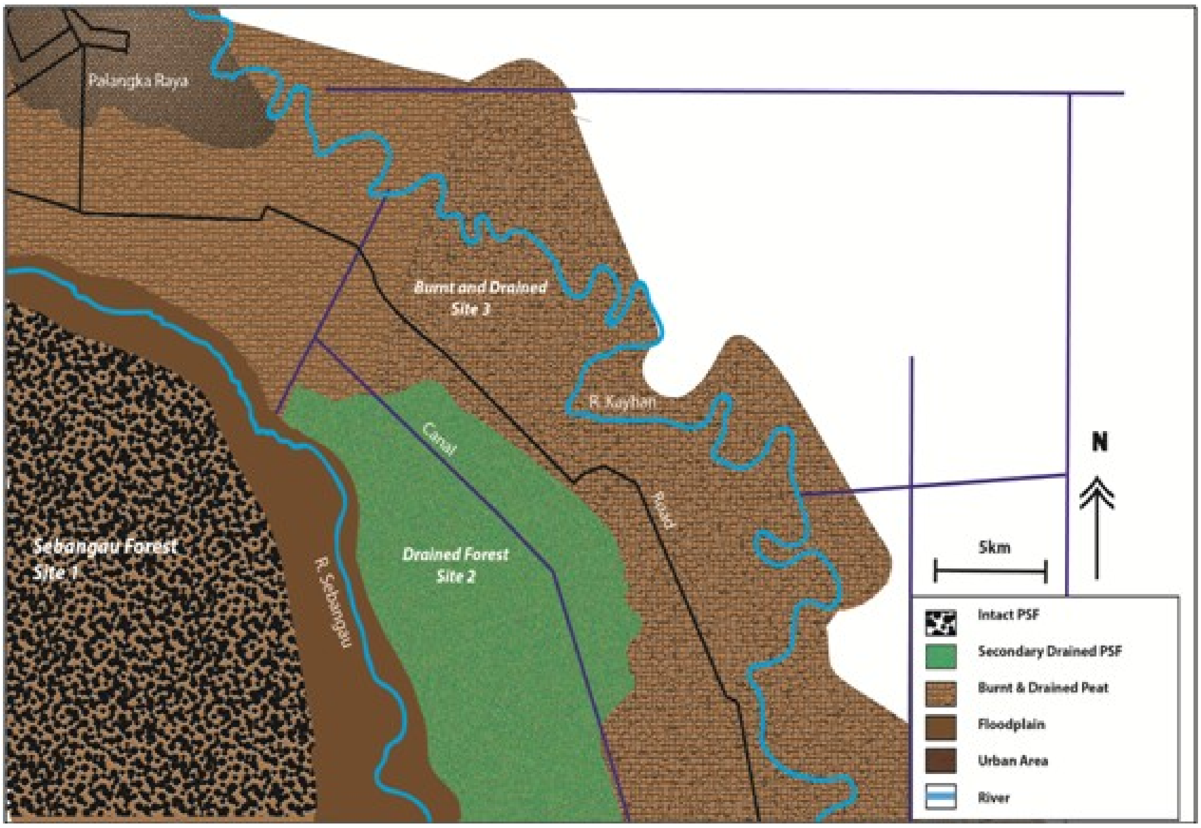


Fig.8: Location Map of sampling areas (1, 2 and 3). Site 1: Intact peat swamp forest. Site 2: Drained peat swamp forest. This area has been selectively logged and the peat drained but this area has not been burnt. Site 3: Burnt and degraded area.

3.1.1 Site 1: Intact Peat Swamp Forest (Sebangau Forest).

The Sebangau Forest has a relatively intact cover of peat swamp forest. This area was selected as a control site as most of this forest, beyond a narrow fringe close to the river, has not been affected by fire. There is also a small area within the tall pole forest vegetation that was burnt during the 1997 fires; however, neither the burnt riverine zone nor this latter burnt area were within the sampling location.

Site 1 was located within Mixed Swamp Forest (MSF) vegetation developed on the shallower peat (1 to 6 m) of the peat dome (Fig.9). This forest was analogous with the forest type sampled on the other side of the River Sebangau in the MRP (Site 2). The level of the peat water table in the MSF is typically at or above the peat surface during the 'wet season' (October – May) and reaches a maximum depth of 40 cm below the surface during the 'dry season' (June – September) (Takahashi *et al.*, 2003).The micro-topography of the peat surface is heterogeneous due to variation caused by hummocks and hollows, with trees rooted on the hummocks. The peat matrix is also spatially variable as it is composed of a random array of partially decomposed vegetation ranging from leaves to woody material, with the bulk of the peat matrix formed from root litter..

Fig.9: Upper; Mixed Swamp Forest (MSF) during wet season (March 2011), Right; Tall Interior Forest 12km from edge of peat dome (March 2011).

3.1.2 Site 2: Drained Peat Swamp Forest (Kalampangan).

This site is located in the northern part of Block C of the former MRP. This block is bordered by the River Sebangau to the west and the River Kahayan to the east and spans an area of ~4,600 km^2 equivalent to 40 % of the total former MRP area (Hoscilo *et al*, 2011). The peat in this location has been subject to extensive drainage by a series of canals constructed during the ill-fated MRP. All of this area was previously covered with peat swamp forest, but only small remnants now survive, the rest having been lost as a result of logging and frequent wildfires.

Site 2 is located in an area of drained but unburnt MSF vegetation; thus the vegetation cover is analogous to that at Site 1 (Fig.10). This site was selectively logged during the implementation of the former MRP and up until the end of the 1990s. The forest has since recovered and is referred to as secondary forest. This area of forest has not been burnt. The wet season water table at this Site is on average 25 to 40 cm below the peat surface (Hooijer *et al*., 2010), but dropping well below this during the dry season. Drainage at this site has not been managed since the MRP was abandoned, therefore large annual fluctuations in water table depth have been recorded (1.57 ± 0.03 m, Jauhiainen *et al*., 2012) During the dry season of 2006, for example, the water table was 160 cm below the peat surface in some locations (Ballhorn *et al*., 2009). The average annual water table depth measured between 2002 and 2009 was 53 cm ± 11cm (Hirano *et al*., 2012).

Fig.10: Site 2: Drained secondary peat swamp forest, Block 'C' of the former MRP. Source: Hoscilo, (2006).

3.1.3 Fire affected Site 3: Burnt and degraded peatland (Kalampangan).

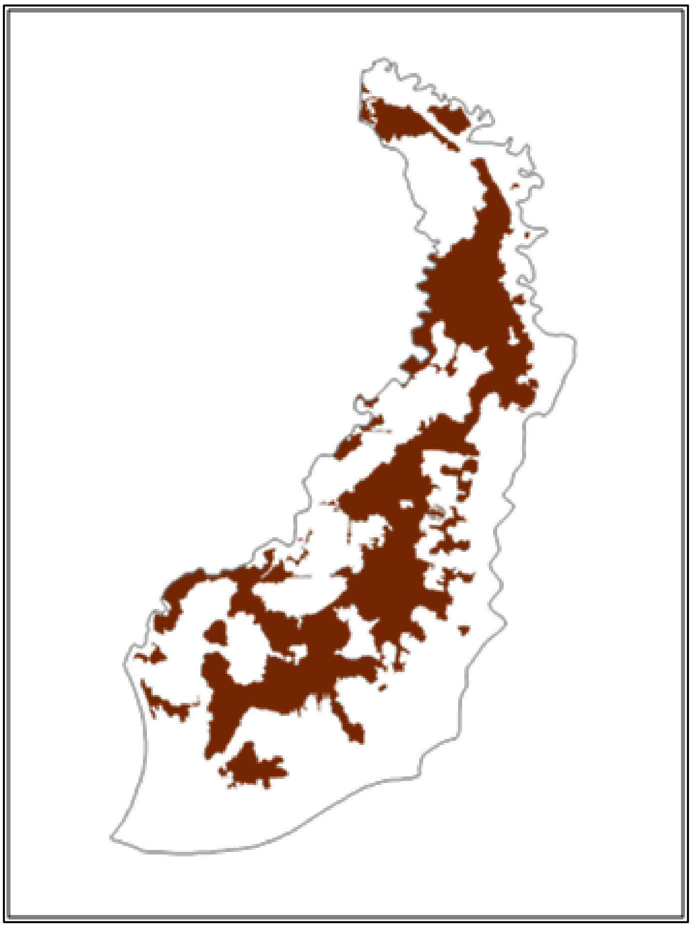
This site is also in the northern most section of Block C close to the village of Kalampangan. This area has been heavily drained by both the Kalampangan Canal and the MRP Canal. The Kalampangan Canal is ~ 20 m wide and about 12 km in length from the river Sebangau to the river Kahayan. The MRP canal runs 150 km south and perpendicular to the Kalampangan Canal. Site 3 therefore experiences a lower water table depth than Site 1, with the water table below the peat surface during all months of the year, but somewhat higher than at Site 2 where there are greater evapotranspirational losses from the forest biomass compared with the fern-dominated vegetation at Site 3.

Fig.11: Examples of the range of vegetation types and conditions in Block 'C' of the former MRP. Recently burnt (2009) secondary forest (upper left). A recovering area of peatland that was burnt during the 1997 fires; the fern Stenochlacena palustris *occupies the foreground (upper right). An area of peatland adjacent to a canal which had burnt on four different occasions (lower left). An example of recolonisation by non-woody vegetation in an area of Block 'C' that burnt during the fires in 1997 and 2006 (lower right).*

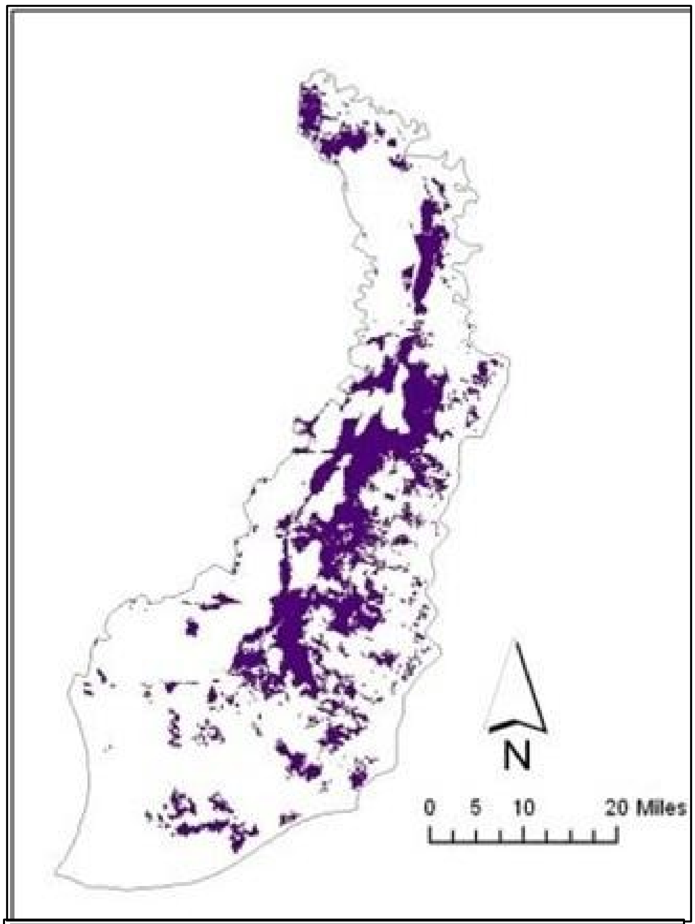
The water table was measured at a maximum depth of ~ 80 cm and ~ 50 cm below the peat surface during the dry seasons of 2004 and 2005 and respectively (Hirano *et al*., 2013). Mixed peat swamp forest formerly occupied this location before the implementation of the MRP. Subsequently, logging followed by repeated fires have led to total loss of the forest and the site now supports a mosaic of different non-woody vegetation types and, in the most recently burnt locations, bare peat. The average peat thickness in this site is around 4 m and in some places up to 5 m (Hooijer *et al*., 2006). Fern communities are the most widespread vegetation, with *Stenochlacena palustris* and *Blechnum indicum* as the principal species; there are also patches dominated by grasses, sedges, shrubs and a scattering of recolonizing tree species including; *Combretocarpus rotundatus* and *Cratoxylon glaucum.*

Site 3 has experienced a range of fire events since the implementation of the MRP and there have been previous studies that have mapped the extent and frequency of these events (e.g. Hoscilo, 2009; Yunos, 2010) (Fig.12). Fires occurred during the dry seasons of 1997, 2002, 2006 and 2009. Burned areas were mapped for the 1997 and 2002 events by Hoscilo (2009) and for the 2006 and 2009 events by Yunos (2010). Fires also occurred in Block C during the dry seasons of 2004 and 2005; however, burning did not extend to any of the areas selected for sampling during this study. Using data from these sources a variety of sampling locations were selected within Site 3 that ensured that a range of different fire events and frequencies could be investigated.

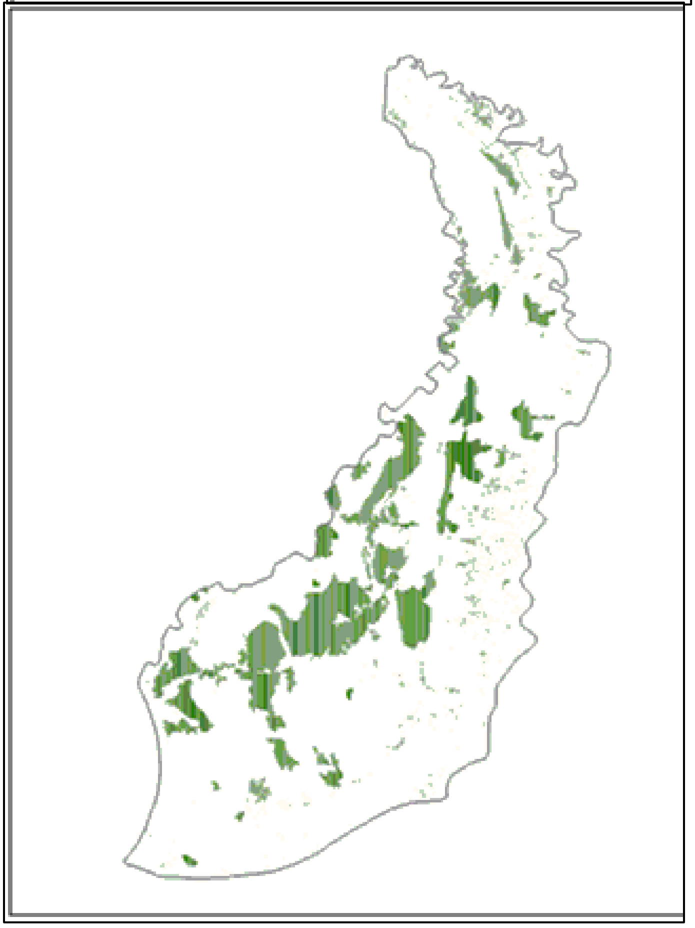
a)



b)



c)



d)

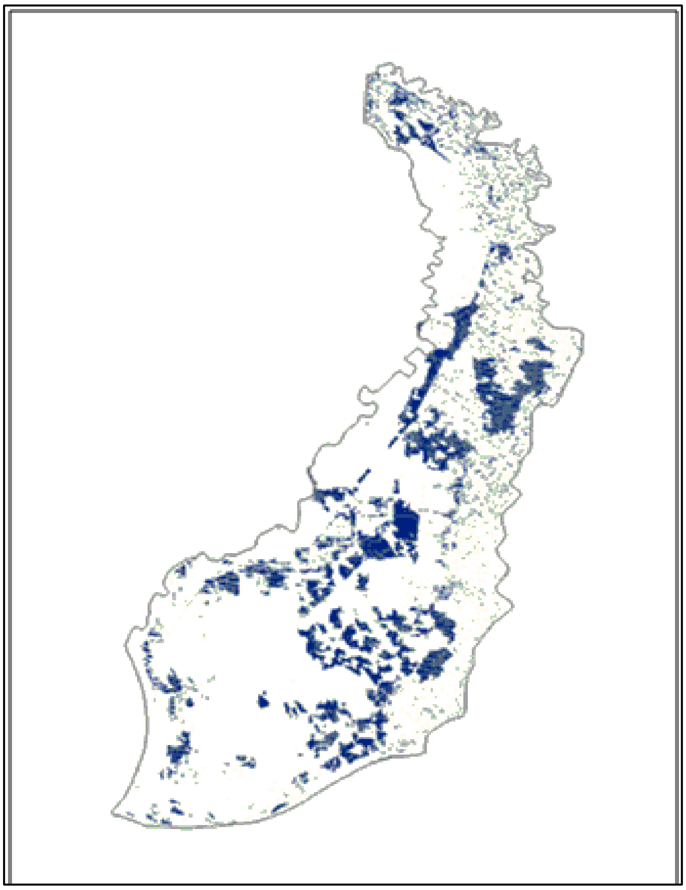


Fig.12: Burnt area of Block C of the former MRP area from the following years a) 1997, b) 2002, c) 2006 and d) 2009. Burn scar data was derived by using a series of pre and post-fire satellite images (Landsat MSS, TM and ETM+) of the area and calculating the Normalized Burn Ratio (dbnr) to derive the burnt area for each year. Source adapted from, Hoscilo, (2009.) and Yunos, (2010).

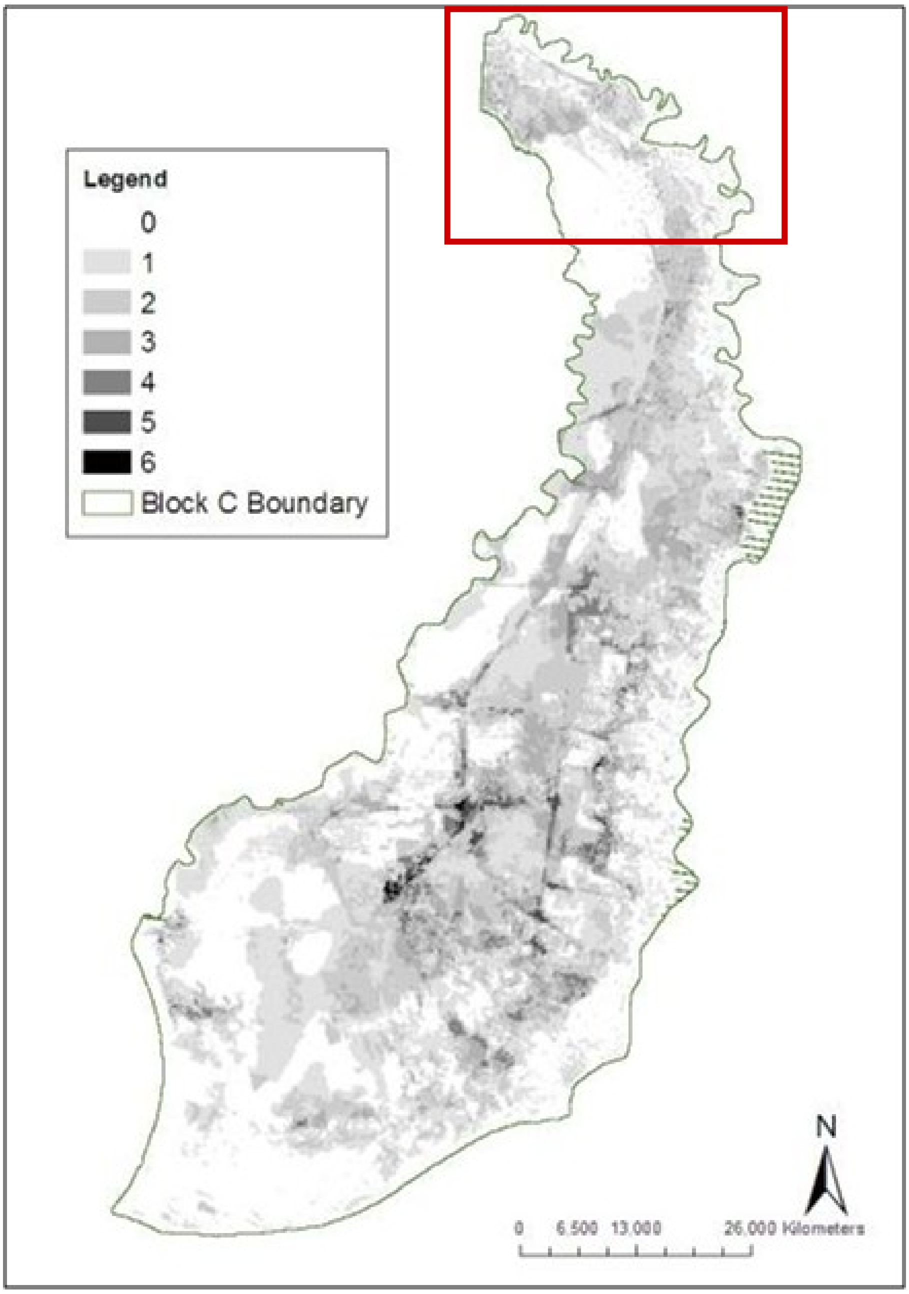


Fig.13: Map of fire frequency in Block 'C' of the former MRP area. Burnt area data was combined for fires during 1997, 2002, 2006 and 2009 to determine the fire frequency regime. Data used from Yunos, (2010). Red box respresents the specific study area, also shown in Fig. 8.

Burnt area data were combined to produce a 'fire frequency' map for block 'C' thus allowing a range of sites to be selected for sampling that represented both single and multiple burns (Fig. 13). By analysing samples from a number of different fire events and areas a range of fire regime variables could be considered, including 'Time since last burn' and 'Fire frequency' (Table 1).

3.2 Plot selection

Peat sampling was conducted across each of the three sites, Site 1 (Intact PSF), Site 2, (Drained PSF) and Site 3, (drained and burnt).

A total of three different plots (N1, N2 and N3) were sampled within Site 1, all of which were within the MSF zone. The specific location of plots was selected to be parallel to a pre-existing transect. A series of transects had previously been developed within Site 1 which were predominately used by scientists in this designated research area, the Natural Laboratory for the study of Peat Swamp Forest (Fig. 14). These transects are only present in the intact peat swamp forest site (Site 1) and are predominately used for surveying orangutan nesting sites. The transects form a 3 x 1 km grid, with 1km transects at 0.0, 0.4, 0.8, 1.3, 1.6, 2.0 and 3.0 km from the edge of the River Sebangau. Each plot was sampled on the 0.4 km transect and samples were taken 5 m from the edge of this transect in order to reduce the effects of disturbance caused by this access route through the forest (Section 3.2.1). The 0.4 km transect was selected because it is within the MSF vegetation type but also far enough away from base camp and the River Sebangau as to reduce influence of the human distrubance and fluvial interferences. Site 1 was sampled in August 2009 and March 2011.

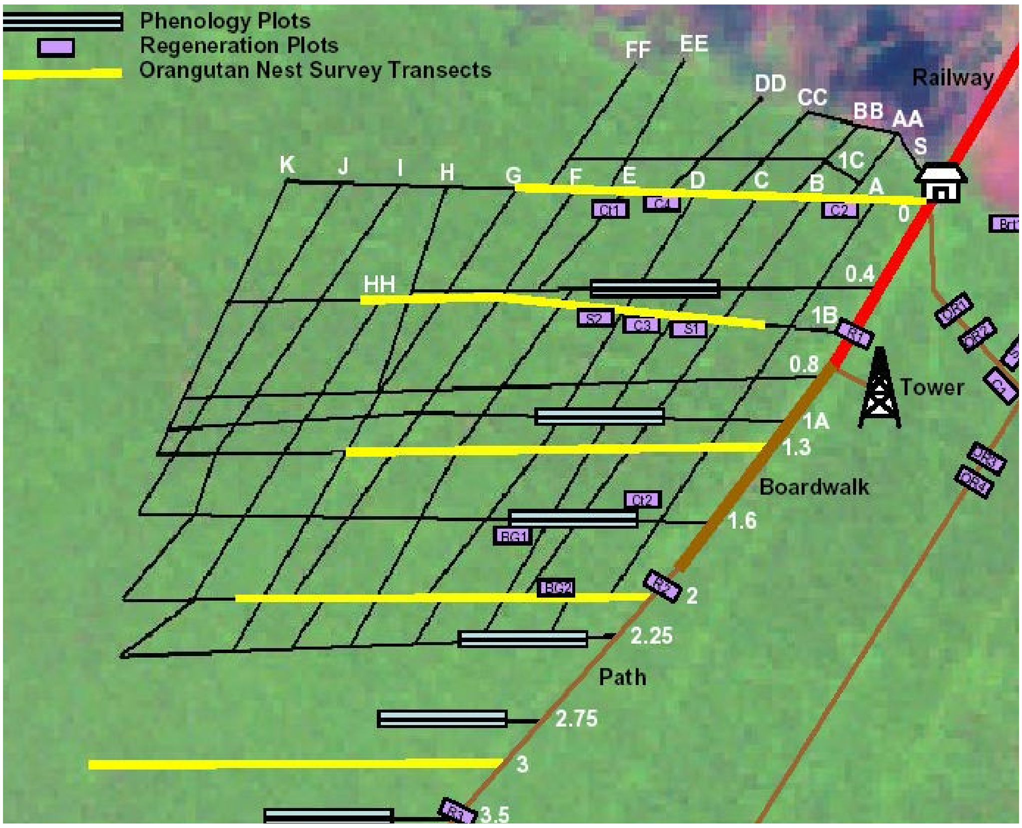


Fig.14. Map of pre-exsiting transects in the intact peat swamp forest area (Site 1). Samples taken at the site was conducted 5 m parallel to transect 0.4 km. Source (http://www.orangutantrop.com/MapofLAHG.pdf - 02/05/2010)

Site 2 was also sampled within the MSF of the secondary drained forest. A single plot (0) was sampled 5 m from the edge of a pre-existing transect that was west of the main logging canal (MRP channel). The MRP canal runs north to south through Block C and through part of the secondary drained forest. Site 2 was sampled in March 2011.

Sampling locations at Site 3 were selected on the basis of their 'fire history'. Using maps of burnt area a total of seven sampling sites were selected that allowed for collection of samples from locations that had experienced different land management and fire regimes i.e. fire events (1997, 2002, 2006 and 2009), frequencies, and time since last burn. A range of plots were selected in both of the Control Sites (i.e. undrained and drained forested sites, sites 1 & 2) (Fig.15) that allowed for comparison of samples collected from Site 3. A variety of different plots with different 'fire histories' were located; their respective land use types and fire histories are depicted in Table 1.

*Table 1: Peat sampling locations (November 2009) using point sampling strategy. Fire regime variables including, 'Fire Event', 'Fire Frequency', 'Time since last Fire' are included. Geographical locations of samples are displayed in Fig. 15. * Full lists of all samples collected for the fire regime analysis are included in Chapter 5.*

Location	Depth (cm)	Sample ID	Fire History	Time Since last burn	Fire frequency
Site 1 Sebangau Forest *(undrained & unburnt)*	0-5	SN1	Unburnt	n/a	0
	5-15	N1C			
	15-30	N1B			
	30-50	N1A			
	0-5	SN2	Unburnt	n/a	0
	5-15	N2C			
	15-30	N2B			
	30-50	N2A			
	0-5	SN3	Unburnt	n/a	0
	5-15	N3C			
	15-30	N3B			
	30-50	N3A			
Site2 Block 'C' (*drained, unburnt secondary forest*)	0-5	1D	Unburnt	n/a	0
	5-15	1C			
	15-30	1B			
	30-50	1A			
Site 3 Block C Kalampangan (*burnt and drained)*	0-5	SF1	Burnt	1 month	1
	5-15	F1C			
	15-30	F1B			
	30-50	F1A			
	0-5	SF2	Burnt	1 month	1
	5-15	F2C			
	15-30	F2B			
	30-50	F2A			
	0-5	SF3	Burnt	1 month	1
	5-15	F3C			
	15-30	F3B			
	30-50	F3A			
Site 3* Block C Kalampangan *(burnt and drained)*	0-5	/	Burnt	Various	1-4
	5-15	/			
	15-30	/			
	30-50	/			

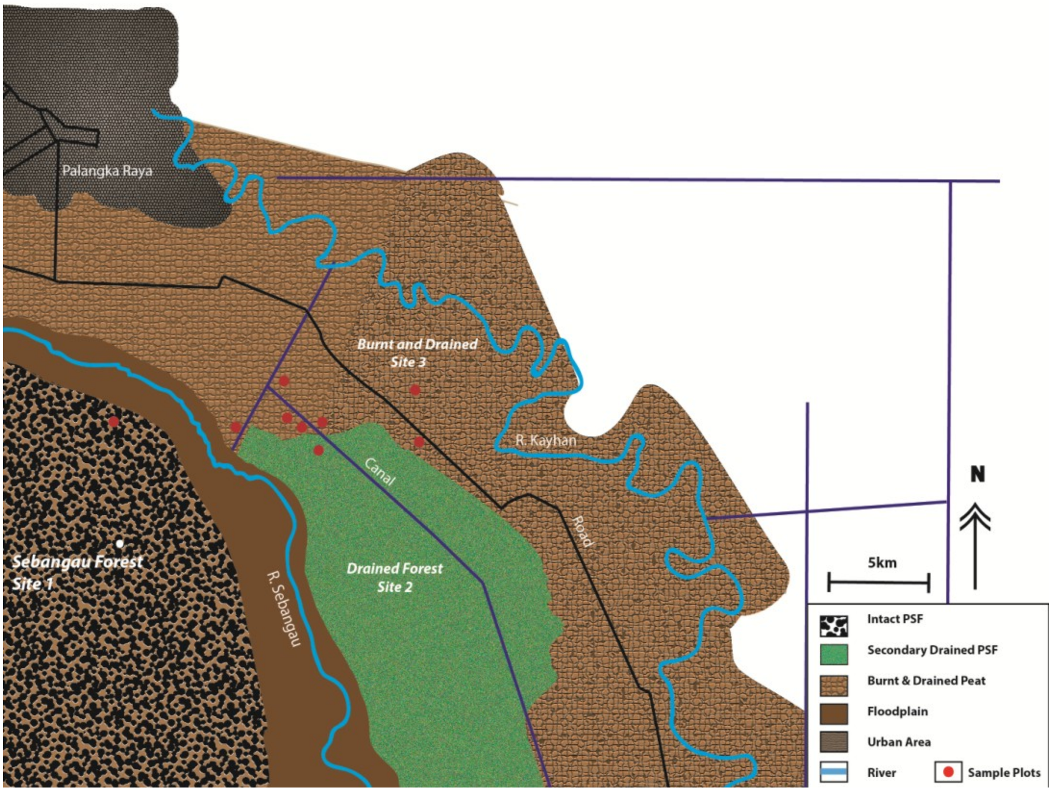


Fig.15: Map of plot locations in Sites 1-3. Adapted from Landsat imagery using Adobe Illustrator.

3.2.1 Preliminary Sampling Regime

Sampling was conducted over three separate field expeditions; November 2009, March 2010 and March 2011. The November 2009 visit represented a preliminary sampling visit. The purpose of this was to collect peat samples from areas that had been affected by the wide-spread fires that occurred in the former MRP area during June and July of 2009. While it was not possible to collect samples shortly (1 month) after the 2009 fires (preliminary sampling regime), as this was prior to the official commencement of my own studies, I advised a colleague (Dr. Sam Moore, University of Oxford) who was working in nearby sites during this time, to collect samples on my behalf. By conducting research in the Natural Laboratory of Peat Swamp Forest for my BSc dissertation (July 2008) I had already gained valuable experience of the field sites described in this thesis, therefore, despite not being able to conduct the preliminary sampling myself, I was knowledgeable about the study area and was responsible for the choice of sampling locations and method of sampling collection.

During the preliminary sampling regime, three point samples (three 50 cm cores) were collected from both Site 1 and Site 3. At Site 1 samples were collected from within the MSF zone of the Sebangau PSF, 5 m distant from and perpendicular to the pre-existing transect. At Site 3 samples were collected from an area in the northern section of Block C that had been affected by the recent fires (June/July 2009). No sampling was conducted at Site 2 during this preliminary sampling campaign. For each core, peat samples were obtained at four depth intervals (i.e. 0-5 cm; 5–15 cm; 15-30 cm; 30-50 cm). Each core was divided into the each of the four depth intervals and all of the peat was collected into polyethylene sampling bags and refrigerated before being transported to the University of Leicester.

3.2.2 Subsequent Sampling Regime

Following the preliminary sampling campaign in November 2009, a revised sampling regime was employed for the fieldwork expeditions that took place during March 2010 and March 2011. In addition to Sites 1 and 3, Site 2 was also sampled during these fieldwork expeditions.

The preliminary sampling campaign allowed an initial set of data to be produced. There were no further fires in the study area between the first (November 2009) and last of the field expeditions (March 2011). Therefore, in order to answer research question 1, (**To provide evidence for change in OM composition after a single fire event in the chosen study area**) the samples from the preliminary sampling regime have been used.

In order to address the research questions and assess the biogeochemical effects of fire at the landscape scale, the original sampling strategy was adapted to remove small scale variability at the individual plot level introduced by the general heterogeneity of the peat substrate and/or variation in fire spread and intensity. The aim of the subsequent sampling strategy was to improve the reliability and reproducibility of the results.

During the second and third field campaigns, sample collection (Table 1) was undertaken using an intensive plot sampling strategy that is typically used for soil analyses (Bird *et al*, 1999). Plots were established based on the locations that had been burnt during each of the fire years (1997,2002,2006 and 2009) as identified from burnt area data produced from Landsat images (Fig. 12). Each of the plots were 100 m by 50 m in dimension. From within each plot a peat core (to 50 cm depth) was taken using a 50 cm Russian soil corer, at 25 m intervals across the width (100 m) of the plot. A further two rows of core samples were taken in the same manner resulting in a total of 15 peat cores for any one plot. The average burn depth in peatland fires in the MRP area had previously been estimated at up to 50 cm (Usup *et al.*, 2004) 33 ± 18 cm Ballhorn *et al.*, 2009) and 51 ± 4 cm (Page *et al.*, 2002) therefore 50 cm cores were collected for analysis allowing the full effects of burning to be assessed. This depth range was also comparable to the average water table depth, i.e., above the surface and maximum depth, 40 cm at Site 1, (Takahashi *et al.*, 2003) 53 ±11 cm at Site 2 (Hirano *et al.*, 2012) and maximum of 50-80 cm at Site 3 (Hamada *et al.*, 2012) and the depth of peat that would have been heated by the burning i.e. below the water table heat transfer will be inhibited therefore burning is there unlikely to have any effect. For each core, peat samples were obtained at four depth intervals (Fig. 16) (i.e. 0-5 cm; 5–15 cm; 15-30 cm; 30-50 cm). Each core was divided into the each of the four depth intervals and all of the peat was collected into polyethylene sampling bags and refrigerated before being transported to the University of Leicester. Prior to sampling the 15 cores from each plot were bulked to form a composite sample for each depth interval. Thus, there were a total of four samples from each plot location, one from each depth depth interval.

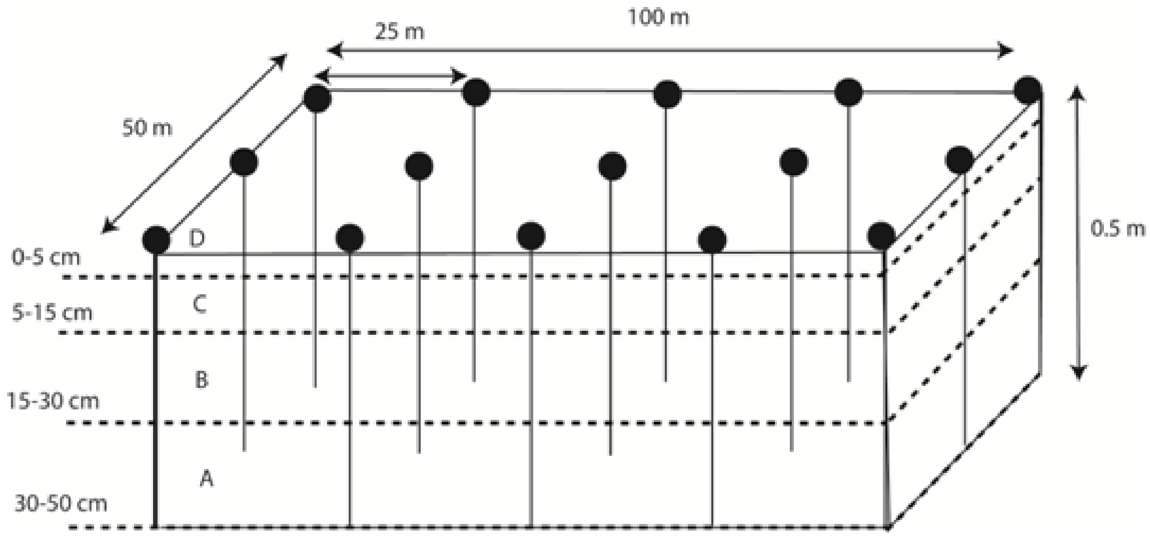


Fig.16: Schematic diagram of intensive plot sampling strategy. Each of the locations was sampled using this method. Circular dots represent location of each 50 cm core.

3.3 Analytical pyrolysis

The analytical data presented in this thesis rely considerably upon use of Py-GC/MS as a technique to assess the OM composition of the peat samples. It is, therefore, appropriate to explain the key scientific theory regarding the application of this method for soil and, in particular, soil OM analysis.

'Pyrolysis' is essentially the breaking apart of large macromolecules into smaller fragments by using high temperatures and the exclusion of oxygen (Wampler, 2006). Analytical pyrolysis is the characterisation of a material by chemical degradation reactions induced by thermal energy (Moldoveanu *et al.*, 1998). Under a set temperature regime macromolecules will fragment in a characteristic pattern and the breakdown products are separated and identified by a GC/MS system. Analytical pyrolysis typical takes place at relatively high temperatures, usually between 500 and 800 °C and greater during vigorous pyrolysis (Moldoveanu *et al.*, 1998). The resulting pyrolysis products or pyrolysate is used as chemical markers of the original OM.

The main advantages of Py-GC/MS as a method to analyse the chemical composition of OM are as follows: Very little sample preparation is required, unlike conventional

GC/MS analysis which requires extraction of a refined organic solution; analysis is relatively quick; bulk samples can be analysed, e.g. soils and sediments pyrolysed directly so that the often complex OM is analysed in its entirety and only a small amount of sample (< 1 mg) is needed. Pyrolysis is often used in combination as a sample preparation technique prior to analysis by gas chromatography, mass spectrometry and Fourier Transform Infrared (FTIR) spectrometry.

Pyrolysis is not without its disadvantages, the most significant problem being that it is a destructive technique that causes fragmentation as well as side chain reactions that may form ring structures (Sáiz-Jiménez, 1994). However, organic compounds breakdown in a characteristic way under set temperature conditions, and therefore it is possible to reveal information about the parent material even though pyrolysis is a destructive method that causes fragmentation (Wampler, 1999).

3.3.1 Pyrolysis-GC/MS Background and Applications

Many different methods have been employed in the past to characterise SOM including spectroscopic methods (e.g. ^{13}C NMR, infrared spectroscopy and UV light spectroscopy) (Buurman *et al.*, 2006).

Analytical pyrolysis has a variety of applications across many different industries, including analysis of art materials, biological samples (Schulten, 1998), fuel sources and in forensics, as well as analysis of environmental samples (Bruchet *et al.*, 1990). Pyrolysis-Gas Chromatography (Py-GC/MS) has become a popular method as it reveals information on the chemical composition of soil OM more specifically the macromolecular composition of OM. Therefore, enabling comparisons to be made across different types of environments (Nierop *et al.*, 2001). ^{13}C NMR, infrared spectroscopy and UV light spectroscopy although providing information about the chemical composition of soil OM they do so by presenting the relative abundance of certain functional groups e.g. ^{13}C NMR measures specific spectral regions that relate to biochemical groups such as alkyl-C and aromatics, as opposed to Py-GC/MS that gives compound specific information about the samples. Analysis of soil OM by GC/MS alone allows only for the extractable OM to be analysed unlike Py-GC/MS that provides information about the pyrolysis products from the sample in its entirety. Thus, Py-GC/MS allows the insoluble macromoelcular to be observed. Py-GC/MS is potentially a rapid method for detecting changes in the OM composition of soils contrasting with other more lengthy chemical methods often used in soil analysis (Stuczynski *et al.*, 1997)

3.3.2 Theory: Py-GC/MS

Pyrolysis is used as a sample preparation technique but, when coupled to a gas chromatography mass spectrometer (GC/MS) system, it can provide useful data on the composition of soil OM. The application of other analytical tools such as (GC/MS) is not feasible when trying to examine a whole sample such as the total OM in a soil sample. Although extractable fractions of the OM can be analysed in high detail using a GC/MS, A Py-GC/MS systems allows the whole of the OM to be analysed.

A GC/MS uses a Gas Chromatograph (GC) and a Mass Spectrometer (MS). Thermally stable pyrolysis fragments are separated by a gas chromatograph; fragments are swept onto a capillary column by a carrier gas, which in this case is helium. The fragments separate on the basis of their interaction with the column. The molecules will elute from the column at different times dependent on their molecular weight. The MS will then ionise the molecules into mass fragments before detection by an electron multiplier diode based on their mass. Detection of different masses is achieved by measuring the ion currents of the different molecules. The resulting ‘mass spectrum’ displays the mass over charge (*m/z*) of the ions and their intensity.

Alternatively, thermally assisted hydrolysis and methylation (THM) in the presence of tetramethylammonium hydroxide (TMAH) is often used to characterize soil OM (Abbott *et al* 2013, Swain and Abbott, 2013). TMAH derivatises highly polar pyrolysis products (e.g. forming methyl esters of the carboxylic acids) when OM is analysed in pyrolysis gc/ms. This technique can be advantageous when attempting to analyse the lignin and phenol dervived pyrolysis products a that would otherwise, when using convential analytical pyrolysis, be diffilcult to detect. Differentiating between lignin and phenol derived compounds can also be challenging using conventional Py-GC/MS, due to their highly polar chemical structure. For example this TMH in the presence of TMAH was employed during a study of boreal peats (Abbott *et al*., 2013). The aim was to characterise biomarkers specific to *Sphagnum* mosses and quantify the total phenols dervived from *Sphagnum* relative to vascular plants. This technique was not used when in this thesis because this was the first study of burnt tropical peat OM and thus the traditional Py-GC/MS method would provide a wider range of data from which to compare the data to. Since the aims of this study was to gain an overview of the fire induced changes to peat OM and in-depth examination of the lignin and phenol compounds alone was not required at this stage. However, following an intital analysis of the OM further investigation of simliar samples are likely to benefit from a greater insight into the lignin content of the OM.

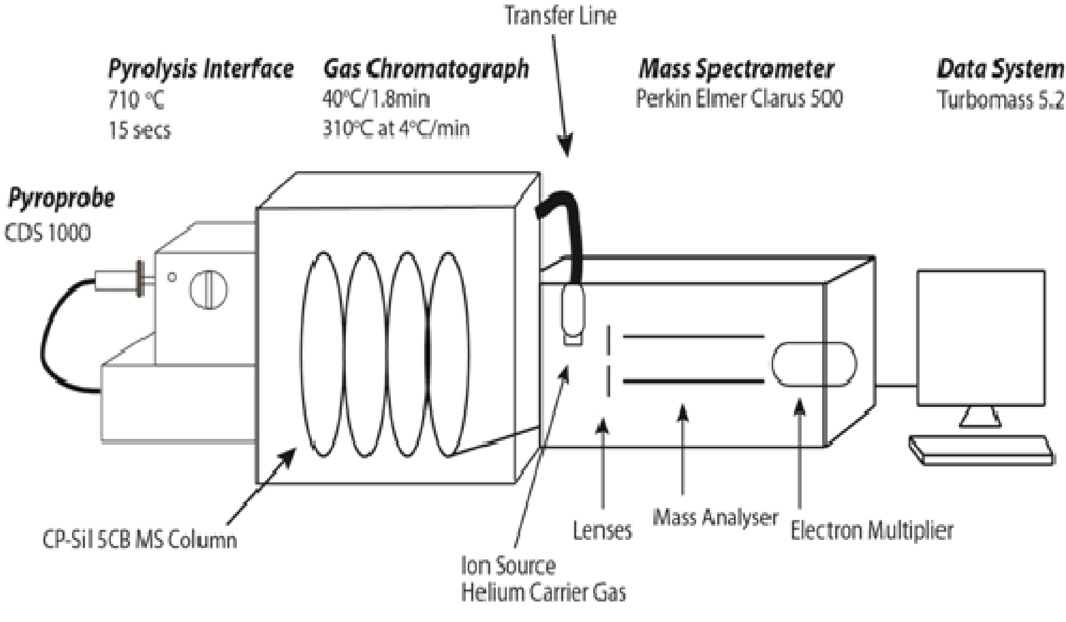


Fig.17: Schematic diagram of a Py-GC/MS setup.

Identification of pyrolysis products utilises the mass spectral information (Fig.21). Mass spectra are composed of a number of peaks which represent fragments of the molecule. The mass spectrum of phenol shows the most intense peak at *m/z* 94. The smaller peaks represent fragments of the phenol molecule. Peak *m/z* 66 is formed by a hydrogen atom shift and a loss of C and oxygen atoms (Fig. 21). Fragment *m/z* 65 is formed by a further loss of a hydrogen radical and formation of a double bond (Fig.18)

The degradation mechanisms that are involved during the pyrolysis step are reproducible allowing information to be revealed about the original material. A free-radical process initiated by bond dissociation at a specific pyrolysis temperature causes the breakdown of larger organic molecules (Wampler, 1995). The nature of the chemical breakdown is determined by the strength of the chemical bonds. The organic molecule will be fragmented by one of three degradation mechanisms; random scission, unzipping and side group elimination (Ranzi *et al.*, 1997; Wampler, 1995). An understanding of the degradation mechanism is required to enable interpretation of results when the composition of an unknown sample is involved.

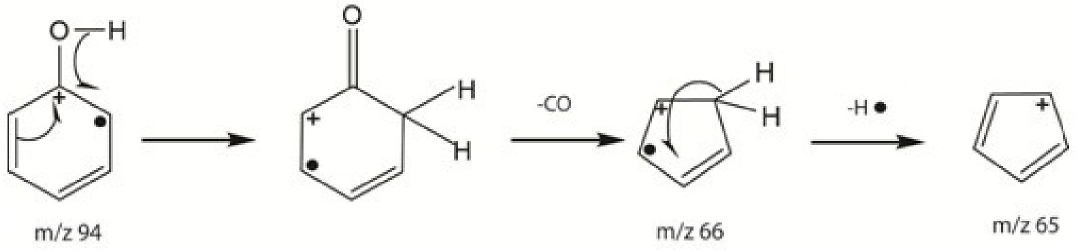


Fig.18: Mechanism of fragmentation for phenol. (m/z) Mass to charge ratio. • Represents a free radical. Arrows represent movement of an electron. Adapted from, Gross, (2010).

3.3.3 Degradation Mechanisms

During analytical pyrolysis compounds degrade by dissociation of a chemical bond and production of a free radical (Wampler, 1997). The manner in which the original macromolecule is degraded depends on the type of chemical bonds that are present and the experimental conditions that are used. When organic materials are pyrolysed different molecular species will degrade in different ways as well as a series of chemical interaction can occur between the different pyrolysis products. This diverse interaction of compounds in material such soil samples make the pyrolysis process highly complex. Many of the pyrolysis products, particularly the larger fragments will contain structural information about the source material. The three most common degradation methods will now be explained.

Random chain scission

Random chain scission involves the random degradation of a polymer's carbon chain backbone (Moldoveanu, 1998). In a C-C chain, all of the chemical bonds between the C atoms are of equal strength therefore they will fragment in an identical way. Pyrolysis products such as alkanes and alkenes of varying molecular weight can form in this way. The fragmentation of carbon chains produces hydrocarbons with terminal free radicals. This molecule can be stabilised by extracting a hydrogen atom from a neighbouring molecule. The end of this molecule then becomes saturated and creates another free radical in the neighbouring molecule. The process of beta scission will then stabilise this free radical by producing a hydrocarbon with an unsaturated end and new terminal free radical. Beta scission continues and further saturated hydrocarbons molecules with either a double terminal bond or double bonds at each end (Wampler, 1997) (Fig. 19).

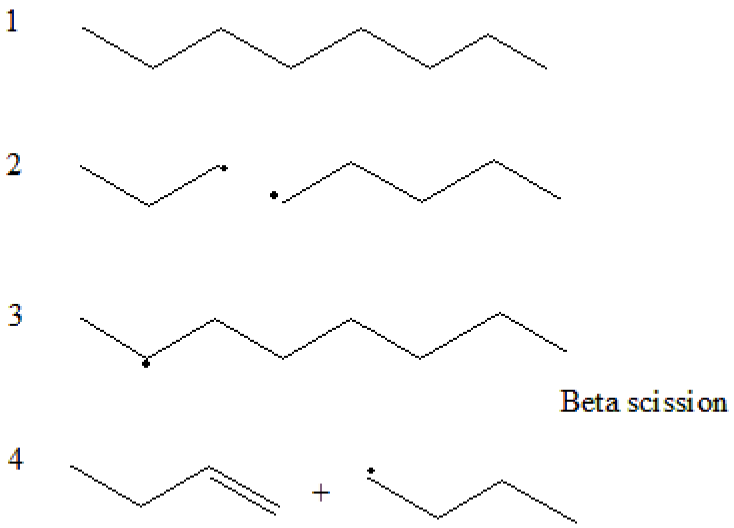


Fig.19: Diagrammatic example of random scission. Figure adapted from Wampler, (1997).

Side-group elimination

Side-group elimination is common and usually occurs before random scission of polymers. Side-group elimination does not affect the polymer chain therefore when this degradation step is complete it is often followed by random chain scission (Moldoveanu, 1997). An example of a polymer that undergoes side-group elimination is poly-vinyl chloride (PVC). Aromatics, such as benzene, toluene and naphthalene are formed from the unsaturated backbone that is left after the side-groups have fragmented from the original polymer (Wampler, 1997). In the case of PVC, HCl side-groups are fragmented from the original polymer chain and an unsaturated C backbone remains that then transforms into a variety of aromatic structures (Fig.20).

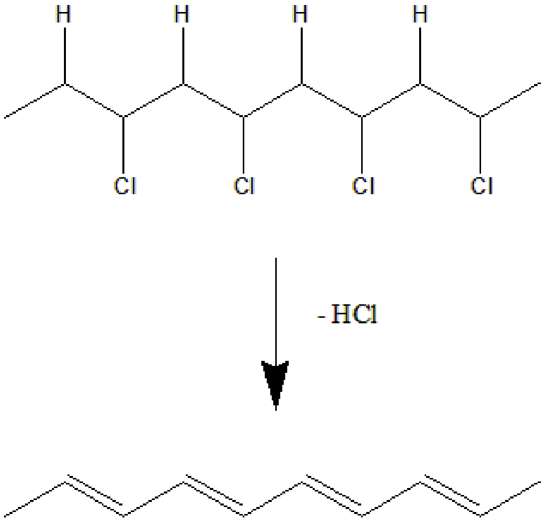


Fig.20: Diagrammatic example of PVC undergoing side-group elimination.

Unzipping

Unzipping or monomer reversion is the reversal of a polymer back to its original monomer, a process often known as depolymerisation. Compounds including polymethylmethacrylate and polyoxymethylene are known to undergo unzipping (Stauffer, 2003). The resulting monomers give an indication of the chemical structure of the original polymer. Unlike random scission, which produces a variety of different fragments of different chain lengths, unzipping fragments a polymer to the original monomers from which the polymer was formed.

3.3.4 Interpretation of results

Results have been analysed using MS software and in this study Turbomass 5.2.0 software (Perkin Elmer) was used. The output from this analytical technique is a series of peaks on a ‘pyrogram’. This fingerprint of the original OM provides information about the nature of the characteristic organic fragments and the relative concentration of one fragment compared to another. Peaks represent pyrolysis products of a particular molecular weight. Identification begins with matching the detected mass spectra with published data in spectral libraries e.g. the National Institute of Standards and Technology (NIST). (Fig.21)

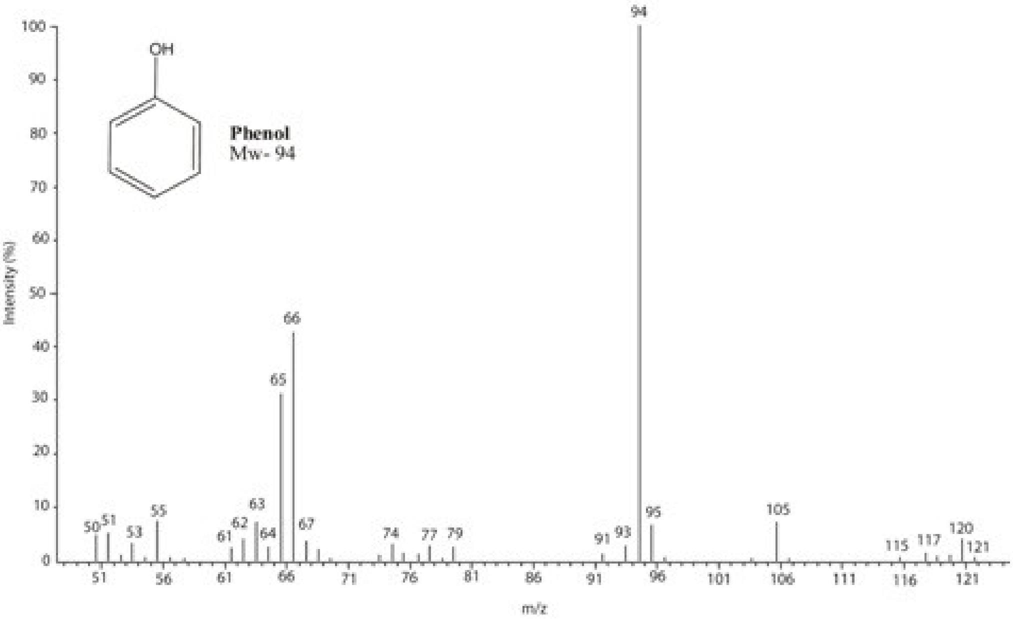


Fig.21: Mass spectrum of Phenol. (Source: Indonesian peat sample from Site 1).

The ‘Retention Time’ (RT) is dependent on the time taken for the compound to elute from the column. This value can be used to aid in identification; however, retention times are concurrent with the GC conditions and are therefore not strictly comparable with other published data. The Kovat’s retention index allows retention times to be compared between different types of GC in different laboratories. Values are conversion of retention times into system-independent constants. The RTs are converted according to those of adjacent eluting n-alkanes. Kovat’s values become useful when GC conditions change, e.g. after trimming the column. Kovat's retention indices were calculated (Equation. 1) for all identified pyrolysis products. Although retention times and Kovat's index was used to aid identification, all compounds were checked by manually in order to indentify the exact compound.

Equation 1: Kovat's Retention Index

$$K = \quad 100\, X\, n + (N - n) \qquad \left[\frac{r.t.(unknown) - \ r.t.\ n}{r.t.(N) - \ r.t.(n)}\right]$$

K = Kovat's Retention Index
n = Number of Carbon atoms in smaller alkane
N = Number of Carbon atoms in larger alkane
$r.t.$ = Retention Time

The dominant peaks in the pyrolysates were identified and the relative contribution was calculated based on the sum of the total identified pyrolysis products. The abundance was calculated based on results from peak integration (Fig.22). The area under the peak is equal to its intensity. The baseline was altered manually if the automated baseline produced by Turbomass 5.2.0 was unsatisfactory, i.e. if the resulting pyrogram revealed there was poor chromatographic separation of peaks with baseline 'noise'.

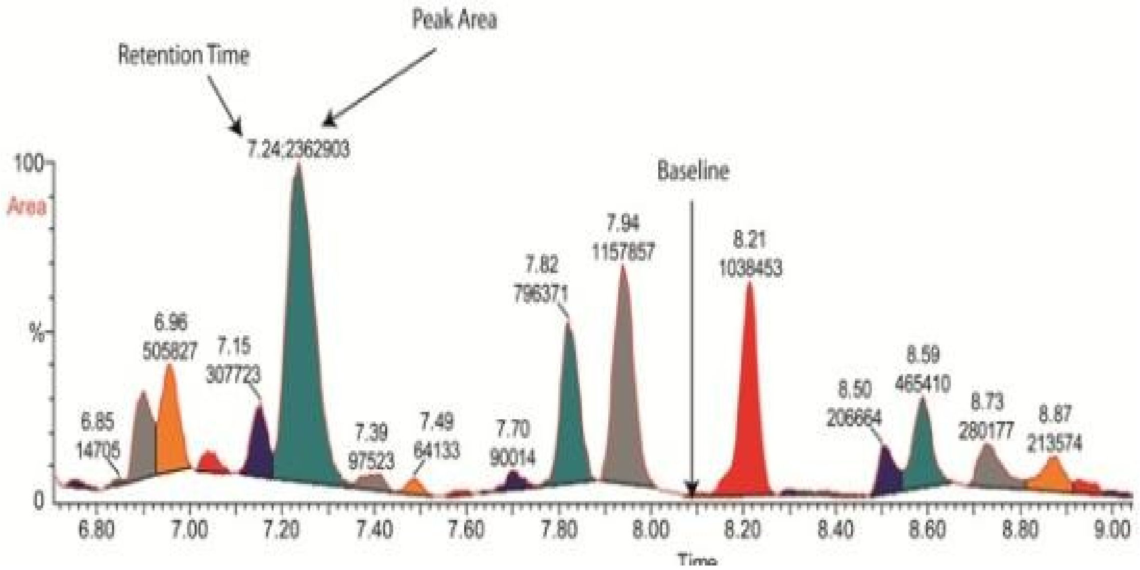


Fig.22: An example of peak integration. Each peak represents of different molecule. The area under the peaks represents the contribution of that molecule relative to the total ion current.

Some compounds of similar molecular weight will elute from the column at almost the same time and therefore appear on the chromatogram as one undefined peak. Inspection of the mass spectrum reveals that the peak is impure as there is more than one compound present; a process called co-elution. There were a small number of compounds that co-eluted with each other and each compound could be detected by examining the 'mass chromatogram' for each of the compounds. The mass chromatogram is extracted from the original chromatogram by searching for the base peak (the characteristic or most intense) of each of the co-eluting compounds. Then, in order to accurately determine the abundance of each of the compounds, the ratio is calculated between the base peak intensities of the two compounds.

Pyrolysis products were used as markers for the original macromolecules in peat OM. An understanding of the fragmentation patterns caused during the pyrolysis step allowed for inferences to be made regarding their likely origin, e.g. Guaiacol is a pyrolysis product formed from the fragmentation of lignin. The organic fragments are then be assigned to known biochemical groups in the soil (Schnitzer, 1991) and to plant residues (Nierop *et al*., 2001). Compounds were grouped according to their likely origin using groups and assigning compounds based on previously published studies (Buurman *et al.*, 2006, Schellekens *et al.*, 2009). The following compound classes have been used; Lignins, Polysaccharides, Phenols, Nitrogen containing compounds, Polyaromatic hydrocarbons, Aliphatics and Aromatics.

Initially it could be reasonable to presume that Py-GC/MS is not a suitable method for analysing the effects of fire on soils due to the pyrolysis step, which creates a second phase of rearrangement of molecular substances. This difficulty can be overcome, however, if there is an understanding of all of the pyrolysis products as the presence of one type of compound may reveal information about another. For example, if furans are much less abundant than levosugars the most likely source of both is polysaccharides (Kaal *et al.*, 2009b). Therefore careful analysis of all pyrolysis products allows conclusions to be drawn on the degradation step that has occurred.

3.4 Statistical Analyses

A variety of different statistical techniques have been applied to the data in this thesis, with detail of the specific statistical tests provided in each of the data chapters (4-6).

The data generated by Py-GC/MS contains a complex mixture of organic molecules resulting in a large number of variables within each of the samples. Due to this highly complex dataset multivariate statistics were applied. Principal Components Analysis (PCA) is a statistical method used to explore highly complex data sets by transforming the original variables into new variables or principal components.

PCA can present results using insightful plots allowing rapid graphical interpretation of the results. Plots of both the samples (plot of cases) and variables (plot of compounds) were used to display the results of the analysis in Chapters 4 and 5. The plot of compounds is divided into four quadrants and displays the correlations between each of the individual variables (i.e. pyrolysis products). Variables that plot close to the origin of the two selected principal components do not vary with regard to either such components. The further a variable plots from the origin the greater the variability with regard to that principal component, i.e. a variable that plots several absolute numbers on the horizontal axis has significant variability with regard to principal component 1. Variables that plot close to one another are similar, i.e. pyrolysis products that plot close to one another are chemically similar. The plot of cases is also divided into four quadrants and displays the correlations between the samples (each peat sample). As with the plot of variables the further a case plots from the origin the greater the variability that sample has with regard to that principal component. Also, samples that plot closely to each other are similar, i.e. peat samples that plots closely to each other have peat pyrolysates that are chemically similar. Comparing the plot of variables with the plot of cases allows deductions to be made about which variables are relevant to which sample i.e. a pyrolysis product that plots in the same quadrant as a particular sample is likely to have a relatively high contribution in that sample.

By plotting the highly complex pyrolysis data generated by the Py-GC/MS analysis of the peat samples, single points were plotted in multidimensional factor space. Firstly, this was used as a data reduction method, since clustering of the variables in factor space reduced the dimensionality of the dataset without significant loss of information. In the case of the Py-GC/MS dataset many of chemical compounds that are no longer significant due to reduced dimensionality revealed by the PCA had little significance on the overall variation between samples. Secondly, PCA also allowed patterns in the dataset to be identified that would otherwise not have been visualised using graphical techniques which are very limited when analysing data with large numbers of variables. Following PCA, inferences were made regarding the organic compositional differences and significance of such differences between samples.

These linear principal components represent the maximum variation in the data with the first principal components representing the largest contribution of the total variance. All principal components are uncorrelated to all other principal components and in turn each principal component shows the direction of the next largest variance. PCA can be used to determine the origin of an unknown compound by assessing the location of the variable in the variable plot, relative to clusters of known compounds. Separation of the compounds and samples in principal component space allows deductions to be made as to the processes that are likely to have caused the OM composition of the peat samples to be altered from their original state.

In the PCA all data from pyrolysates were added to a universal dataset. Initially data obtained from the samples analysed of Site 1 and Site 3 were analysed (see Chapter 4, Section 4.3.2) this analysis was followed by the addition of data from Site 2 (see Chapter 4 Section 4.3.3). Data presented in Chapter 5 was then added to this universal dataset. All samples and compounds were included in the analysis, none were removed or grouped. Each sample and compound was assigned a code used for the purposes of idnetification (See Apppendix 1).

Other statistical techniques applied to the data include linear and logarithmic regressions, and Analysis of Variance (ANOVA) (Two-way and two-way repeated measures). Details of these techniques are described in the relevant data chapters.

Chapter Four - Effects of fire on the organic matter composition of tropical peat

4.1 Introduction

The aim of this chapter is to address the following research objective: **To provide evidence for change in OM composition after a single fire event in the chosen study area.**

The chapter begins with a brief rationale for the research followed by a description of the methods, summarising information covered in greater detail in Chapters 2 and 3, respectively. The remainder of the chapter explains in detail the results of Py-GC/MS analysis of a range of peat samples from Sites 1, 2 and 3. Finally the short-term effects of fire on peat OM composition are discussed in sections 4.4 and 4.5. A general discussion of the wider implications of this dataset is provided in Chapter 7.

4.1.1 Rationale

Fires in terrestrial ecosystems can have various environmental and ecological implications. Burning of above ground biomass releases C as CO_2 to the atmosphere (Kasischke *et al.*, 1995). Fire also has a range of effects on soil properties (Schmidt *et al.*, 2000; González-Pérez *et al.*, 2004; Certini, 2005), including alteration of the OM composition (Almendros 1997; González-Vila and Almendros, 2003).

Peat fires are known to have an impact on the substrate nutrient status (Dikici and Yilmaz, 2006; Smith *et al.*, 2001), but relatively few studies have focussed on the effects on peat OM (Buurman *et al.*, 2006; Schellekens *et al.*, 2009; Rollins *et al.*, 2003; Knicker*,* 2007). Peat OM contains an array of organic compounds derived from plant residues and microbial biomass, all of which are susceptible to fire-induced alteration (charring). Compositional transformations include: reduction in carbohydrate content, including depletion of furans, which often results in a relative increase in lipid compounds (Kaal and Rumpel, 2009), and an increased aromatic content and neoformation of heterocyclic N compounds as a result of heating (Knicker *et al.*, 2005). Charred OM predominantly consists of refractory aromatic and alkyl C (Knicker *et al.*, 2005).

The effects of fire on the OM composition of mineral soils are reasonably well documented (Leinweber and Schulten, 1999, González-Pérez *et al.*, 2004; Certini, 2005), but there is a knowledge gap with regard to peatland systems and, in particular, tropical peats. Future climatic change is expected to contribute to an increasing incidence of peatland fire (Turetsky *et al.*, 2002; Li *et al.*, 2007), so it is critical to understand how fire influences these concentrated C stores. Improved knowledge of how fire alters the C forms and OM quality of tropical peat should aid understanding of the stability of this C store, longer term C cycling and post-fire ecosystem recovery.

The aim of this chapter is to report the changes in the OM of tropical peat as a result of fire. Py-GC/MS results for recently burned tropical peat are compared with unburned 'controls' in order to reveal fire-induced biogeochemical modifications. Previous studies have often used controlled burning or heating experiments to assess alteration to the OM composition of soil (Campo *et al.*, 2011), but these may not be directly comparable with natural fire events due to the variable environmental conditions that are inevitably found in the field. In contrast, this study examines the impact of fire on peat OM composition by analysing samples collected in the field immediately following a fire event. This is the first study to describe fire-induced alteration of the organic chemistry of tropical peat.

4.2 Methods

4.2.1 Site Selection

Three sampling sites were selected for investigation; firstly, an area of relatively intact peat swamp in the Sebangau forest (Site 1), secondly, a drained area of forest within Block 'C' of the MRP (Site 2) and finally a degraded area of peatland, also within Block 'C' (Site 3)) that had been subject to a single fire event during the dry season of 2009. Further details regarding each of the sites are included in Chapter 3 Sections 3.1.2, 3.1.3 and 3.1.4.

4.2.2 Sampling Strategy

The peat samples used for the analyses reported in this chapter were obtained from three sets of point samples from Sites 1 and 3 (sampled in November 2009) and also composite samples from a total of 15 cores from a single plot in Site 2 (sampled in March 2010). Further details regarding the specific sampling strategies are included in Chapter 3, Section 2.3. A full list of samples used in this chapter is provided in Table 2.

Table 2: Peat sample information including site locations, sample codes, depths and fire history. + Samples at Sites 1 and 3 were collected in November 2009; in the case of Site 3 the samples were collected one month after fires in that year. 3 cores were collected in Sites 1 and 3. Details of sampling are provided in Chapter 3, Section 3.2.1. Site 2 a single plot was sampled (15 cores) in March 2010. Details of sampling strategy-see Chapter 3, Section 3.2.2.*

Table 2. – Peat Sample Information

Location	Sample ID	Depth (cm)	Fire History
Site 1 **Intact Peat Swamp Forest** $^{+}$	SN1	0-5	Not burnt
	N1C	5-15	
	N1B	15-30	
	N1A	30-50	
	SN2	0-5	
	N2C	5-15	
	N2B	15-30	
	N2A	30-50	
	SN3	0-5	
	N3C	5-15	
	N3B	15-30	
	N3A	30-50	
Site 2 **Drained Peat Swamp Forest***	1D	0-5	Not burnt
	1C	5-15	
	1B	15-30	
	1A	30-50	
Site 3 **Burnt and Degraded Peatland** $^{+}$	SF1	0-5	Burnt 2009
	F1C	5-15	
	F1B	15-30	
	F1A	30-50	
	SF2	0-5	
	F2C	5-15	
	F2B	15-30	
	F2A	30-50	
	SF3	0-5	
	F3C	5-15	
	F3B	15-30	
	F3A	30-50	

4.2.3 Characterising Peat Organic Matter: Py-GC/MS

Bulk samples were pyrolysed using a CDS 1000 pyroprobe coupled to a Perkin Elmer Clarus 500 GC/MS. Approximately 1 mg of freeze-dried and homogenized sample was encapsulated into a clean quartz tube plugged at either end with quartz wool. The samples were pyrolysed at 710 °C for 15 s. A higher temperature of pyrolysis was chosen in order to ensure that the sample in the quartz tube reached 610 °C. Typically a lower temperature has been used (610 °C) in other pyrolysis studies however many of these studies were based on Curie Point pyrolysis where the sample is in direct contact with the filament coil. By encapsulating the sample in a quartz tube the sample is not heated to the same degree therefore pyrolysis was conducted 100 °C higher to allow for this reduced heat transfer (Wampler pers. comm). The GC/MS temperature programme consisted of an initial temperature of 40°C for 1.8 min which was then ramped to a final temperature of 310°C at 4°C min^{-1}.The GC/MS instrument was fitted with a CP-Sil 5CB MS column (30 m x 0.25 mm x 320 µm). Compounds within the pyrograms were identified based on their mass spectra and retention times. Peak integration was performed using Turbomass software 5.2.0 and the relative abundance of each pyrolysis product was determined in relation to the relative proportion of all identified pyrolysis products. Pyrolysis products were grouped according to compound class; aliphatics (Al), aromatics (Ar), lignins (Lg), N compounds (N), phenols (Ph), polyaromatics (PAHs) and polysaccharides (Ps).

4.2.4 Statistical Analysis

Comparisons between compound classes were made using average relative proportions of the total identified pyrolysis products. Within class variation was assessed using multivariate analysis in the form of Principal Components Analysis (PCA). Data were entered into an Excel spreadsheet and analysed using Statistica® software. PCA was used to establish differences in peat OM composition. Two principal components were extracted and factor loadings were plotted for individual variables as well as factor scores of cases (samples). Clustering of cases based on the factor scores on the principal components axes related to the loadings of the original variables.

4.3 Results

Py-GC/MS is a powerful analytical tool that allows for a detailed interpretation of OM in soils and sediments. Analysis of bulk peat samples provide data (pyrolysates) that reveal details regarding the likely sources or types of compounds present in the original OM. Comparison of many pyrolysates from different sites allows convincing interpretations to be made and inferences can also be made about the relative OM quality. The results presented in this chapter will interpret the peat pyrolysates for the following sample categories; undisturbed peat from intact peat swamp forest (Site 1); peat from drained peat swamp forest (Site 2); peat samples from a site affected by both drainage and a recent fire (samples were collected one month after the fire) (Site 3). Direct comparisons are made between the burnt and unburnt peat samples in order to determine the changes in OM composition caused by fire.

4.3.1 Characterisation of intact PSF peat (Site 1)

Overview

In the peat samples collected from intact PSF (Site 1) 122 pyrolysis products were identified in the MSF pyrolysates. The samples from this location displayed little variation across the 0 to 50 cm depth range (Table 3). Py-GC/MS analysis of surface peat samples resulted in an array of different pyrolysates derived from a range of different source materials. There are contributions from all compound classes including lignins, polysaccharides, aliphatics, aromatics, nitrogen containing compounds, phenols and polyaromatic hydrocarbons. The complete list of pyrolysis products and their respective compound classes are listed below (Table 3)

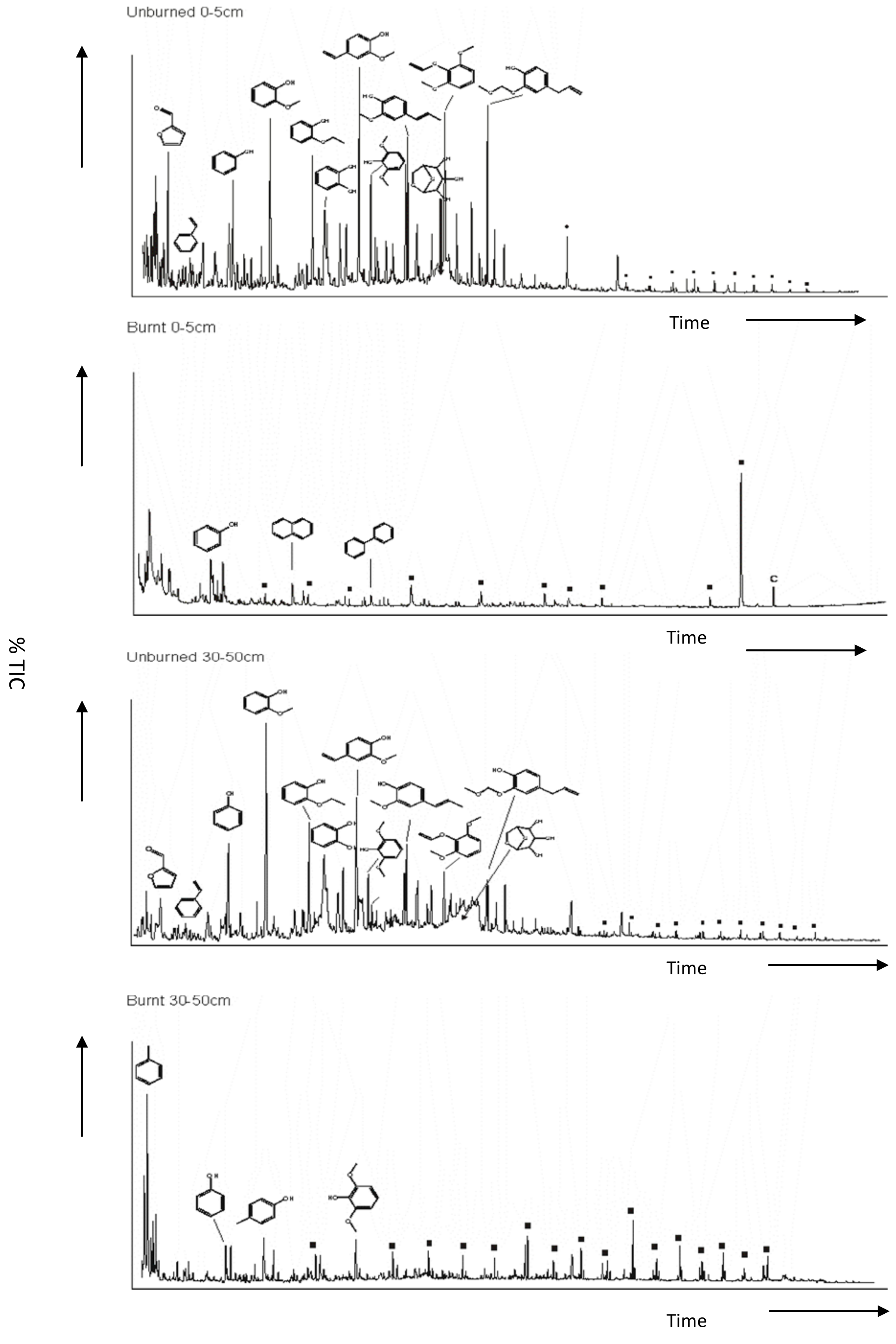


Fig. 23: Examples of pyrograms of sample from Site 1 (Intact peat swamp fores) and 3 (burnt peat swamp fores). Pyrograms represent the following depth and sites: Site 1 0.-

5 cm, Site 3 0-5 cm, Site 1 30-50 cm and Site 3 30-50 cm. Black squares represent aliphatics (alkene/alkanes).

Table 3: Average abundances of compound classes (%) of total identified pyrolysis products*$^{+}$**.** ** Sites 1 & 3 : Each sample is an average of three samples. Site 2 results of bulked sample .+ Al, aliphatics, Ph, Phenols; PAH, polyaromatics; N, nitrogen containing compounds; Lg, lignins; Ar, aromatics; Ps, polysaccharides.*

Site N^{o}	Sample	Ps	Lg	Ar	Ph	N	PAH	Al
Site 1	Surface N	30.8 (± 6.7)	36.1 (± 9.1)	4.5 (± 0.7)	10.7 (±0.4)	2.8 (±0.4)	0.3 (±0.0)	14.7 (±1.8)
	NC	27.9 (± 12.7)	19.9 (±6.6)	4.6 (±2.5)	17.9 (±7.2)	3.8 (±1.7)	0.8 (±0.6)	24.0 (±6.6)
	NB	24.50 (±4.3)	29.05 (±4.1)	5.0 (±1.1)	15.2 (±4.6)	3.6 (±1.0)	0.7 (± 0.0)	22.0 (±5.2)
	NA	24.6 (± 6.3)	35.2 (±2.1)	4.4 (±1.2)	15.0 (± 4.4)	3.5 (±0.3)	0.7 (±0.3)	16.5 (±3.0)
Site 2	Surface 1	22.6	10.1	4.5	16.0	4.1	1.2	41.5
	1C	16.5	13.1	7.8	13.2	3.3	1.6	44.5
	1B	2.7	7.0	5.7	7.1	4.9	1.7	70.8
	1A	6.9	10.6	4.5	9.0	4.3	2.0	62.6
Site 3	Surface F	0.1 (±0.1)	0.8 (±1.2)	12.0 (±5.3)	6.2 (±0.9)	4.1 (±3.8)	5.5 (±2.6)	71.3 (±12.9)
	FC	4.4 (±1.1)	19.3 (±7.9)	6.8 (±0.1)	10.2 (±5.2)	3.0 (±1.8)	0.8 (±0.4)	55.5 (±16.1)
	FB	5.4 (±0.9)	10.2 (±10.4)	7.8 (±0.8)	10.5 (±3.4)	3.4 (±2.2)	1.3 (±0.1)	61.5 (±9.7)
	FA	4.1 (±1.4)	13.8 (±3.6)	8.0 (±1.3)	13.4 (±5.5)	2.1 (±0.8)	1.7 (±0.0)	57.0 (±6.6)

Lignins

Lignin derived pyrolysis products (36.1± 9.1 %), which are biomarkers for woody material, and polysaccharide-derived compounds (30.8 ± 6.7 %) provide the largest contributions to the OM composition of the surface samples from Site 1. The total lignin-derived compounds show a reduction from 36.1 ± 9.1 % at 0-5 cm depth to 19.9 ± 6.6 % at 5-15 cm depth in the 0- 50 cm profile. At the 30-50 cm depth interval relative lignin derived pyrolysis product concentrations increase to 35.2 ± 2.1 %. Molecules derived from lignin such as guaiacol (Lg1), methyl guaiacol (Lg2) and ethyl guaiacol (Lg16) are dominant. Coniferyl monomers make a significant contrirbution to the lignin of the bulk OM. The relative concentrations of guaiacol increases with depth; ranging from 5.5 ± 0.4 % at 0-5 cm depth to 7.2 ± 1.3 % at a depth of 30-50 cm. Shortening of lignin alkyl side chains, particularly in guaiacol structures, has previously been suggested as a parameter by which to judge decomposition (Schellekens *et al.*, 2009). Increased abundance of guaiacol compared with alkyl side chain guaiacols (Lg 2, Lg 4 and Lg 9) implys some evidence of decomposition in the peat in the 30-50 cm depth interval. As a consequence some larger molecular weight lignin derivatives such as acetyl syringol (Lg14) show a relative decrease with depth from 2.3 ± 1.0 % at the 0-5 cm depth to 0.5 ± 0.4 % at the 30-50 cm interval. However, the majority of the higher molecular weight lignin compounds do not comply with this trend but remain relatively consistent with increasing depth. The near-constant inundation experienced by the peat at Site 1 ensures that lignin derived compounds which would otherwise decompose under oxic conditions, remain intact.

Polysaccharides

Polysaccharides contribute the second largest abundance to pyrolysates for peat samples from Site 1 (26.95% average 0-50 cm). The majority of this contribution is made by Levoglucosan (Ps3), a pyrolysis product believed to be derived from fresh lignocellulose material (Poirer *et al.*, 2000). Relatively large contributions of Levoglucosan are present in the Site 1 pyrolysates at all depth intervals. The average relative concentration across all four depth intervals is 17.8 ± 6.3 %. Relative contributions decline with depth (20.3 ± 6.8 to 16.8 ± 5.3 %) between the 0-5 cm and

30-50 cm depth intervals. Levoglucosan is the most prevalent polysaccharide pyrolysis product and therefore its relative concentration significantly influences the total proportion of polysaccharide pyrolysis products in the peat. The total contribution by polysaccharides varies from 30.8 ± 6.7 % at the 0-5 cm interval to 24.6 ± 6.3 % at the 30-50 cm interval. Other polysaccharide compounds are also present in the pyrolysates, including furan derivatives. The likely source of such compounds is microbial organic matter (Buurman and Roscoe, 2011). Some seven different furan/furanone compounds can be identified. Furfural (Ps1) is the most dominant of these compounds and is present in all peat samples. Contributions of this microbial-derived polysaccharide range from 2.6 ± 1.2 % at the surface to 1.81 ± 2.1 % at the 30-50 cm depth interval.

Phenols

Eight phenol-derived compounds were identified (Appendix 1). Overall phenol contribution increased slightly with depth from 10.7 ± 0.4 % to 15.0 ± 4.4 % at the deepest interval. Phenol itself is the most abundant compound (Ph1), although its source is somewhat unknown. There are some phenol compounds that are believed to be breakdown products of lignin compounds; including methyl phenols (Ph2, Ph3 and Ph4). Phenol compounds have also been attributed to algal and microbial polyphenols as well as proteins (tyrosine) (Fabbri *et al* 1998). Due to the variety of possible sources of phenol pyrolysis products this compound class is not particularly diagnostic in OM analyses.

Aliphatics

There is a slight depth variation in the proportion of aliphatics with an average across the 0-50 cm depth although there is no consistent trend with depth. The greatest contribution by aliphatic derived pyrolysis products was from the 5-15 cm depth interval (24.0 ±6.6 %) and the least from the 0-5 cm depth interval (14.7 ±1.7 %). Aliphatics remain relatively consistent across the 50 cm depth range (14.7 ±1.8 to 16.5 ± 3.0 %). Aliphatic compounds are predominately composed of *n*-alkane and *n*-alkene doublets with C chain lengths ranging from 7 to 33. The ratio of short chains (C8-C 15) to long chains (C24 – C33) remains unchanged throughout the depth profile with only a slight increase from 1.9 at the 0-5 cm depth interval to 3.2 at the 30-50 cm depth interval (Table 3). Short chains are present in relatively greater amounts compared with long chains at all depth intervals. Long chain aliphatic compounds are derived from lipids (Bracewell *et al.*, 1989) from a range of potential sources including, leaf waxes, microbial products and biopolymers such as cutan and suberan (Tegelaar *et al.*, 1995). Prist-1-ene (Al22) is a pyrolysis product derived from chlorophyll and this compound is present in all of the pyrolysates suggesting preservation of fresh plant material at all depths (Buurman *et al.*, 2006) Inundation of the peat at Site 1 is likely to have inhibited decompositional processes that would lead to an accumulation of aliphatic and, particularly, *n*-alkane and *n*-alkene pyrolysis products.

Aromatics

The aromatic contents of the peat pyrolysates show no consistent changes with depth, with an average value across all depths of 4.6 ± 0.3 %. Aromatics, like other compound classes, can be derived from a range of different sources including proteins (Furhmann *et al.*, 2004) as well as incomplete combustion during charring and thermal alteration of polysaccharide derived compounds (Baldock and Smernik, 2002). Aromatics may also accumulate under anaeroobic decomposition conditions (Schellekens *et al.*, 2009), reflecting the typical, waterlogged conditions as Site 1. There are some conflicting ideas on the sources of such aromatics as toluene and benzene; both have often been used as indicators of past wildfire events as they are products of charred materials (Campo *et al.*, 2011).

Nitrogen- containing compounds

Total N-containing products, which include pyrroles, indole and benzamide, have low a relative contribution and show no consistent trend with depth in the peat pyrolysates from Site 1. Relative contributions range between 2.8 ± 0.8 and 3.8 ± 1.7 % of the total identified pyrolysis products. The sources of N-containing compounds are varied, for example, pyrroles and pyridine are derived from proteinaceous material (Schulten and Schnitzer 1998; Buurman *et al.*, 2007), while indole has been acknowledged as a marker of undegraded plant material (Buurman *et al.*, 2007). Indole contributes an average 0.24 ± 0.1 % across all depth intervals. Pyridine is the most dominant N-containing compound at this site (0.54 ± 0.2). The presence of nitriles is often used to imply charring (Kaal and Rumpel., 2009) hence their insignificant contributions at all depths at this site confirm that this site has not experienced fire in the recent past. The N-containing pyrolysis products are indicative of the organic N fraction and their relatively low contributions support the results of previous studies, that ombrotrophic tropical peatlands are a poor source of N for the biota (Page *et al.*, 1999). Mineralization of N compounds to inorganic forms is likely to be impeded because of the anaerobic site conditions. (Note: further N data are included and discussed in Chapter 6).

Polyaromatics

This group of compounds is commonly used to imply burning of vegetation (Kaal and Rumpel., 2009; Buurman and Roscoe, 2011 Campo *et al.*, 2011). Compounds including napthalene (PAH1) may indicate the presence of charcoal in soils or peats (Kaal *et al.*, 2008; Schellekens *et al.*, 2009). In the dataset from Site 1, six polyaromatic compounds were identified, mainly of the naphthalene type. The relative concentration of polyaromatics is very low in the peat pyrolysates (< 1 %) from Site 1 and there is no consistent trend with depth (Table 3). It is likely that these insignificant contributions of polyaromatics are derived from the pyrolysis step itself during Py-GC/MS rather than from the peat OM.

Summary

There are no significant differences in pyrolysis products with increasing peat depth, although there are some subtle differences in the relative amounts of the individual compounds. It is likely that the depth of the water table is a controlling factor in maintaining the organic state of the peat by inhibiting aerobic decomposition. Fluctuation of the water table between wet and dry seasons along with anaerobic decomposition may influence subtle chemical changes with depth, but aerobic decomposition is generally low in inundated tropical peatlands as a result of a high water level throughout much of the year (Jauhiainen *et al.*, 2005). There is a slight variation in the lignin products within the 50 cm range, with an overall declining contribution with depth. Lignin has been found to be readily decomposed under aerobic conditions (Schellekens *et al.*, 2009) and decay in acidic soil can be rapid (Buurrman and Roscoe, 2011). In tropical soil, it is believed that lignin is part of the fresher rather than the refractory organic pool and so is readily decomposed (Kiem and Kögel–Knaber, 2003). However, the prolonged seasonal inundation in peat swamp forests likely favours anaerobic conditions that suppress the rate of lignin decomposition.

4.3.2 Characterisation of drained peat (Site 2)

Overview

Site 2 has not been affected by fire therefore the differences in OM between this site and Site 1 are likely due to the drainage effects. The enhanced oxic conditions present in the upper layer of peat, resulting from lowering of the natural water table has lead to an alteration of the peat OM in Site 2. Comparisons with pyrolysates from Site 1 indicate the nature of these changes caused by the enhanced of oxic conditions.

Lignins

Many lignin derived pyrolysis products are present in the drained peat samples but relative contributions remain moderately unchanged with depth (9.5 – 10.0 %). There is evidence that large MW lignin derived compounds are present in greater abundance at the surface than at depth. Guaiacol (Lg 1), methylguaiacol (Lg 2), vinylguaiacol (Lg 4) and acetylguaiacol (Lg 9), for example, all show a decline in relative abundance with depth. Degradation of the guaiacol C3 side chain has previously been used a parameter to judge aerobic decomposition in peats (Schellekens *et al.*, 2009). Upon calculation of the ratio between the total C_3 side chain guaiacols and the total guaiacol abundance these data conform with previous findings by displaying an increasing ratio with depth (from 2.62 at the surface to 19.2 at a depth of 30-50 cm) (Table 3) suggesting enhanced decomposition over this depth range. On balance, the variation of these lignin derived compounds provides evidence for enhanced decomposition in the sub-surface peat compared with the surface peat. Previous research has found that warm oxygenated environments cause an increase in lignin degradation (Nierop *et al.*, 2001; Carr *et al.*, 2010) and this is supported by these results.

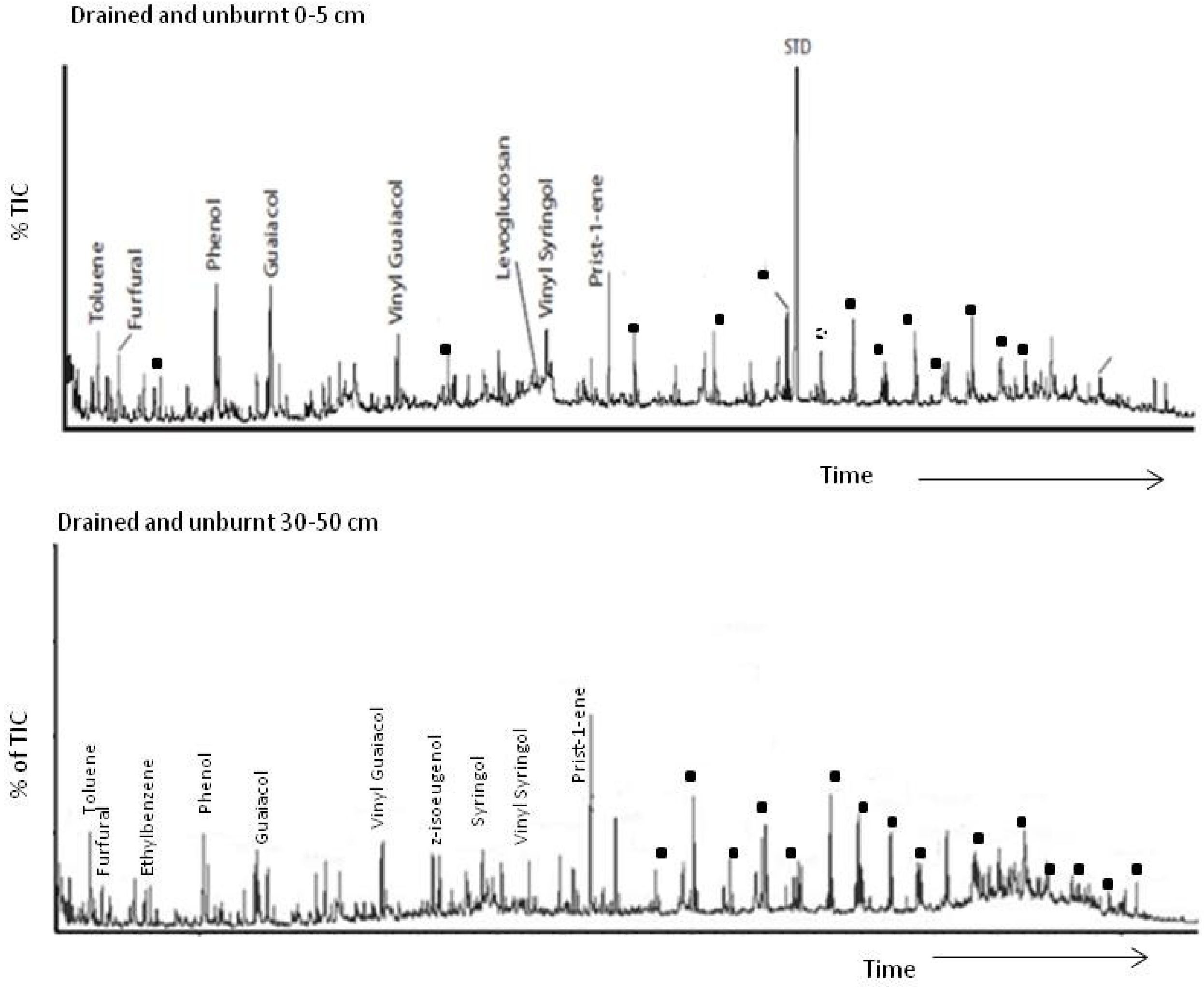


Fig. 24: Examples of pyrograms of sample from Site 2 (Drained and unburnt peat swamp forest). Pyrograms represent the following depth and sites: Site 2 0.-5 cm, Site 2 30-50 cm Site 1. Black squares represent aliphatics (alkene/alkanes).

Polysaccharides

Compounds derived from polysaccharides are present in the drained peat samples, however there are several compounds that are reduced or absent compared with the undisturbed peat samples from Site 1. There is an overall reduction in total polysaccharide content with depth (22.6 – 6.9 %). For example, the contribution of levoglucosan declines from 18.2 % in the pyrolysates of surface samples to 4.8 % at the 30-50 cm depth interval. Levoglucosan (Ps3) is likely sourced from the input of fresh cellulose material hence its greater abundance in the surface than in the sub-surface samples where it is likely to have been exposed to a longer period of decomposition. The considerable decline in polysaccharide pyrolysis products from the 5-15 cm to the 15-30 cm depth interval suggests that at this depth the peat is more decomposed than in the upper 15 cm. Increased residence time at depth coupled with inputs of litter to the surface may explain this higher state of decomposition with depth.

Aromatics

The average aromatic contribution across the 50 cm profile is 5.6 ± 1.6 % compared to that of the average of 4.6 ± 0.3 % for the profile at Site 1. Results suggest there are processes occurring between the 5-15 cm and 15-30 cm depth intervals that have caused modifications to the OM composition of the peat. Typically aromatics are produced during the charring process and as this site has not burnt, relative contributions are low. However, as noted by some other authors (Fabbri *et al*., 1998; Buurman *et al*., 2007) the accumulation of aromatic compounds such as Benzene (Ar1) and Toluene (Ar2) may imply decay of OM (Schellekens *et al*., 2009). There are similar contributions of aromatics, on average, throughout the upper 50 cm of the undisturbed peat profile from Site 1, therefore these data do not support the idea that aromatics are created by decomposition processes.

Aliphatics

As with other compound classes, aliphatic contributions show distinct differences between the 0-15 cm and 15-30 cm depth intervals. Aliphatics, which include *n*-alkene/alkane doublets, increase considerably with depth, from 44.8 % at the 5-15 cm interval to 70.8 % at the 30-50 cm depth. This result supports the data for other compound classes which suggest a shift in OM composition below a depth of 15 cm. The increase in aliphatics below this depth can in part be attributed to the isoprenoid hydrocarbons, Prist-1-ene (Al22) and Prist-2-ene (Al23), which are produced by the pyrolytic cleavage of chlorophyll-a (Ishiwatari *et al*. 1991). At 5-15 cm, Prist-1-ene is found at a lower concentration (2.77 %) than at the 30-50 cm interval (5.43 %). These Pristene compounds are also present in the Site 1 peat pyrolysates, although in reduced relative contributions. The remaining aliphatic pyrolysis products consist of *n*-alkane/*n*-alkene doublets and their contributions increase with depth. The ratio of short to long chain *n*-alkene/*n*-alkanes is lower in peat pyrolysates from Site 2 compared to those from Site 1 (Table 4) indicating that there is a greater abundance of long chain *n*-alkane/*n*-alkanes compared with shorter chains at Site 2. A greater proportion of short to long chain compounds has previously been suggested as an indicator of aerobic decomposition which causes a shift in chain length from long to shorter homologues (Almendros *et al*., 1998) however this data was generated using GC-MS analysis of lipid extracts which provides a more detailed examination of the lipid fraction than Py-GC/MS. The data derived from my study do not support previous findings; on the contrary there are a greater proportion of long chain homologues in the drained peat compared with the undisturbed peat (Table 4). The considerable aliphatic content of the drained peat pyrolysates compared with the undisturbed peat supports the statement that the peat is more decomposed at Site 2 as aliphatic compounds are typically resistant to microbial breakdown (Schellekens *et al*., 2009). Therefore their relative abundance appears to be occurring at the expense of a reduced presence of other compound classes which are more readily decomposed.

Table 4: Chain length distributions of n-alkyls (n-alkenes, n-alkanes, n-alkene/alkane doublets in undisturbed, drained and recently burnt peat. Ratios have been calculated by finding the average sum of the short chain alkene and alkanes respectively (C8-C15) and dividing by the sum of the long chain alkene and alkanes (C24-C33). Coloumn six was calculated by determining the ratio between the total short and long chain aliphatics (alkenes and alkanes).

Site	**Sample**	**Depth (cm)**	**Average Short/Long Alkenes**	**Average Short/Long Alkanes**	**Ratio Short: Long chain *n*- alkenes/ *n*-alkanes**
Site 1	Surface N	0-5	4.7	0.8	1.9
	NC	5-15			2.3
	NB	15-30	2.2	0.8	1.4
	NA	30-50			3.2
Site 2	Surface 1	0-5	0.7	0.9	0.8
	1C	5-15			0.6
	1B	15-30	0.5	0.3	0.4
	1A	30-50			0.5
Site 3	Surface F	0-5	17.5	0.3	0.7
	FC	5-15			1.8
	FB	15-30	1.3	0.6	0.9
	FA	30-50			1.8

Nitrogen- containing compounds

The relative abundance of identified N-containing compounds in the pyrolysates shows no consistent trend with depth (Table 3). The average across the 50 cm depth range is 4.2 % which is a ~27 % increase over corresponding data from Site 1. Pyridine is the dominant N-containing compound in these pyrolysates; in surface samples pyridine contributes 0.43 % to the pyrolysates and at 30-50 cm it contributes 0.90 % of the total identified products. Pyridine has been suggested as a parameter by which to judge decomposition in peat (Schellekens *et al.*, 2009). Increasing abundance of Pyridine with depth may suggest greater levels of decomposition in the deeper peat compared with the surface. Other N-containing compounds include pyrroles and indene which collectively have a greater abundance in the drained peat from Site 1 vs. the inundated peat from Site 1.

Phenols

Phenol-derived pyrolysis products show a decreasing trend with depth (Table 3). At the surface phenols contribute 16.0 % of the identified pyrolysis products and, at 30-50 cm, only 9.0 %. The source of phenol compounds is contested in previously published studies and they do not originate from one specific source (Kaal *et al.*, 2008), therefore an explanation for this decreasing trend with depth may not be particularly diagnostic. Phenol (Ph1) is the most dominant of the phenol compounds at all depth intervals contributing an average of 4.4 ± 2.0 %. Other significant compounds in the 0-5 and 5-15 cm pyrolysates include 2-methyl phenol (Ph2), 3-methylphenol (Ph3) and 4-methylphenol (Ph5).

Polyaromatic Hydrocarbons

The relative contribution of polyaromatic hydrocarbons of the pyrolysates from Site 2 is negligible although greater than that from Site 1 (Table 3). There are no consistent trends with depth. Naphthalene is the most dominant compound which contributes an average 0.30 ± 0.07 %) across the four depth intervals. As this site has not been burnt it is unlikely that these compounds are derived from charred biomass, as has been previously determined in other studies (Grandy and Neff, 2008; Kaal *et al.*, 2009b). The relatively low contributions of polyaromatics in these pyrolysates are most likely derived from the pyrolysis step itself and therefore are not diagnostic of the OM composition.

Summary

Typical trends in decomposition involve reduction in polysaccharides, increase in non-oxygenated aliphatics and aromatics with depth (Pontevedra-Pombal *et al.*, 2001). Comparison of data for Site 2 with Site 1 implys the modifications in OM composition brought about by drainage. Pyrolysates from a 50 cm depth profile from Site 2 reveal that there are, 117 pyrolysis products present in the sample. This is a reduced number of pyrolysis products compared Site 1. Of the compounds present in Site 1 that are not present in Site 2 pyrolysates, many are derived from polysaccharide sources. Compounds include; maltol, (*5H*)furan-3-one and acetylfuran. Furan structures can be attributed to polysaccharide sources (Fabbri *et al.*, 1998; Vancampenhout *et al.*, 2012). There are significantly reduced levels of polysaccharides at Site 2 vs. Site 1 including levogluscosan particularly at the 15-30 and 30-50 cm depth intervals (Table 3). The reduced abundance of polysaccharide derived pyrolysis products suggests that they are an important component of inundated tropical peat (Site 1) and that introduction of oxygen to the peat causes degradation of these types of compounds.

Other compounds identified in Site 1 pyrolysates that are not present in these Site 2 pyrolysates include ethyl phenol, guaiacylacetone and acetyl syringol. Absent compounds allow deductions to be made about the impacts of drainage on peat composition. Predominately polysaccharide derived compounds and some lignin derived compounds are not detected in the pyrolysates of drained peat. Across the depth profile there is some variation between compound classes (Fig.24). The surface of the drained peat displays evidence of the addition of fresh organic material in the form of cellulose (levoglucosan) derived material, however at depth (> 15 cm below the surface) this fresh organic material is not preserved in the manner presented at Site 1 (Fig.23). The surface of the samples collected and analysed from Site 2 generally have a similar organic composition to those of the corresponding samples from Site 1.The upper most layers of peat at this site have previously been described as humic whereas more decomposed peat has been identified at depth (Jauhiainen *et al.*, 2008, 2012). Pyrolysates analysed from depths >15 cm from the surface support this previous finding as this study provides evidence for increased decomposition at depths greater than 15 cm.

4.3.2 Effects of Fire

The remainder of this chapter presents and discusses data that assess the changes in OM composition of peat that occur immediately post-fire. Fires were widespread across much of the MRP during the dry season of 2009 and the data analysed in this section focus on the pyrolysates from peat samples collected from locations affected only by this single fire event. By comparing the data from the fire-affected peat pyrolysates (Site 3) with those from undisturbed (Site 1) and drained (Site 2) locations, the fire-driven modifications to peat chemical composition can be assessed. Although under natural conditions tropical peat swamp forest is subject to almost permanently waterlogged conditions, the peat at both Sites 2 and 3 has been drained and therefore the peat will have been subject to higher rates of peat oxidation (decomposition). Comparison of data from Sites 2 and 3 will enable separation and interpretation of modifications caused by decomposition alone and those caused by a combination of both decomposition and fire.

4.3.3 Immediate effects of fire

Overview

Samples F (Surface F, FC, FB and FA) were collected at Site 3 one month after the end of a fire that occurred during the 2009 dry season (i.e. during November 2009). The data derived from analysis of these samples can therefore be taken to be representative of the 'Short Term' effects of fire on peat organic geochemistry. Total pyrolysis products in the burnt surface samples from Site 3 ranged from 72-75 compared with 109 in the peat pyrolysates of surface peat from the drained site (Site 2) and 122-127 compounds in surface samples from intact peat (Site 3), suggesting that decomposition followed by burning reduces the number of OM compounds.

Many of the compounds detected in the peat samples from the inundated and drained forest sites were not detected in the samples from the recently burnt site. Compound diversity was particularly modified in the (0-5 cm) surface peat pyrolysates (Fig.24) whereby pyrolysis products were dominated by aromatic and aliphatic compounds. In the subsurface peat samples, burning also modified the peat OM but to a lesser extent than in the surface peat. The samples from the burnt sites are dominated by aliphatics and have an increased aromatic content particularly in the surface (0-5 cm). The surface samples are also depleted of all polysaccharides and almost all lignin derived compounds (0.8 ± 1.2 %) although these compound classes are present in subsurface (5-15; 15-30; 30-50 cm) samples.

*Table 5: Parameters of decomposition as used in Shellekens et al., (2009). Average values are used for Sites 1 and 3. * C16-C23. ¹- Average polysaccharide content.*

	Site 1 Intact PSF		**Site 2 Drained PSF**		**Site 3 Drained and Burnt**	
Parameter	**0-5 cm**	**30-50 cm**	**0-5 cm**	**30-50 cm**	**0-5 cm**	**30-50 cm**
Levoglucosan/sum of Ps[1]	1.51	1.46	0.81	0.70	0	1.57
Sum C3 guaiacol/guaiacol	1.56	2.53	1.7	19.2	0	1.76
Sum C3 syringol/syringol	1.62	0.98	1.57	7.5	0.13	0.66
Sum mid chain* alkanes	1.87	1.35	3.12	5.68	9.25	5.77
Pyridine (%)	0.68	0.57	0.43	0.90	1.36	0.2

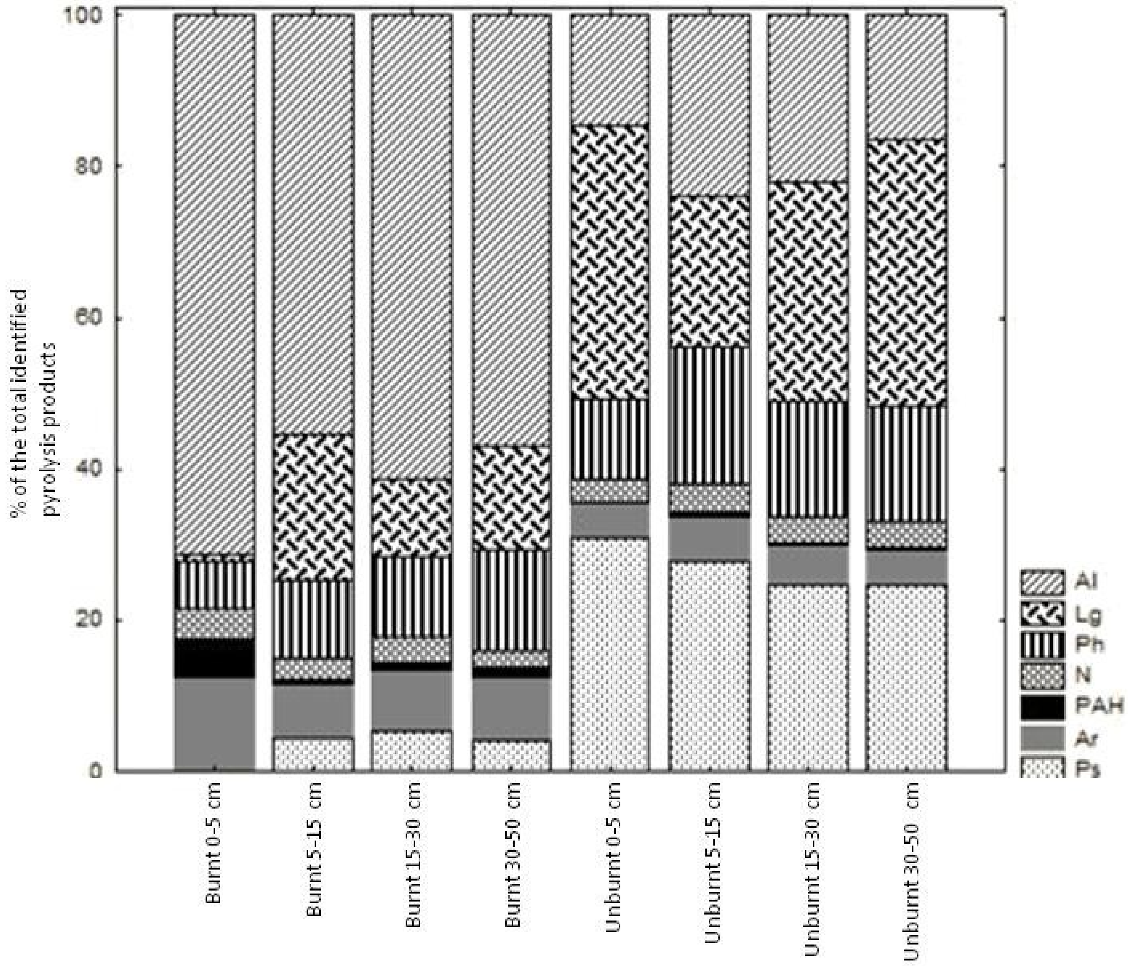


Fig.25: Relative proportions of pyrolysis products (% of the total identified pyrolysis products) in recently burnt and unburnt peat.

Lignin

Low concentrations of lignin compounds are often indicative of fire events due to a loss of methoxy groups during the burning process (González-Pérez *et al.*, 2004). The data from Site 3 support this as lignin-derived products are virtually absent from the pyrolysates of surface peat samples (0.80 ± 1.2 %) and are present in all subsurface samples (19.3 ± 7.9 - 13.8 ± 3.6 %) but in lower abundance than at Site 1 (Fig. 25). Guaiacol (Lg1) has the most prominent peak of the lignin-derived compounds. Shortening of lignin alkyl side chains, particularly of guaiacol structures, has previously been suggested as a parameter by which to judge decomposition (Schellekens *et al.*, 2009). An increased abundance of guaiacol compared with C3 alkyl side chain guaiacols (Lg 2, Lg 4 and Lg 9) (Table 5) implys some evidence of decomposition in the unburned peat. Syringol derivatives were less significant than those of guaiacols at all depth intervals in pyrolysates of recently burnt peat. Lignin degradation likely began soon after the peat was drained and underwent aerobic decomposition hence, the reduced abundance in this compound class observed in the Site 2 pyrolysates. Burning has further decreased the contribution of lignin compounds suggesting that these types of compounds are thermo labile.

Polysaccharides

Polysaccharide-derived pyrolysis products are particularly low (0.1 ± 0.1 %) at the surface of burnt peat. Such compounds are present in the subsurface pyrolysates (4.1 ± 1.4 %) at the 30-50 cm depth interval but are in lower abundance compared with inundated and drained forest peat (Sites 1 and 2). Contributions of polysaccharides are greater in the subsurface peat, (Table 3) however, as with other thermo labile OM components such as lignins, the upper layer of peat presents the greatest differences chemically from the peat in a natural, intact, inundated state (Site 1). Levoglucosan (Ps3) typically dominates the unburned samples, however it is not present in the post-fire samples suggesting that this labile primary polysaccharide is either volatilized or converted to some other organic form during fire. There are small contributions of this primary polysaccharide further down the peat profile at the burnt site. From analysis of the drained forest peat it is was found that Levoglucosan abundance was reduced at all depth intervals compared to peat from Site 1. At Site 3, both the introduction of oxic conditions and the limited supply of OM additions from above ground biomass have resulted in reduced abundance of this primary polysaccharide while burning has caused further removal of levoglucosan due to preferential combustion.

Aromatics

Aromatic content contributes an average of 8.67 % to pyrolysates throughout the 50 cm depth range at the burnt site. However, by far the greatest contributions come from the surface (0-5 cm) pyrolysate (12.0 ± 5.3 %). It is well documented that burning or heating of OM causes an increase in aromatic content (Almendros *et al*., 1992; Certini 2005) which is caused by a selective enrichment of aromatic compounds as well as the alteration of polysaccharide-derived compounds by endothermic reactions (Baldock & Smnerik 2002; Freitas *et al*., 1999; Knicker *et al*., 2006). The findings of this study support this interpretation, as there is an apparent decline in polysaccharide content with increasing aromatic content (Fig.25).

Nitrogen- containing compounds

Nitrogen-containing compounds as indicated by the surface peat pyrolysate at the burnt site comprise 4.1 ± 3.8 % of the total assigned pyrolysis products. Total N-containing compounds show no consistent trends, between the 0-5 cm and 30-50 cm (2.1 ± 0.8 %) depth intervals. Comparable contributions of N-containing compounds were determined in the peat pyrolysates from the intact (Site 1) and drained (Site 2) locations. The presence of the N-containing compound pyridine suggests an accumulation of heterocyclic N in the peat OM which is often considered to be an indicator of fire (Campo *et al*., 2011). The data show there is a presence of nitrile compounds such as Benzonitrile (2.38 ± 2.14 %) that occurs only in the pyrolysates of the burnt surface peat. Nitriles are commonly found in charred materials (Kaal *et al*., 2007), which may further suggest elevated burning intensity at the surface of Site 3. The sources of N compounds are varied, for example, pyrroles and pyridine are derived from proteinaceous material (Schulten and Schnitzer 1998), and indole has been acknowledged as a marker of undegraded plant material (Burrman et al., 2007). Indole was not present in the pyrolysates from any of the samples from Site 3 but it was detected in the peat pyrolysates from Sites 1 and 2.

Phenols

Phenols contributed 6.2 ± 0.9 % of the total identified pyrolysis products in the surface sample (0-5 cm) from the recently burnt site, increasing to 13.4 ± 5.5 % at the 30-50 cm interval (Table 3). Phenol (Ph1) is the most dominant of the phenol derived compounds. Although phenols are not particularly diagnostic it is thought that they may be the degradation products of lignin compounds, hence their increased abundance compared to that of peat from the drained forest site. Dehydroxylation of lignins may be related to the increased contribution of phenol derived compounds.

Aliphatics

Aliphatic derived compounds are the dominant compound class in the peat samples from the burnt site (Table 3) contributing 71.3 ± 12.9 % to pyrolysates from the surface samples and 57.0 ± 6.6 % to those from the 30-50 cm depth range. *n*-Alkene/*n*-Alkane doublets heavily influence the contribution of aliphatics which dominate all samples from the burnt site, resulting in a C rich OM through the expulsion of other atoms, particularly oxygen. Relatively large contributions from aliphatic derived compounds at Site 2 suggest these compounds have a high resistance to thermal degradation. The ratio of short to long chain *n*-alkanes is reduced compared to those in the peat samples from both Sites 1 and 2 (Table 4). Long chain (C24-C33) *n*-Alkene/*n*-Alkanes display greater resistance to decomposition and fire as implyed by this reduction in the ratio. Previous studies of soil heating have also observed aliphatics to be resistant to thermal treatment (Campo *et al.*, 2011). Aliphatic compounds are dominant in the pyrolysates from Site 2 suggesting that long-term aerobic decomposition prior to burning caused preservation of this compound class. Aliphatics are further preserved post-fire as they are highly resistant to thermal degradation.

Polyaromatic Hydrocarbons

At 5.5 ± 2.6 %, pyrolysis products that are indicators of polyaromatic hydrocarbons such as naphthalene (PAH1) and biphenyl (PAH3) are present in greater proportions in peat samples from the recently burnt compared with the unburned sites (Sites 1 and 2), with the burnt site samples containing 3.14 ± 1.8 % and 1.93 ±0.7 %, respectively. Such compounds are often detected in fire-affected OM and are considered to be derived from charcoal (González-Vila *et al.*, 2001; Knicker *et al.*, 2007; Pastrova *et al.*, 1994), although Kim and Kögel-Knaber, (2003) found an enhanced PAH content only immediately post-fire and, after 5 months, concentrations were similar to unburned samples. Further analysis of longer term impacts of fire are discussed in Chapter 5.

4.3.4 Principal Components Analysis (PCA)

The PCA reveals that there are statistical differences between the pyrolysis products in the peat samples from the recently burnt peat site (Site 3) compared with those from the unburned, inundated, forested site (Site 1). The results indicate that two factors explain 46.77 % of the total variability in the OM composition. The compound loadings on Factors 1 and 2 are shown in Fig.27 and indicate there is specific compound variation separating the samples via their pyrolysates. The plot of cases (Fig.26) reveals three clusters of samples; unburned inundated peat (Site 1), surface drained and burnt peat (Site 3), and subsurface drained and burnt peat (Site 3). Assessment of the compound loadings (Fig. 26) in relation to these three sample clusters allows an interpretation about the processes that have lead to the differences in OM composition.

There is also separation of the loadings of the three individual point samples for any given peat depth e.g. Surface F1, F2 & F3 (Fig. 26). This implys that these samples have statistically different OM composition despite being collected from within very close range of each other. Due to the heterogeneous nature of both the peat itself and the burning process the OM composition is likely to be different even over small spatial range.

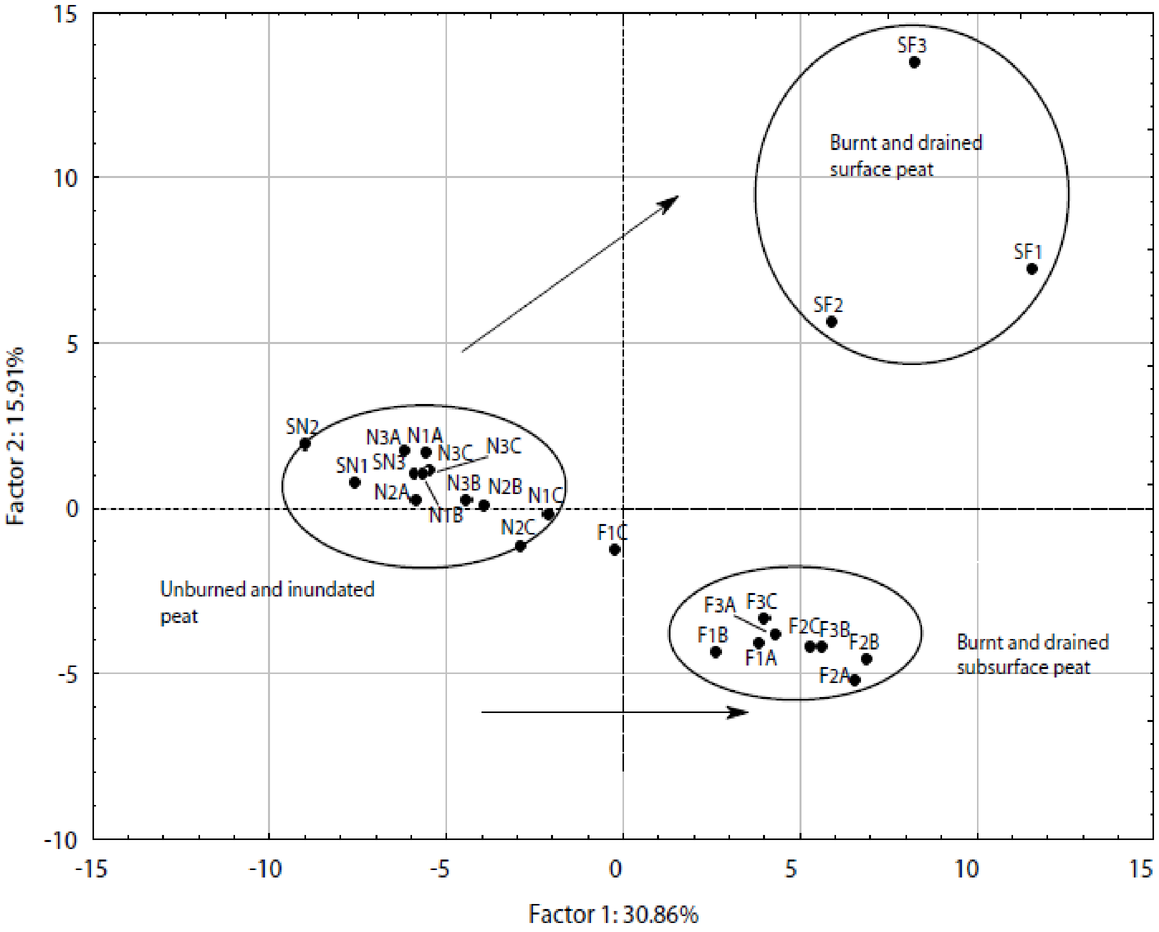


Fig.26: Plot of cases (samples) in factor space. Loadings based on factors 1 and 2. Circled areas highlight statistical separation between burned (Site 3) and unburned (Site 1) surface samples.

A plot of compound loadings (Fig. 26) highlights that Factor 1, which contributes 30.86% of the variation statistically, differentiates between the aliphatic pyrolysis products and the lignin/polysaccharide products. Factor 2, however, accounts for a further 15.91 % of the total variation which is produced by most of the aromatic and aliphatic products. Lignin compounds group together in the left of the diagram and have a negative loading on Factor 1 corresponding with peat surface samples from Site 1 (Fig. 25). Polysaccharide-derived compounds also cluster just above the lignin compounds and all have a negative loading on Factor 1.

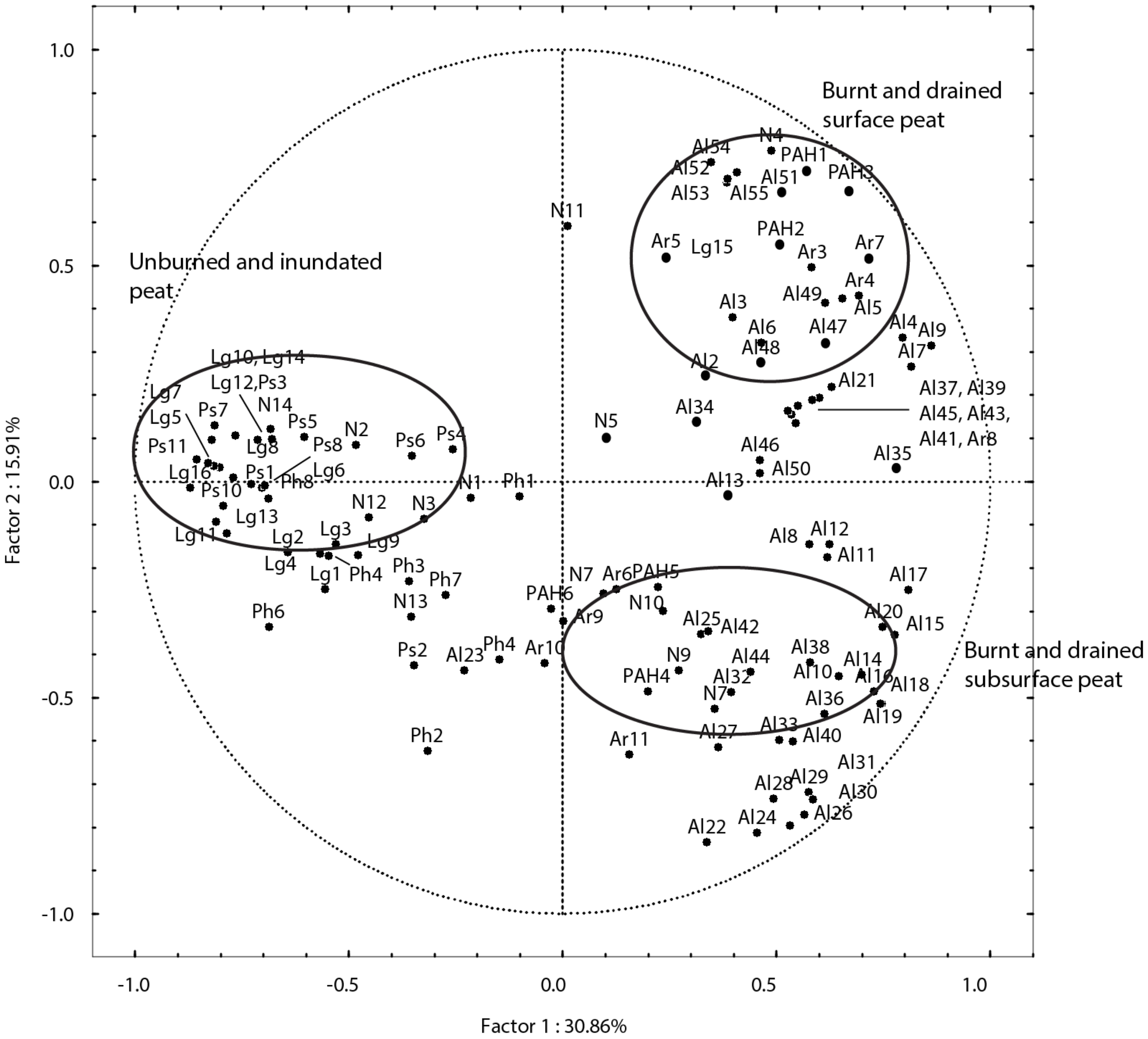


Fig. 27: Plot of compounds, loadings based on factors 1 and 2 which explain 46.92% of the total variance (Factor 1, 30.86 %; Factor 2, 15.91 %).

Aromatics, including ethyl benzene, xylene and propylbenzene (Ar 3, 5 & Ar 7), plot in the top right of the diagram and have a positive loading on both component axes. However, there are some aromatic derived compounds that plot with a negative loading on Factor 2, including acetophenone and *m*-methyl indene (Ar 9 & 11). Indene plots with a positive loading on Factors 1 and 2. There is conflicting information on the source of indene-based compounds in the literature. Although they have been classed as aromatics in this study, in agreement with many other Py-GC/MS studies (Schellekens *et al*., 2009; Vancampenhout *et al*., 2012), there are examples where they have been classed as polyaromatics (Buurman & Roscoe, 2011). Polyaromatics are typically associated with burning (Kaal *et al*., 2009b) which is in agreement with the loadings of the burnt sub-surface peat samples. Both aromatic and polyaromatic pyrolysis products are associated with thermal processes in OM (Campo *et al.*, 2012).

N-containing compounds have varied origins. For example, pyrroles such as N1 N2 N3, which plot in the left of the diagram with the polysaccharide compounds, may be attributed to fresh plant material (Buurman *et al.*, 2007) and, as expected, therefore plot close to the most labile components. Benzonitrile (N4), although this is an N compound, is believed to be a marker of charred protein components (Kaal *et al.*, 2007). It is only present in the pyrolysates of the surface samples of burnt peat from Site 3.

Aliphatics, including almost all of the *n*-alkanes and *n*-alkenes, have positive loadings on Factor 1 and the majority have a negative loading on Factor 2 (Fig. 27). They plot in similar component space to the sub-surface samples from Site 3 (Fig. 26). Aliphatics in the pyrolysates are most likely derived from leaf lipids and the cuticle-derived aliphatic biopolymer cutin (Nierop, 1998; Gupta *et al.*, 2007)**.** A relatively high concentration of aliphatic compounds, resulting from a relative decrease in other compound classes, is indicative of decomposition in both soil and peat (Kaal *et al.*, 2007).

The presence of aliphatic and aromatic compounds in both of the right hand side quadrants indicates relatively recalcitrant source material that is likely caused by burning and/or long term decomposition. Surface burnt samples (Surface F1-F3) are clearly associated with aromatic-derived compounds as they plot in similar component space, however the subsurface burnt samples are associated with the majority of the aliphatic compounds. Surface samples from Site 1 (Surface N1, N2 and N3) are most closely associated with lignin and polysaccharide compounds. Almost all aliphatic derived compounds have a positive loading on Factor 1, as do most of the burnt samples across all depths. The high aliphatic content is evident from Fig.27 and is likely an impact of burning.

Using the PCA scores, cases were plotted in Factor 1 and 2 space (Fig.26). Clear differences are revealed between the recently burnt and unburned samples. The short term effects of burning results in the surface samples (Surface F1, F2 & F3) plotting positively on Factors 1 and 2. Samples at depth all have a positive loading on Factor 1. Site 1 samples, however, have a negative loading on Factor 1 with the surface unburned samples (Surface N1, N2 & N3) loading most negatively on Factor 1. Factor 1 can therefore be attributed to burning. Factor 2 differentiates between the surface and subsurface effects of decomposition. There appears to be major modification of the peat OM during burning with results suggesting in the short term (one month post-fire) that most modification takes place in the surface layer.

Compounds located in the lower left quadrant represent well preserved plant derived OM, such as lignin and cellulose, which is associated with inundated, unburned peat swamp forest (Fig. 27) Samples from Site 3 separate into two clusters, with the surface vs. subsurface pyrolysates separating out on Factor 2 (Fig.26). The surface burnt pyrolysates consist mainly of aromatic and polyaromatic classes, while the subsurface burned and drained peat pyrolysates comprise mainly the aliphatic compound class. As explained above, under aerobic conditions, lignin degrades rapidly and the results for Site 3 likely indicate the combined effect of a long term lowering of the water table, as well as the 2009 fire event. Smouldering fires are known to occur in tropical peatlands and so the peat analysed here is material remaining after the upper layers have already been partially combusted. Surface samples from Site 3 show more pronounced OM change due to fire compared with subsurface samples. OM change at depth (5-50 cm) could be attributed to long term aerobic decomposition. Drainage resulting from the implementation of the MRP in the mid 1990s has caused aeration of the surface peat to a depth of at least 50 cm and therefore microbial oxidation of the peat had already occurred in advance of the 2009 fire event. Based on their associated compound loadings, it is proposed that Factor 1 can, therefore, be attributed to changes caused by decomposition following a lowering of the water table and Factor 2 can be attributed to changes caused by burning. Section (4.3.3) of this chapter consists of further statistical analysis of data from Site 2 in an effort to validate this hypothesis; results from the analysis of peat samples from this site will reveal the modifications brought about solely by aerobic decomposition.

There are several statistically significant relationships between different compound classes (Table 6). Results of a correlation analysis reveal that there are eight strong relationships ($p < 0.05$) between recently burnt and drained (Site 3) and unburned, inundated (Site 1) peat samples.

Table 6: Pearsons correlation matrix of average N and F plots. (n = 24) Significant correlations are highlighted in ***bold****, p= < 0.05.*

Correlation Matrix – Site 1 and 3 (F plots)							
	Ps	Ar	PAH	N	Ph	Lg	Al
Ps	1.00	**-0.70**	-0.54	0.13	0.25	**0.69**	**-0.88**
Ar	**-0.70**	1.00	**0.82**	-0.39	-0.22	**-0.68**	**0.60**
PAH	-0.54	**0.82**	1.00	0.37	-0.37	**-0.63**	0.53
N	0.13	0.39	0.37	1.00	-0.03	-0.13	-0.15
Ph	0.25	-0.22	-0.37	-0.03	1.00	0.40	-0.53
Lg	**0.69**	**-0.68**	**-0.63**	-0.13	0.40	1.00	**-0.89**
Al	**-0.88**	**0.60**	0.53	-0.15	-0.53	**-0.89**	1.00

One of the strongest relationships is between Aliphatic (Al) and Polysaccahride (Ps) groups ($r = -0.88$ $p < 0.05$). This supports the findings that polysaccharides are severely reduced in burned and drained peats, while there is a dramatic rise in contribution by aliphatic compounds. Other significant relationships are evident between Aliphatic and Lignin (Lg) classes ($r= -0.89$ $p < 0.05$); Aromatic and Lignin classes ($r= -0.68$ $p<0.05$) as well as many others (Table 6) providing evidence for the changes in OM composition that occur during burning. There are no significant relationships between the N- containing and phenol compound class and all other classes.

From the analysis of samples collected one month after the 2009 fire it is evident that there are many short term changes to OM composition when compared to peat from the undisturbed site. The data in the next section of this chapter will provide a statistical analysis of the differences between pyrolysates from Sites 1, 2 and 3 in orderto investigate the modifications to OM that are brought about by aerobic decomposition rather than burning.

4.3.5 PCA; Intact inundated vs. drained vs. drained and recently burnt peat samples: Sites 1, 2 and 3

Addition of the data from the Site 2 pyrolysates (drained peat forest) into a PCA reveals that drainage is contributing to statistical differences between the three sites (Fig. 28). Results show that two factors explain 45.4 % of total variability in OM composition. A plot of variables in Factor 1 & 2 space highlights differences between compound classes. Factor 1, which contributes 30.36 % of the variation, differentiates between the aliphatic pyrolysis products and the lignin/polysaccharide products. Factor 2 accounts for a further 15.04 % of the total variation and explains variability produced by the major aromatic and aliphatic products. Compounds plot in similar factor space to the output in (Fig.26) despite the addition of the Site 2 pyrolysate data.

General trends include, firstly, lignin compounds have a negative loading on Factors 1 and 2, therefore similarly to the results plotted in Fig.26 these compounds also plot in the lower left quadrant. Secondly, Factor 1 separates the aliphatic derived compounds as they have a positive loading on Factor 1. The results of this analysis suggest that the correlations between variables are alike regardless of the addition of data from Site 2. Therefore, the variables associated with each of the site pyrolysates can be used as evidence that Site 2 pyrolysates are statistically different from those from Site 1.

Cases were plotted in Factor 1 & 2 space (Fig. 28). As previously displayed in Fig. 26 the short term effects of burning result in the surface samples (Surface F1, F2 & F3) plotting positively on Factors 1 and 2, while samples at depth all have a positive loading on Factor 1. Site 1 samples, however, have a negative loading on Factor 1 with the surface unburned (Surface N1, N2 & N3) loading most negatively on Factor 1. Site 2 peat samples plot in similar factor space to the subsurface Site 2 samples, with a positive loading on Factor 1 but a negative loading on Factor 2. Factor 2 differentiates between the surface and the subsurface effects of burning. There appears to be major modification of the peat OM during burning with results suggesting in the short term (one month post-fire) that most compositional changes take place in the surface layer. Subsurface burnt pyrolysates are not statistically different to drained peat pyrolysates, hence their similarities in factor space. It can be implyed therefore that, as a result of fire, there is significantly greater modification to the OM composition at the peat surface than at depth. Due the clustering of Site 2 and subsurface Site 3 samples, Factor 1 is likely to represent the effect of aerobic decomposition on OM composition rather than the effect of burning.

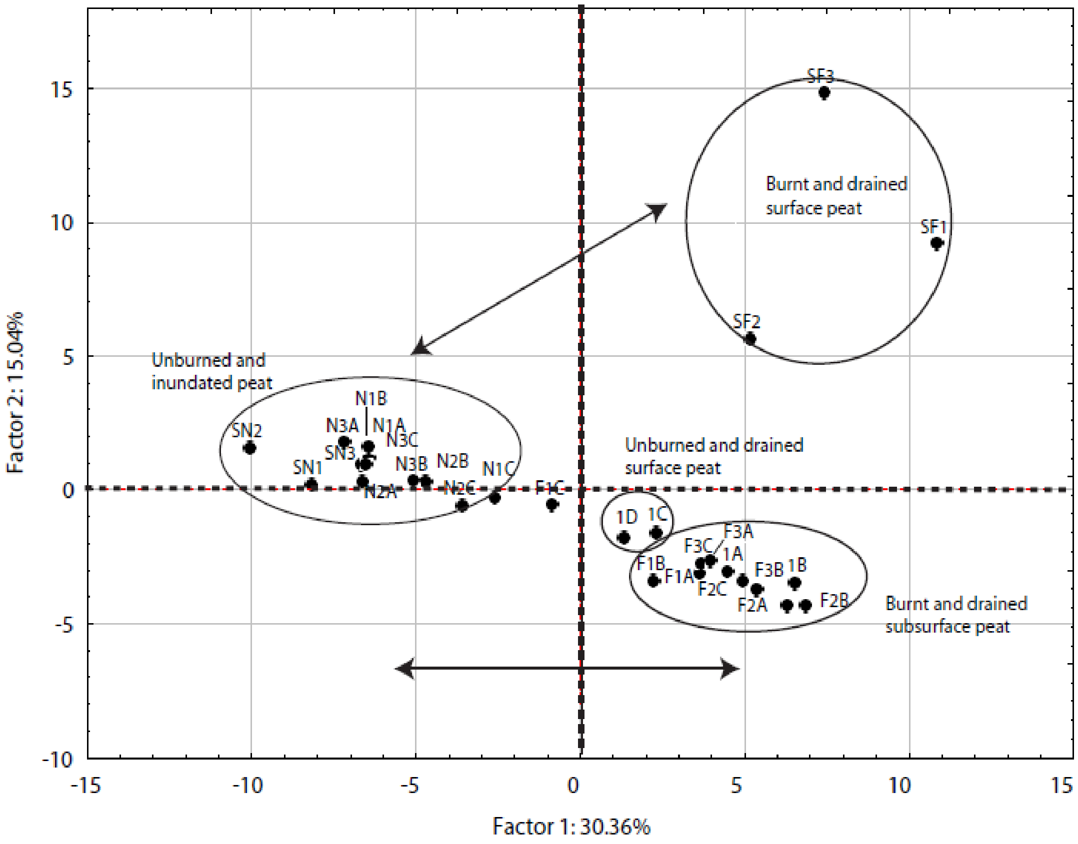


Fig. 28: Plot of cases in factor space. Pyrolysates from Sites 1 (N), 2 (1) and 3 (F) plotted on factors 1 (30.36 %) and 2 (15.04 %).

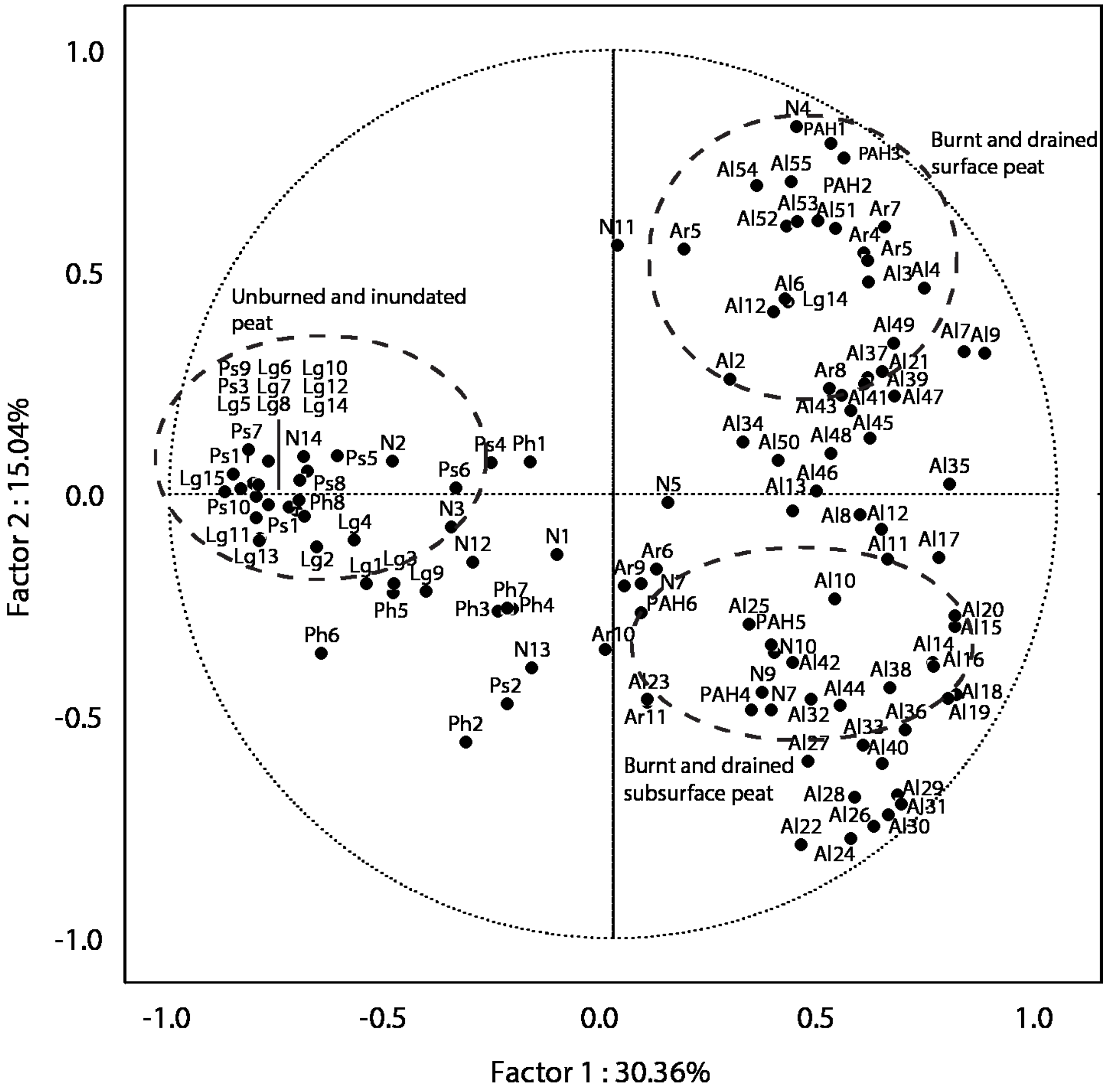


Fig. 29: Plot of compounds in factor space. Pyrolysates from Sites 1 (N), 2 (1) and 3 (F) plotted in factors 1 (30.36 %) and 2 (15.04 %).

4.4 Discussion

The aim of this chapter was to understand the changes that occur in peat OM composition as a result of fire through an assessment of the pyrolysates of both burnt and unburned peat samples across a 0-50 cm depth range. However, the areas of peatland in the study area that had been burnt had also been subject to drainage. The data presented in this chapter therefore go on to reveal the modifications induced by aerobic decomposition as well as by fire. Fires in peatlands in Central Kalimantan typically occur when the peat is dry and the water table lowered; it is therefore undoubtedly the case that burnt peat will have already undergone some level of aerobic decomposition prior to burning. The change in peat OM composition that occurs in the transition from natural undisturbed peat (Site 1) through to drained, burnt peat (Site 3) is a two step change; firstly, enhanced aerobic decomposition occurs due to lowering of the water table and secondly, thermal modification takes place as a result of fire. Analysis of peat from the drained but unburnt forest (Site 2) allowed this intermediate step of aerobic decomposition to be examined more closely. Any differences between Site 2 and 3 can be largely attributed to fire, since prior to the fire event Sites 2 and 3 had similar environmental conditions. To understand the complete OM change in the transition from intact inundated peat swamp forest through to fire-affected peatland, a comparison between the pyrolysates from Sites 1 and 3 was made.

High water table levels in the intact inundated site (Site 1) favoured preservation of the OM in the upper 50 cm of peat. There is relatively little variation in compound class abundance between the peat surface and the 30-50 cm depth interval (Table 3). Ratios used in a previous study to judge the state of OM decomposition (Schellekens *et al.*, 2009) (Table 3) highlights that there is also limited differences in decomposition state with depth. Significant presence of labile components such as lignin and polysaccharide- derived compounds at all depth intervals indicate that the peat at this site is in a state of lower decomposition compared to the peat pyrolysates from Sites 2 and 3.

Aerobic decomposition over a 16 year period following implementation of the MRP (1995-2011) brought about by severe drainage caused a change in OM composition and quality at Site 2. The effects of this are two-fold; firstly, there is a general decline in the most labile components and enhancement of recalcitrant components. Secondly, the relative decomposition state is higher than that of peat from Site 1. Furthermore, the OM is distinctly more decomposed at depths greater than 15 cm; this is supported by relatively greater abundance of aliphatic compared with lignin and polysaccharide compound classes in the 15-30 and 30-50 cm intervals. Pyridine and aliphatic compound abundances are higher in the drained (Site 2) as opposed to the intact inundated (Site 1) peat pyrolysates (Table 3), supporting the contention that severe drainage conditions have enhanced peat decomposition.

Comparisons of pyrolysates from the peat at the intact inundated site (Site 1) with recently burnt peat (Site 3) do not allow a clear depiction of the effects of fire on OM composition. As a result of both aerobic decomposition and burning, aliphatic derived compounds are evident in the pyrolysates. It is likely that these types of compounds are resistant to both aerobic decomposition and fire suggesting that the peat has become more recalcitrant during the two step process from intact inundated peat swamp forest to burnt peat swamp forest. In addition, compound classes associated with the more labile organic fractions, such as polysaccharides and lignin-derived compounds, are significantly reduced compared to peat from both the drained and the burnt sites. It has been previously suggested that aliphatic-rich soil OM is associated with recalcitrant soils (Vancampenhout *et al*., 2009; Lorenz *et al*., 2007). Recalcitrant soils have also been positively correlated with lower rates of heterotrophic respiration and methanogensis (Reiche *et al*., 2010) while recalcitrant peats are often described as being of 'low quality' (Waddington *et al*., 2001). The implications of my data are that the peat in intact peat swamp forest, such as Site 1, has a greater potential for CO_2 emissions, although sustained high water tables in such areas will inhibit microbial activity and therefore the rate of heterotrophic respiration. By comparison, the more recalcitrant peat at the recently burnt site (Site 3) would be expected to have a lower rate of heterotrophic respiration owing to the lower availability of suitable C sources for microbial oxidation. It must, however, also be noted that elevated peat surface temperatures, as will be found in recently burnt areas as a result of the removal of the vegetation cover, have also been shown to increase peat surface CO_2 emissions arising from heterotrophic respiration (Lafleur *et al* 2005; Scanlon and Moore, 2000). In addition, fire results in the addition of charred material to the peat surface, resulting in a 'black body' effect which is also likely to increase the post-fire temperature of the peat surface and thereby enhance the rate of heterotrophic respiration.

A recent study has, indeed, demonstrated that burnt peat in the former MRP (e.g. Site 3) is experiencing lower rates of soil respiration compared to other areas such as drained PSF (e.g. Site 2) (Hirano *et al*., 2013). During a fire, labile C in the upper layers of peat is preferentially burnt and recalcitrant compounds remain. This shift in chemical composition of the upper layers of peat reduces the oxidative CO_2 emissions from burnt and drained peatlands (e.g. Site 3). Peat pyrolysates from sites that experienced burning (Site 3) contained increased contributions from aromatic and polyaromatic compounds compared with those from the site that had only been drained (Site 2). Thermo labile components such as polysaccharides and lignins were virtually absent in the surface layer of the recently burnt peat compared with the surface of the drained peat where these compound classes were simply at reduced abundance. Previous research estimated an average burn scar depth of 0.33 ± 0.18 m during the 2006 fires in the MRP area (Ballhorn *et al.*, 2009). It would therefore be expected that although the upper layers of peat may be fully combusted during a fire there would be vertical transfer of thermal energy causing substantial heating of the peat and subsequent OM change at depth. The maximum temperatures reached at the surface would be greater than at depth. Maximum temperatures of 275 °C were recorded in surface peat layers burnt in 2002 and were maintained for 4-5 hours (Usup *et al.*, 2004). However, observed temperatures decreased with depth; at 10 cm the maximum temperature was 75 °C and at 40 cm it reduced to 30 °C (Usup *et al.*, 2004). OM change is temperature dependent (González-Pérez *et al.*, 2004) and hence, as expected, the greatest change in peat OM was found in the surface peat samples. If temperatures at Site 3 were comparable to those recorded by Usup *et al.* (2004), then it is not surprising that there is little OM change below the peat surface (i.e. below 5 cm). Distillation of volatiles and loss of organic C do not begin until temperatures are between 100 °C and 200 °C (Kang and Sajjapongse, 1980; Giovannini and Lucchesi, 1997).

The PCA analysis revealed that the recently burnt subsurface (Site 3) peat pyrolysates were of a similar composition to those of the drained subsurface peat pyrolysates (Site 2). This suggests that temperatures at depth were insufficient to cause considerable peat OM change during the 2009 fire and that long term aerobic decomposition, rather than fire, is responsible for the OM change observed in the subsurface peat compared to Site 1. Fires in the study area have been categorised as ‘surface’ or ‘deep peat’ fires (Usup *et al.*, 2004) and the evidence from these data suggests that the area sampled

either experienced a surface fire **or** that there had been loss of the surficial peat as a result of combustion during the fire but that there had been insufficiently high temperatures at depth to bring about significant changes in OM composition.

4.5 Conclusion

Data obtained using Py-GC/MS can be used to assess the impact of fire on peat OM as it allows a detailed investigation at the molecular level. Compositional differences between burnt and unburned (inundated and drained) peat sample pyrolysates suggest that a combination of both fire and drainage causes alteration of the OM composition. The main observations are summarised as follows:

(i) Peat pyrolysates from an unburned, inundated site contain contributions from all compound classes. Lignin products such as guaiacol, methyl guaiacol and ethyl guaiacol are dominant.

(ii) Lowering of the peat water table by drainage induces oxic conditions in the upper peat layers causing a reduction in OM diversity particularly below 30 cm from the surface. Peat pyrolysates from the drained, unburned site are dominated by aliphatic components.

(iii) Peat pyrolysates from the drained, recently burnt site are composed predominantly of aromatic and aliphatic compounds and are significantly reduced or depleted in all other compound classes, including lignin and polysaccharide derived compounds. A high aromatic and aliphatic content, including a large contribution from *n*-alkene/alkane doublets, suggests that the burnt peat is highly refractory and that much of the labile component has been lost or converted to other C forms.

(iv) Subsurface peat pyrolysates from the recently burnt site are associated with aliphatic moieties with considerable variance from the surface samples. Differences in surface vs. subsurface burnt and drained peat are attributable to differences in the impact of fire and decomposition.

(v) Although fires in tropical peatlands are often considered to be smouldering, thereby penetrating the peat substrate, data from this analysis suggest that the effects on the OM composition were predominately experienced in the surface peat layer (0-5 cm). Any differences in the OM composition between intact inundated peat and the subsurface peat at the recently burnt site are likely to be caused by decomposition processes rather than fire.

Understanding how tropical peatland fires modify peat OM composition can contribute to an improved knowledge of post-fire C and nutrient cycling. Thermally induced alteration of peat OM may be a factor inhibiting ecosystem recovery, ultimately influencing the global C balance. Retrogressive succession of burnt peatlands to fern and sedge dominated vegetation, rather than back to forest, may be a response to alteration of the OM caused by burning. The results of this chapter demonstrate that fire has caused the most labile OM components to be removed from the upper peat layer alongside the neoformation of aromatic structures, thus increasing the recalcitrance of the peat substrate. This could explain the reduced rate of post-fire peat oxidation measured in Site 3 (Hirano *et al.*, 2013). Alteration of the OM composition may also have implications for physical properties of the peat soil, for example enhanced water repellence, which would impact upon post-fire surface runoff and solute transport.

Chapter Five - Effects of fire regime on the organic matter composition of tropical peat

5.0 Introduction

Results presented in the previous chapter provided a detailed molecular analysis of peat OM in order to investigate the short term (one month post-fire) effects of burning. The results showed that fire caused distinct modification of peat OM; some of the changes could be attributed to the direct effects of the fire, while others were the result of aerobic decomposition through the drainage that had occurred some years prior to the fire. There was a shift from relatively labile peat OM, in the intact peat swamp forest, to a relatively recalcitrant peat in the drained site. The composition of peat pyrolysates from the intact peat swamp forest was dominated by lignin and polysaccharide compounds, reflecting the continual inputs of fresh litter from aboveground vegetation. In contrast, the drained, burnt peat was considerably modified, being highly aromatic and containing significant contributions of polyaromatic hydrocarbons (PAHs) that indicated the presence of charcoal.

Fire regime can be defined as the characteristics of a particular fire event, which may include a variety of variables, such as: burning duration, temperature, rate of spread and frequency (Cochrane and Ryan, 2009). Wildfires are typically unpredictable in their regime and are highly variable, making reporting on their effects quite challenging. Many regime variables cannot be determined unless *in situ* measurements are taken i.e. burn temperature and rate of spread. Some aspects of a fire regime are often defined by the consequences or impacts on the vegetation (Keely, 2009). For example, ‘fire severity’ is a term used to describe the impact of a particular fire although the term is not used consistently. It is measured by the change in aboveground biomass (Agee, 1993; Odion and Hanson, 2008), however the belowground OM consumption is sometimes also included in measurements of fire severity (Ryan & Noste, 1985). ‘Burn severity’ is a term coined by the remote sensing community to assess the change in above-ground biomass that occurs during a fire. Both ‘fire severity’ and ‘burn severity’ are correlated to ‘fire intensity’ (Keely, 2009), which is defined as the amount of energy released by a flaming front (Drysdale, 1999; Morgan *et al.*, 2001). OM composition in soils is affected by the temperature at which burning occurs (González-Pérez *et al.*, 2004), therefore an assessment of the OM chemistry may be an indicator of the fire intensity.

The aim of this chapter is to extend the biogeochemical analysis presented in Chapter 4 to investigate if different fire regimes cause differential alteration of peat OM composition, in addition to the changes that were observed in the short term (i.e. one month post-fire). Information about the effects that different fire regimes have on peat OM will be important when considering the effects of peat fires on a larger spatial scale. Previous studies have confirmed that the fire regime in the former MRP area is dynamic and variable (Hoscilo *et al.*, 2011), however it is not currently known if and how this variability, in terms of fire frequency and time since last burn, influences the OM composition of the peat. Following single fires in block 'C', the regenerating vegetation can undergo succession to secondary forest, although Hoscilo (2009) found that only 10-15 % of the primary biomass of intact peat swamp forest was restored over a 9 year period (1997-2006). As the amount and type of aboveground biomass changes over time it may be that the composition of the peat OM will reflect the vegetation successional stage thus the peat OM composition may be expected to change with 'time since last burn'. Many areas of block 'C' have been burnt more than once; between 1997 and 2006, 45 % of block 'C' was affected by multiple fires (Hoscilo, 2009). This chapter investigates the effects of different 'fire frequencies' on peat OM. Many fire-affected areas of block 'C' have experienced burning during different fire events, thus they have had different recovery periods. It is not currently not known if the short term chemical changes caused by fire are temporary or if these changes are maintained over the longer term, therefore the effect of 'time since last burn' on peat OM composition is also investigated in this chapter.

In order to understand the landscape scale impacts of fire in the MRP area a range of variables must be investigated. There are many variables previously investigated by other authors, (see Chapter 2 section 2.2.3) however for this research two have been selected; 'time since last burn' (fire chronosequence) and 'fire frequency'. The data presented in this chapter are split into two sections; one for each of the regime variables studied. Results from a fire chronosequence analysis are presented in Section

5.1, with results from a fire frequency analysis in Section 5.2. The results are collectively discussed in Section 5.7.

5.1 Fire Chronosequence Analysis

Most studies of fire-affected soils have focused on the short term effects of burning (see Chapter 2), however these effects may be irrelevant in the medium or long term because subsequent inputs of OM to the soil from regenerating vegetation could conceal any thermally induced changes caused by burning. For example, in the short term (two weeks post-fire) burnt soils of forest wildfires in northwest Turkey were significantly depleted in carbohydrate (polyscaccharide) compounds (Kavdir *et al.*, 2005). A slight decrease in carbohydrate compounds in burnt soils from Asturias (NW Spain) were observed seven years post-fire, however in the long term (23 years post-fire) o-alkyl compounds from carbohydrates were dominant in both burnt and unburnt soils (Santín *et al.*, 2008). In some cases the evidence of fire can still detected in the longer term suggesting that fire can have a lasting impact on soil OM composition. For example, at a location in shrubland in Valencia, NW Spain, at nine years post-fire the proportion of recalcitrant C forms remained greater than in soils that had not been affected by fire, although the immediate reduction in the proportion of carbohydrates caused by burning was not maintained as concentrations returned to pre-fire levels nine years post-fire. In this case it was likely that the regenerating vegetation provided a fresh input of litter to the soil surface increasing the carbohydrate content (Rovira *et al.*, 2012). Fires are common in Mediterranean ecosystems and so some vegetation has become relatively resilient to burning and will often recover rapidly post-fire, thus the effects of burning are often detectable only in the short term. Despite a number of fire events between 1976 and 1999 in the Alcant province in eastern Spain, there was no detectable shift towards more recalcitrant soil OM compared to unburnt soils. Thus in this example, post-fire short term chemical changes were not evident, indicating recovery of the soil OM over the order of decades (Duguy and Rovira, 2010).

There are very few studies of the medium and longer term effects of fire on soil OM composition and those that have been published are all from non-peatland environments where wildfires have been historically more frequent. It is therefore not yet understood what the medium and longer term impacts of fire may be on tropical peat OM composition. The vegetation dynamics have been studied over the medium term in block 'C' (Hoscilo, 2009) and these may be linked to the OM composition of the underlying peat and thus provide some indication of the associated changes in the peat OM composition. Peat OM composition may show signs of recovery back to pre-fire status over a 10 year period following a single fire given the aboveground vegetation's ability to regenerate over this time frame (Hoscilo *et al.*, 2011). In contrast, Hoscilo (2009) found that sites experiencing multiple fire regimes did not undergo succession to secondary forest vegetation over the same time period (1997-2006) but became dominated by non-woody biomass. Thus the medium and long term effects of multiple fires on peat OM composition could be different for areas that have been subject to a single fires as opposed to multiple fires as a consequence of different trajectories for vegetation recovery.

This study was undertaken approximately 15 years since the initiation of the MRP and the subsequent high fire frequency affecting this study area allowed for an investigation of the effects of fire on peat OM across a 14.5 year fire chronosequence (1996-2011). The first aim of this chapter is, therefore, to investigate the OM composition of peat under a range of time periods since the last fire (0, 1.5, 4.5, 8.5 and 14.5 years post-fire). The results for areas that burnt 14.5 years prior to sampling are taken to represent the longer-term effects of fire on peat OM composition, while sites that burnt more recently than this are considered to indicate the medium term effects of fire (i.e. from 1.5 years and up to 4.5 years post fire). Changes in the OM composition based on the results of Py-GC/MS are analysed across the chronosequence of burnt areas in order to elucidate the influence of post-fire recovery. It is postulated that this is likely to be linked to the quantity and types of above-ground biomass which provide the OM inputs, with peat OM composition changing with time after burning as the vegetation recovers. The OM composition could then be used as an indicator of the peat OM recovery and thus of overall ecosystem rehabilitation.

5.2 Method

5.2.1 Sampling strategy

The same three sampling locations were used as in the previous chapter for this part of the investigation. Namely: Site 1, Sebangau peat swamp forest; Site 2, Drained secondary forest in Block ‘C’ of the former MRP area; and Site 3, representing a variety of fire-affected locations within Block ‘C’ (Table 7). The ‘time since last burn’ for locations at Site 3 was determined utilising data from previous remote sensing studies (Hoscilo, 2009; Yunos, 2010) which allowed the selection of burnt sites across a 14.5 year chronosequence (Table 7). Sampling plots were selected at locations that had only experienced a single fire event during each of the major fire events since the implementation of the MRP, i.e. the 1997, 2002, 2006 and 2009 fires. The short term effects of fire were investigated using samples from sites burnt in 2009; medium term effects were investigated using samples from sites burnt in 2009, 2006 and 2002, while longer term effects were elucidated from sites burnt in 1997.

5.2.2 Characterising Peat OM: Py-GC/MS

Bulk samples were pyrolysed using a CDS 1000 pyroprobe coupled to a Perkin Elmer Clarus 500 GC/MS. Approximately 1 mg of sample was encapsulated into a clean quartz tube plugged at either end with quartz wool. The samples were pyrolysed at 710°C for 15 s. The GC/MS temperature programme consisted of an initial temperature of 40°C for 1.8 min which was then ramped to a final temperature of 310°C at 4°C min^{-1}.The GC/MS instrument was fitted with a CP-Sil 5CB MS column (30 m x 0.25 mm x 320 µm). Compounds within the pyrograms were identified based on their mass spectra and retention times. Peak integration was performed using Turbomass software 5.2.0 and the relative abundance of each pyrolysis product was determined in relation to the relative proportion of all identified pyrolysis products. Pyrolysis products were grouped according to compound class; aliphatics (Al), aromatics (Ar), lignins (Lg), N compounds (N), phenols (Ph), polyaromatics (PAHs) and polysaccharides (Ps)

Table 7: List of sample identifications used for the fire chronosequence analysis. The 'fire history' i.e. burnt/ unburnt for each sampling location is also provided.

Location	Sample ID	Depth (cm)	Fire History	Time Since Last Burn (yrs)	Recovery Period
Site 1 **Sebangau Peat Swamp Forest**	Surface N1 N1C N1B N1A	0-5 5-15 15-30 30-50	Not burnt	n/a	n/a
	Surface N2 N2C N2B N2A	0-5 5-15 15-30 30-50			
	Surface N3 N3C N3B N3A	0-5 5-15 15-30 30-50			
Site 2 **EMRP – Drained Swamp Forest***	Surface 0 0C 0B 0A	0-5 5-15 15-30 30-50	Not burnt	n/a	n/a
Site 3 **Kalampangan – Burnt Area** +	Surface F1 F1C F1B F1A	0-5 5-15 15-30 30-50	Burnt (2009)	1 month	Short Term
	Surface F2 F2C F2B F2A	0-5 5-15 15-30 30-50			
	Surface F3 F3C F3B F3A	0-5 5-15 15-30 30-50			

Location	Sample ID	Depth (cm)	Fire History	Time Since Last Burn (yrs)	Recovery Period
Site 3 Kalampangan – Burnt Area $^{+}$	Surface 1 1C 1B 1A	0-5 5-15 15-30 30-50	Burnt 2009	1.5	Medium Term
	Surface 2 2C 2B 2A	0-5 5-15 15-30 30-50	Burnt 2006	4.5	Medium Term
	Surface 3 3C 3B 3A	0-5 5-15 15-30 30-50	Burnt 2002	8.5	Longer Term
	Surface 4 4C 4B 4A	0-5 5-15 15-30 30-50	Burnt 1997	14.5	Longer Term

5.2.3 Statistical Analysis

Data were entered into an Excel spread sheet and analysed using Statistica® software. PCA was used to establish statistical differences in peat OM composition, with the view to determine if peat OM changed with time since burning. Two factors were extracted and factor loadings were plotted for individual variables as well as factor scores of cases (samples). Clustering of cases based on the factor scores on the Principal Component (PC) axes were related to the loadings of the original variables.

5.3 Results

5.3.1 Fire Chronosequence Analysis

Overview

The results presented in this section link the short term effects of fire (previously discussed in Chapter 4) with data on the medium and long term effects in order to assess the influence of 'time since last burn' on the composition of peat OM. In addition to the effects of fire, the results in this chapter also relate to the time since drainage. Analysis of samples from Site 2 allows inferences to be made regarding the

OM composition of peat that has experienced an artificially lowered water table for approxiametely 15 years. The results in this section are presented in a series on time sequence graphs whereby the ‘drainage only’ period relates to the period from 1995 (when the Site 2 & 3) were drained to November 2009 (date of first sampling).

Py-GC/MS

Calculation of the proportions of each of the seven compound classes for each pyrolysate reveals information regarding the OM composition with increasing time post-fire (Table 8). The relative contributions of each compound class across the 50 cm depth profile at different points in the fire chronosequence are provided in Figs.29-35..

Table 8: Relative contributions of pyrolysis compound classes (%). Results are calculated as a percentage of the total identified pyrolysis products. Standard deviations of means for Site 1 and Site 3 (SF, FC, FB, FA) samples are included. Time since last burn included in italics beneath Site N^{o}.

Site N^{o}	Sample Code	Ps	Lg	Ar	Ph	N	PAH	Al
Site 1	Surface N*	30.6	36.1	4.5	10.7	2.8	0.3	14.7
		(± 6.7)	(±9.1)	(±0.7)	(±0.4)	(±3.8)	(±0.0)	(±1.8)
Unburnt	NC	27.9	19.9	4.6	17.9	3.8	0.8	24.0
		(±12.7)	(±6.6)	(±2.5)	(±7.2)	(±1.7)	(±0.6)	(±6.6)
	NB	24.50	29.05	5.0	15.2	3.6	0.7	22.0
		(±4.3)	(±4.1)	(±1.1)	(±4.6)	(±1.0)	(± 0.0)	(±5.2)
	NA	24.6	35.2	4.4	15.0	3.5	0.7	16.5
		(± 6.3)	(±2.1)	(±1.2)	(± 4.4)	(±0.3)	(±0.3)	(±3.0)
Site 2	Surface 0 (0d)	22.6	10.6	4.5	16.0	4.1	1.2	41.0
Unburnt	0c	16.5	13.1	7.8	13.2	3.3	1.6	44.5
	0b	2.7	7.1	5.7	7.1	4.9	1.7	70.7
	0a	6.9	11.1	4.5	9.0	4.3	2.0	62.1
Site 3	Surface F	0.1	0.8	12.0	6.2	4.1	5.5	71.3
		(±0.1)	(±1.2)	(±5.3)	(±0.9)	(±3.8)	(±2.6)	(±12.9)
One month	FC	4.4	19.3	6.8	10.2	3.0	0.8	55.5
		(±1.1)	(±7.9)	(±0.1)	(±5.2)	(±1.8)	(±0.4)	(±16.1)
	FB	5.4	10.2	7.8	10.5	3.4	1.3	61.5
		(±0.9)	(±10.4)	(±0.8)	(±3.4)	(±2.2)	(±0.1)	(±9.7)
	FA	4.1	13.8	8.0	13.4	2.1	1.7	57.0
		(±1.4)	(±3.6)	(±1.3)	(±5.5)	(±0.8)	(±0.0)	(±6.6)
Site 3	Surface 1	4.6	8.8	5.9	12.1	4.0	1.7	62.9
1.5 years	1c	5.6	9.8	5.5	12.4	5.3	1.3	60.1
	1b	4.2	12.3	4.7	12.4	3.7	1.2	61.6
	1a	6.0	17.6	4.8	19.8	2.6	1.4	47.9
Site 3	Surface 2	12.0	15.1	4.3	14.6	3.2	1.0	49.8
4.5 years	2c	15.5	18.0	5.4	13.6	3.5	0.8	43.4
	2b	15.3	14.3	3.7	8.6	3.5	1.7	52.8
	2a	6.5	10.0	6.1	9.5	4.6	4.2	59.1

Site N^o	Sample Code	Ps	Lg	Ar	Ph	N	PAH	Al
Site 3 *8.5 years*	Surface 3	8.7	6.8	6.9	8.3	3.0	1.3	65.4
	3c	5.4	8.7	8.2	10.4	3.6	1.7	63.4
	3b	9.8	17.1	6.9	14.1	2.4	5.0	43.4
	3a	6.8	14.3	6.6	9.1	4.1	1.2	57.6
Site 3 *14.5 years*	Surface 4	7.6	11.0	5.6	14.3	3.6	1.7	56.3
	4c	8.4	10.5	6.1	8.9	3.8	1.3	61.1
	4b	11.1	7.2	5.6	11.7	3.6	1.3	59.5
	4a	22.5	7.7	6.6	8.8	4.3	1.5	48.7

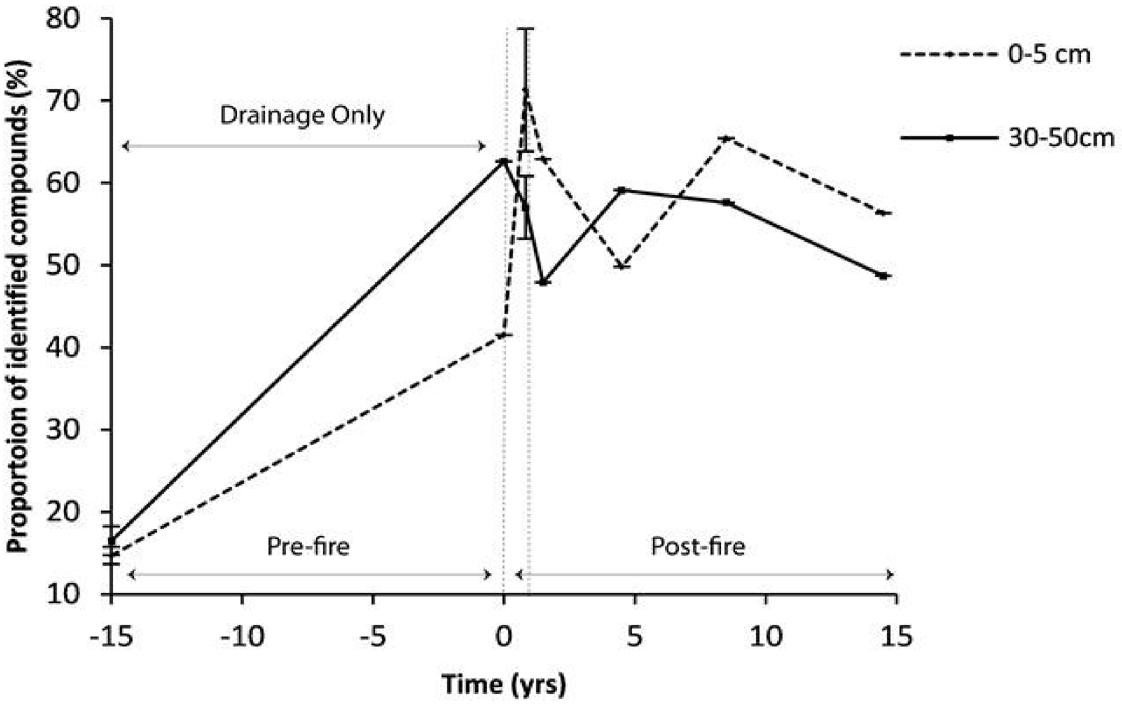


Fig. 30: Total aliphatic content in peat pyrolysates along a pre-fire (drainage only) and post-fire chronosequence (1997- 2011). Sample pyrolysates from the upper 5 cm and at the 30- 50 cm depth intervals are presented. Negative years on the horizontal axis represent time between initiation of drainage and collection of the sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 30 – 36.

The relative contributions of aliphatics in surface (0-5 cm) and subsurface (30-50 cm) peat pyrolysates show a significant increase during the 'drainage only' period. A short term effect of fire (one month post-fire) was observed through an increase in the contributions of aliphatics in the surface peat OM, however these contributions declined in the subsurface peat samples (Fig.30). These short term effects are transitory however, as aliphatic contributions in the surface peat OM decline over the first 4.5 years after fire. This decline is also observed in the subsurface peat pyrolysates, although the decline is only apparent over the first 1.5 years post-fire. While aliphatic contributions fluctuate over the full 14.5 years post-fire chronosequence, in both surface and subsurface peat pyrolysates there is no significant change in their contributions between 1.5 and 14.5 years post-fire. The relative contributions of aliphatic compounds remain higher, however, in peat samples that have been burned compared to those only subject to drainage.

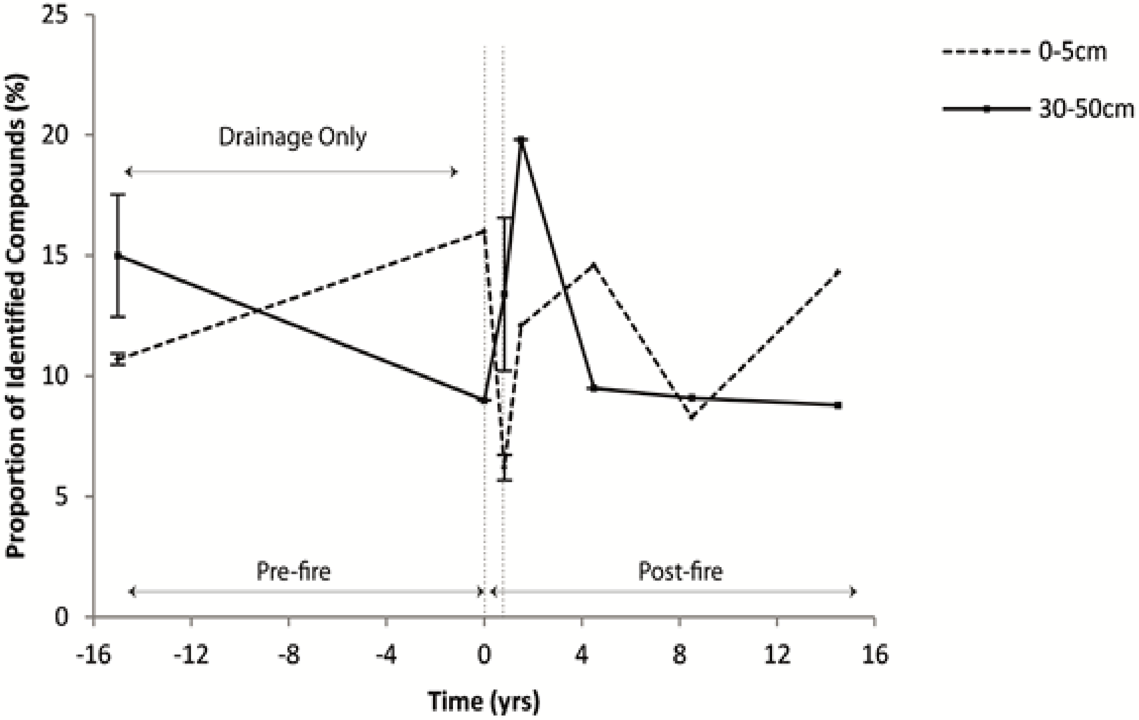


Fig. 31: Relative phenol content in peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 30 –36.

The relative contribution of phenol compounds in surface peat (0-5 cm) pyrolysates increases during the 'drainage only' period (1995-2009), (Table 3), however in subsurface peat (30-50 cm) pyrolysates, the relative contribution of phenols declines over the same period. An immediate effect of the 2009 fire event is a decrease in the contributions of phenols in the surface compared with the subsurface peat (Fig.31). The short term effects of fire on phenol contributions are temporary, however; phenol contributions are greater 1.5 years (12.1 %) than 1 month post-fire (6.2 ± 0.9 %). An increase in and maximum phenol contribution was also observed in the subsurface peat pyrolysate up to 1.5 years post-fire (19.8 %). In both the medium and longer term, phenol contributions fluctuate in the surface peat pyrolysates over the 14.5 year post-fire chronosequence and at the end of the period relative phenol contributions in both surface and subsurface peat pyrolysates are comparable to pre-fire contributions.

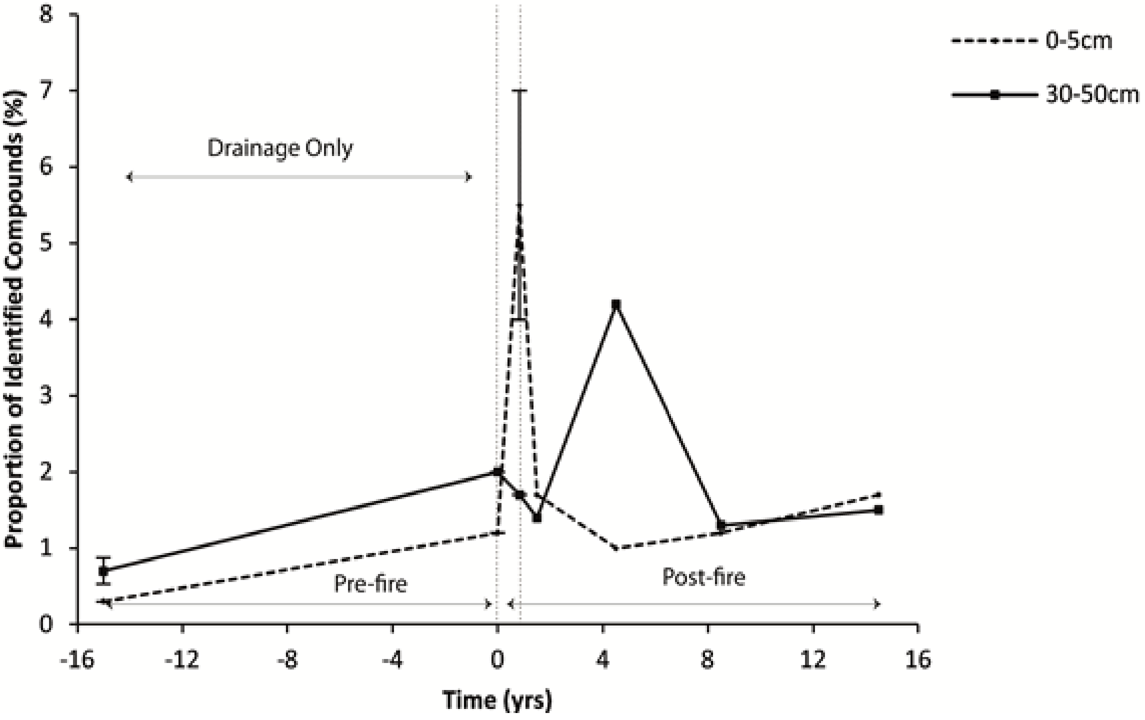


Fig. 32: Total PAH content in peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29 – 35.

Drainage of peat in block 'C' has resulted in an increase in PAHs in the peat pyrolysates. Sample pyrolysates from the upper 5 cm of inundated, intact peat from Site 1 were composed of 0.3 ± 0.0 % PAHs but comprised 2.0 % of the pyrolysates from the drained peat at Site 2. Sample pyrolysates from 30-50 cm below the surface were composed of 0.7 ± 0.3 % PAHs (Site 1) and 2.0 % in drained peat (Site 2). One month post-fire there was a significant increase in the contributions of PAHs to surface peat pyrolysates (5.5 ± 2.65 %), representing the greatest contribution of PAHs identified in any of the samples (Fig.32). The short term increase in PAHs was not, however, maintained; 1.5 years post-fire, their relative contributions were reduced to 1.7 % of the total identified pyrolysis products (Table 3). An increase in PAHs was not observed in subsurface peat pyrolysates one month post-fire (1.7 ± 0.0 %) and contributions of PAHs remain steady up to 14.5 years post-fire. In both surface and subsurface peat pyrolysates, however, there is a peak in relative PAH contributions at 4.5 years post-fire but in the subsurface peat only. At 14.5 years after fire, the contributions of PAHs in both surface and subsurface peat pyrolysates show no significant difference from pre-fire levels.

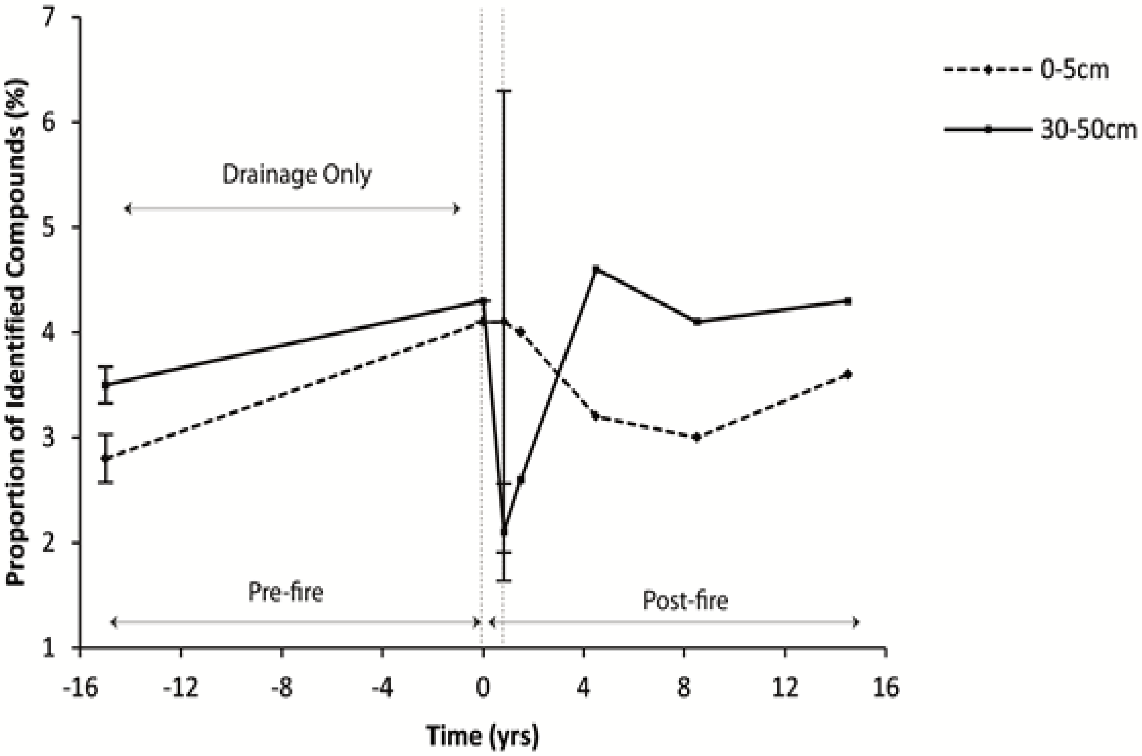


Fig.33: Relative content of nitrogen-containing compounds of peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 30 – 36.

The relative contribution of all nitrogen-containing compounds in both surface (0-5 cm) and subsurface peat pyrolysates (30-50 cm) increased following the 'drainage only' period (Fig.33). In the short- term, nitrogen-containing compounds in surface peat pyrolysates were not significantly affected by fire; however, contributions were considerably reduced in subsurface peat (4.3 vs. 2.1 ± 0.8 %). Between one month and 4.5 years post fire, the relative contributions of N-containing compounds decreased in the surface peat pyrolysates but relative contributions were greater in the subsurface peat pyrolysates. Contributions in both surface and subsurface peat pyrolysates returned to approximately pre-fire levels at 14.5 years post-fire (3.6 and 4.3 %). Burning, therefore, causes a short term reduction in nitrogen-containing compounds within tropical peat OM, but given a 14.5 year post-fire recovery period, the contributions are equal to or greater than pre-fire contributions.

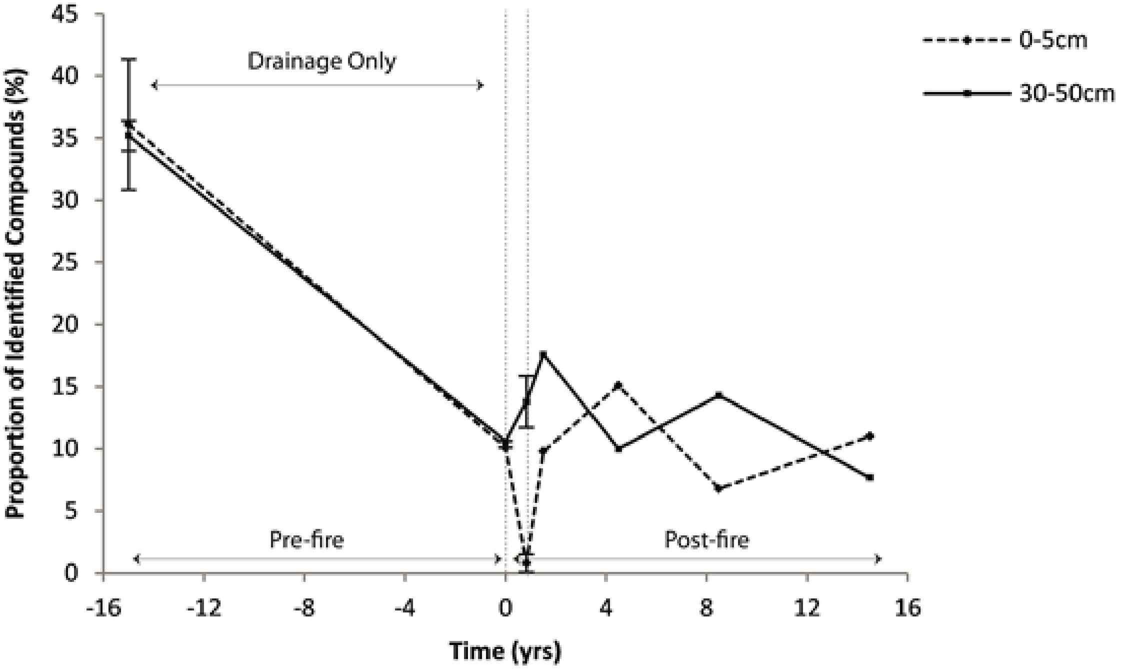


Fig.34: Relative lignin content of peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 30 – 36.

The contributions of lignin-derived compounds in surface (0-5 cm) and subsurface (30-50 cm) peat pyrolysates significantly declined during the ‘drainage only’ period (Fig,34). There was no significant difference between lignin contributions in surface and subsurface peat when exposed to either inundated or drained conditions. Following fire, lignin derived compounds were significantly reduced in the surface peat OM from 10.1 % following drainage to 0.8 (± 1.2) % one month post-fire. In subsurface peat, burning did not result in any significant change in the proportion of lignin-derived compounds. Over the medium term (1.5 to 4.5 years post-fire) contributions of lignins in both surface and subsurface peat pyrolysates returned to pre-fire levels and remained relatively constant over the longer term (14.5 years post-fire). There were minor fluctuations in relative concentrations of lignins at 4.5 and 8.5 years post-fire which could likely be attributed to variations in burning intensity and/or severity between different sites. The overall trend remains clear: drainage severely reduces the relative contributions of lignin-derived compounds in both surface and subsurface peat sample pyrolysates while fire causes further depletion in the upper 5 cm of peat only, but does not alter lignin concentrations in peat below 30 cm.

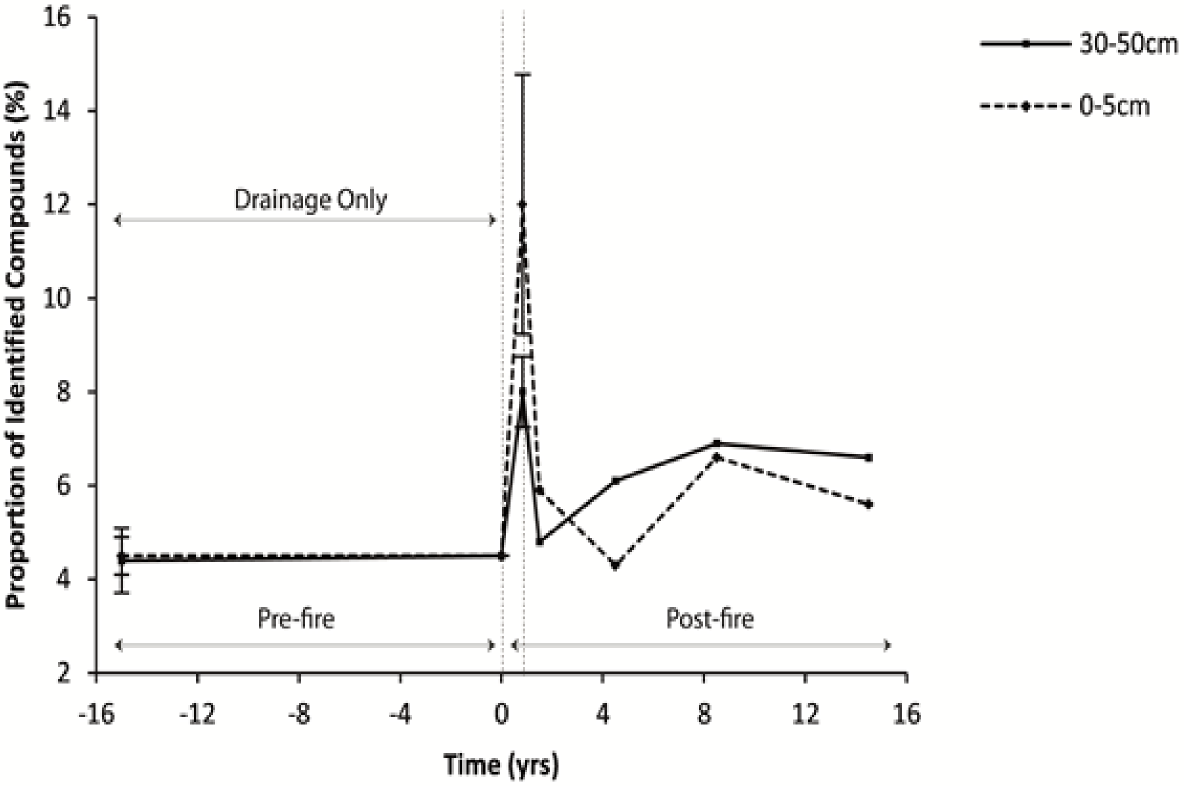


Fig. 35: Relative aromatic content of peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 30-36.

Drainage had no effect on the contribution of aromatic compounds in surface (0-5 cm) and subsurface (30-50 cm) peat pyrolysates (Fig.35). On the other hand, burning led to a significant increase in contributions of aromatic compounds compared to pre-fire levels in both surface (4.5 vs. 12.0 ± 5.3 %) and subsurface (4.5 vs. 8.0 ± 1.3 %) peat pyrolysates, with the increase in post-fire contributions being more significant in the former. Enhanced aromatic contributions as a result of burning were, however, a temporary phenomenon, because at 1.5 years post-fire their relative contributions declined in both surface (5.9 %), and subsurface (4.8 %) peat pyrolysates, although they remained higher than pre-fire levels. Over the longer-term (14.5 years post-fire), aromatic contributions remain greater, albeit insignificantly, than pre-fire levels. Drainage had no impact on the total contribution of aromatic-derived compounds but burning did cause a significant short term increase that was predominantly evident in the upper 5 cm of peat but also at 30-50 cm below the surface.

The contributions of polysaccharides in surface (0-5 cm) and subsurface (30-50 cm) peat pyrolysates significantly declined over the ‘drainage only’ period. Surface peat contributions were relatively high in the peat pyrolysates (30.6 ± 6.7 %) from the intact site (Site 1) but peat pyrolysates from the drained site (Site 2) made a lower contribution at 22.6 % polysaccharides (Fig.36). The effect of drainage was even more pronounced 30-50 cm below the peat surface, with 24.6 ± 6.3 % of all pyrolysis products in intact peat derived from polysaccharide compounds but just 6.9 % detected after over a decade of drainage. An immediate effect of the 2009 fire event was a loss of almost all polysaccharide-derived compounds in the surface peat pyrolysates (0.8 %). Between one month and 4.5 years post-fire, polysaccharide contributions increased in both the surface and subsurface samples and remained relatively unchanged up to 14.5 years post-fire. Polysaccharides in surface pyrolysates remained significantly lower than pre-fire levels despite having up to 14.5 years without being burnt. Polysaccharides are the most labile of all the analysed pyrolysis products but it is evident that fire has had a long, as well as a short-term, impact on the most labile compounds in the peat OM.

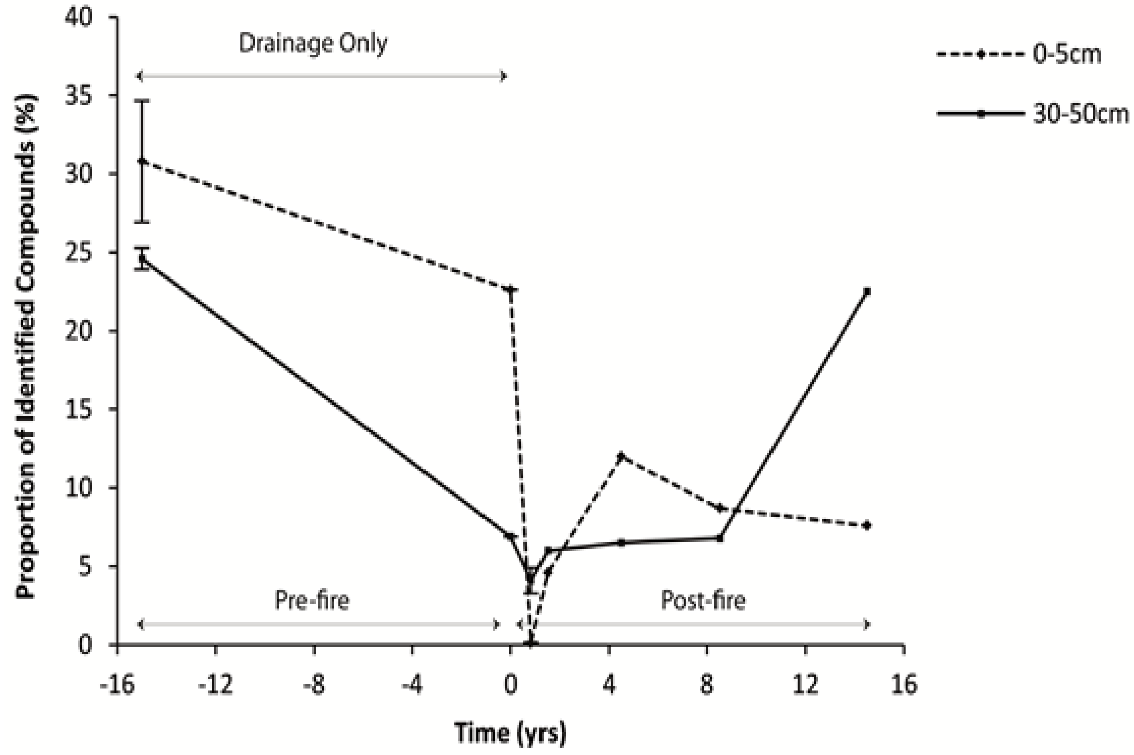


Fig. 36: Relative polysaccharide content of peat pyrolysates along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. N.B. Note the differences in y-axis scale between all compound class contributions in Fig. 29 – 35.

In the short-term (one month post-fire), fire has had a considerable impact on the composition of the peat OM, but there were no significant impacts in the medium (1.5 - 4.5 years) and longer term (up to 14.5 years post-fire). Aromatic, PAH and aliphatic compound classes had significantly larger contributions in samples collected one month after fire compared to unburnt samples, however, short-term increases in the most recalcitrant OM fractions (aromatic, PAH and aliphatic fractions) was not maintained in the medium or longer term. A similar trend was observed for the relatively labile OM fractions; contributions of polysaccharide and lignin classes were less significant in the one month post-fire samples compared to the other samples from burnt sites. This short-term reduction in the most labile OM fractions (polysaccharide and lignin) was not maintained in the medium and long term.

There is some insignificant variability between the contributions of each compound class when assessing peat samples over the 14.5 year post-fire period, although this may be explained by the interaction of other fire regime variables such as 'fire intensity'. The 'fire intensity', i.e. the temperature of each fire was not known, but it is likely that any variability will have an influence on the degree of compositional change in the peat OM. For example, data from the samples collected 4.5 years post-fire (from locations affected by the 2006 fires) show some deviation from the general trends described above. Most noteworthy are variations in the phenol and PAH classes that both show significantly greater contributions compared with other intervals in the fire chronosequence. Polysaccharide concentrations also deviate in the surface peat pyrolysates in that they show a significantly reduced concentration compared with other post-fire plots. This variability in OM composition at 4.5 years post-fire suggests that burning during the 2006 fires may have been of a higher intensity compared with the fires affecting the other plots (i.e. those selected to represent conditions 1.5, 8.5 and 14.5 years post-fire).

Principal Components Analysis (PCA) of the Fire Chronosequence Analysis.

The PCA presented in Chapter 4 revealed that there were significant statistical differences between the contributions of pyrolysis products from peat collected at a site one month post-fire (Site 3) compared with peat samples from the unburnt, intact peat swamp forest (Site 1). However, the data from the fire chronosequence analysis has revealed that there was no difference between drained peat swamp forest (Site 2) and the burnt peat that has undergone ≥ 1.5 years post-fire recovery (Site 3; Plots 3-5). Factors 1 and 2 explain 39.77% of the variation and 5 factors explain 57.8 % of the total variation (Fig.36). This means that fire has a significant short-term effect but in the medium and longer-term, fire has no significant effects on peat OM composition. In contrast, drainage has had considerable long-term effects on peat OM composition, with peat samples affected by 15 years of drainage since the implementation of the MRP showing a markedly different OM composition from peat present at the intact, undrained site.

The relatively low variation accounted for by the first two factors (39.77 %) (Fig.37), coupled with the large number of factors that account for the remainder of the variance, suggests this is a highly complex dataset with many different factors or processes responsible for the differences observed in the OM composition. The loadings on Factors 1 and 2 are shown in Figs.37 & 38 here specific compound and sample variation is presented separating the samples via their pyrolysates.

Factor 1 (Aerobic Decomposition) There is chemical variation in pyrolysates from the intact inundated peat samples, the one month post-fire samples and the samples from the drained site as reported in Chapter 4. The intact sites plot in the lower left quadrant (Fig.36) and have negative loadings on Factor 1. Site 2 subsurface peat pyrolysates are more decomposed than those from the surface. This is reflected in the separation of the surface samples, which have a negative loading on Factor 1, (0d, -0.04) from the subsurface samples, which have a positive loading on Factor 1 (0a + 0.61). Recently burnt sites also plot with a positive loading on Factor 1, however there are no consistent trends with depth. More positive scores on Factor 1 may suggest a more advanced stage of OM decomposition because subsurface samples have a more positive loading than surface samples.

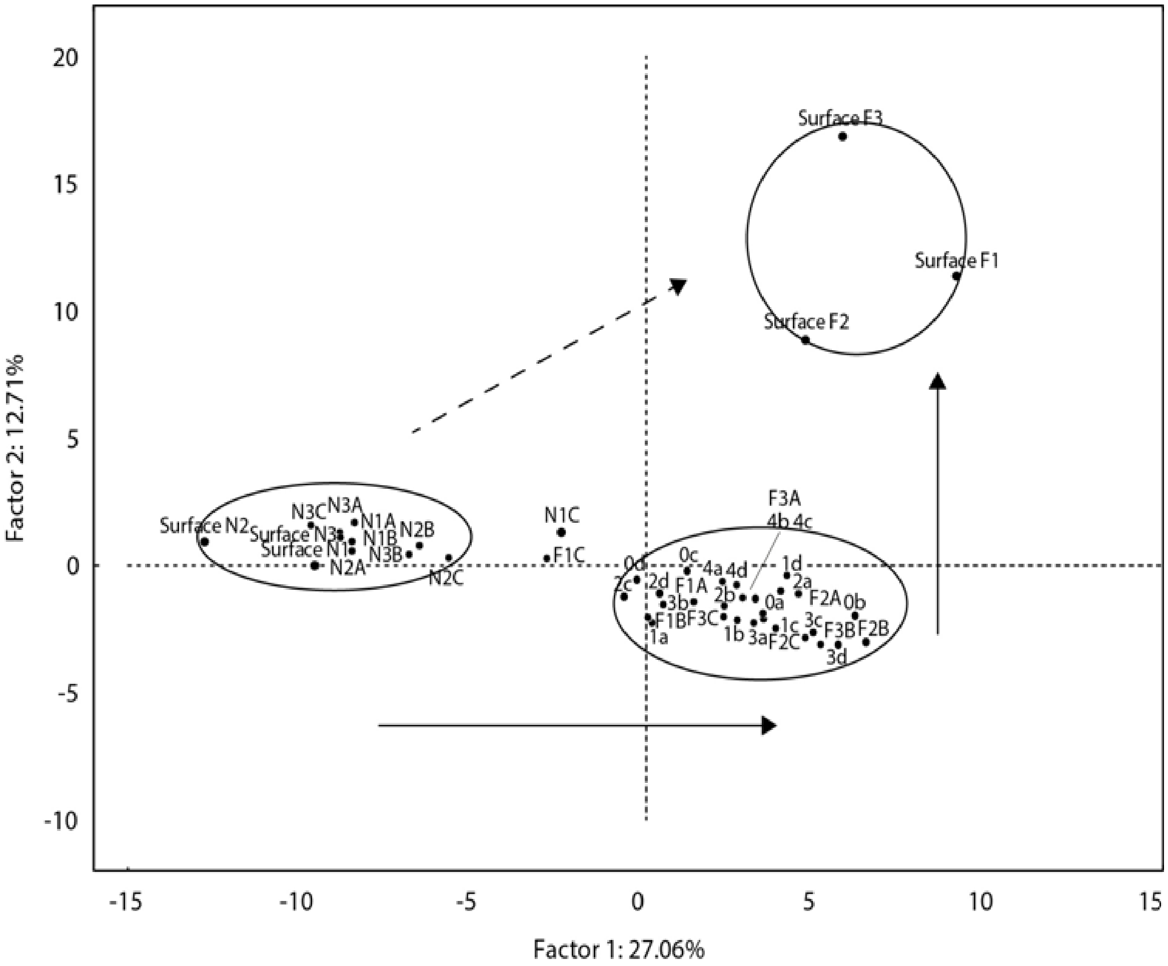


Fig. 37. Plot of cases (samples) in factor space. Loadings based on factors 1 and 2 which explain 39.77 % of the total variation combined. Circled areas highlight separation between intact, drained and drained burnt sample pyrolysates.

Factor 1 therefore may reflect the degree of decomposition, with peat in a higher state of decomposition plotting positively on Factor 1. Almost all samples (with the exception of 2d), from the medium and longer-term post-fire plots, have a positive loading on Factor 1. This implys that although burning has not had a long term effect on peat OM composition, drainage has certainly caused long term if not permanent alteration of the peat OM composition. This is supported by the positive Factor 1 loadings of the aliphatic pyrolysis products (e.g. n-alkanes/alkenes Fig.38), high contributions of which are typically an indicator of relatively decomposed OM since such compounds have high biochemical stability (Lorenz *et al.*, 2007). Further to this, compound classes that showed a significant reduction after drainage and burning typically have a negative loading on Factor 1 (e.g. polysaccharides and lignins). A negative loading on Factor 1 suggests a relatively low state of OM degradation. The compounds which plot most positively on Factor 1 are: Al18 (0.78), Al7 (0.78), Al14 (0.74) and Al20 (0.72). These compounds are all mid and short chain alkenes/alkanes. Compounds plotting most negatively on Factor 1 are: Lg16 (-0.86), Ps10 (-0.84), Ps9 (-0.82) and Lg5 (- 0.81).

Data included in Fig.30-36 can potentially be used to assess the post-fire recovery of peat OM composition over short, medium and longer time scales. In the PCA, the separation of data from peat samples that had been recently burnt from peat samples that had undergone 1.5 years post-fire recovery suggests that the greatest compositional change is observed immediately post-fire (as discussed in Chapter 4) and that at 1.5 years post-fire the OM composition, inferred from the pyrolysates, does not significantly differ from the peat that had only been drained. The PCA did not reveal any significant statistical differences in the peat OM composition over the post-fire chronosequence between 1.5 and 14.5 years. This result indicates that the fires that occurred during 2009 initially had a significant impact on the peat OM composition, as noted at only one month after the fire, but between 1.5 years and 14.5 years post-fire the OM composition returned to its pre-fire state. This suggests that fire only has a short term influence on peat OM composition, while, conversely, the influence of drainage is clearly evident over the longer term, i.e. at 15 years following drainage.

Factor 2 (Fire Intensity)

Factor 2 separates surface samples from the recently burnt site from all other samples, including those from intact, drained and all other burnt locations (Fig.36). Samples from Sites 1 and 2 are not influenced by Factor 2, therefore all samples have either minor positive or negative loadings on Factor 2. Because Factor 2 only separates the short-term chemical changes in peat OM composition it can be implyed that these differences are attributable to the short-term effects of fire.

All peat pyrolysates from the recently burnt site have a strong positive loading on Factor 2 (all samples > 0.8). This difference in OM composition could be explained by ‘fire intensity’, since the upper 5 cm seperate from the sampled subsurface, thus Factor 2 likely indicates the variation in OM composition that is caused by ‘fire intensity’. Higher fire intensity will result in higher burning temperatures and vice versa. Burning temperatures will typically be greater at the peat surface than at depth, thus supporting the results of temperature measurements taken during experimental burns (Usup *et al*., 2004). Distinct separation on Factor 2 of the surface from subsurface peat samples can be attributed to the increased temperature of burning at the peat surface. Between 5 and 50 cm below the peat surface both burning, albeit at lower temperatures (Hamada *et al*., 2012), and aerobic decomposition have contributed to the alteration of the peat OM composition.

The compounds which load most positively on Factor 2 are: PAH3 (0.85), PAH1 (0.79), Ar7 (0.70) and Al51 (0.66). These pyrolysis products are regarded as precursors of relatively recalcitrant macromolecules compared to most other identified compounds. It is not surprising that the PAH compounds plot closely to the recently burnt samples as this result is in agreement with those from a range of studies (Kaal *et al*., 2009b; Campo *et al* 2011) that also identified compounds, such as naphthalene, as products of combustion.

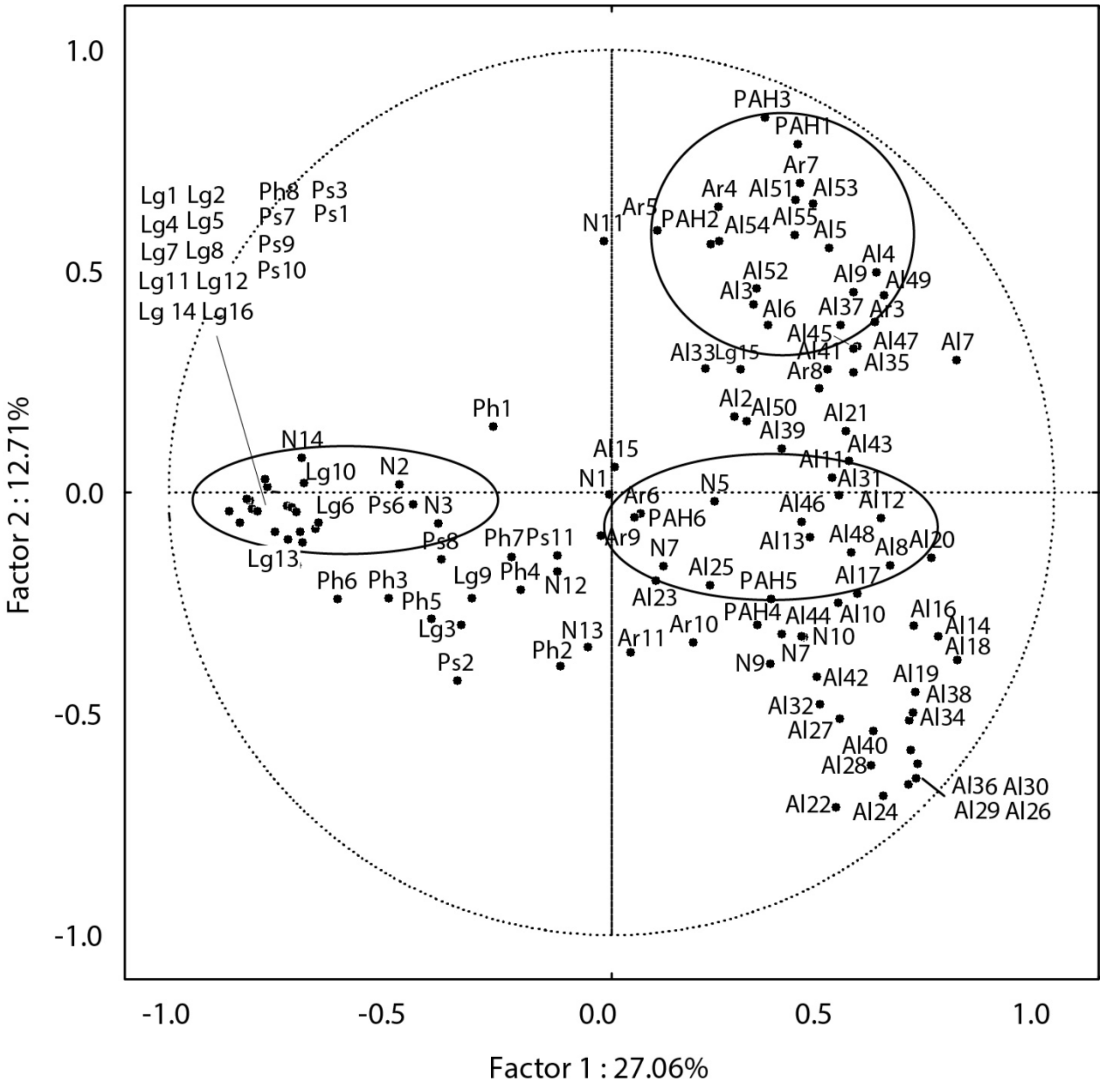


Fig. 38: Plot of variables (pyrolysis compounds) from fire chronosequence analysis in PC factor space. Loadings based on factors 1 and 2 which explain 39.77 % of the total variation combined. Circled areas highlight separation between intact, drained and burned (single and multiple burn) pyrolysates.

PAH compounds are likely to have been accumulated from the thermal alteration of the primary polysaccharide, levogluscosan (Ps3). This cellulose-derived organic compound has a slight negative loading on Factor 2 and is closest to the samples from Site 1 (Fig.37). Laboratory studies have shown that charred cellulose (represented by levoglucosan) forms a variety of PAHs when heated above 310 °C (Pastova *et al.*, 1994). Depletion of levoglucosan coupled with enhanced contributions of PAH supports the idea that greater temperatures were obtained in the upper 5 cm of the fire-affected peat samples.

Compounds loading most negatively on Factor 2 are: Al22 (-0.71), Al24 (-0.69), Al26 (-0.66) and Al30 (- 0.65). These are all mid-chain alkenes with the exception of Al22 (Prist-1-ene); this is an acyclic isoprenoid compound thought to be derived from tocopherols which are long chain aliphatic compounds derived from leaf cuticles. Negative loading of these mid-length aliphatic compounds on Factor 2 suggests that they are not derived from flaming combustion but are biologically resistant compounds selectively preserved during the decomposition of leaf litter (Lorenz *et al.*, 2007) or which increase due to cross-linking during the humification process (Kögel-Knabner *et al.*, 1992). However, positive loadings of long-chain alkenes and alkanes on Factor 1 suggests that these compounds are relatively more resistant to aerobic decomposition than compounds with low Factor 1 scores, meaning that, although the effects of fire are no more than a short-term phenomenon, drainage of the peat has led to long-lasting and possibly irreversible changes to the chemical composition of the peat OM.

Variance of peat OM with time post-fire

The data presented in this chapter provide evidence that burning has a significant short-term impact on the composition of tropical peat OM, but that the OM composition recovers to pre-fire status over a period of up to 1.5 years without further burning. Factor scores of samples collected under a range of different 'times since last burn' show that there are no significant variances between pyrolysates sampled 1.5 and 14.5 years post-fire. All sample pyrolysates over this time period have a positive loading on Factor 1, indicating that the peat samples are relatively more decomposed than those from the intact site, however they do not vary with respect to Factor 2, thus the effects of fire are not evident over the medium or longer-term.

It was hypothesised (Chapter 1 & 2) that fire has a long-lasting impact on the composition of peat OM but it is expected to display signs of recovery if there is a sufficiently long recovery period without further fires, i.e. at 14.5 years post-fire the peat OM composition will be significantly different from that at 1.5 years post-fire. The results of the fire chronosequence analysis do not, however, support this hypothesis. Instead, the data reveal that the recovery of composition of the peat OM back to pre-fire conditions is not linear up to 14.5 years post-fire; the OM composition is comparable to the pre-fire composition at just 1.5 years post-fire and thereafter remains unchanged up to the end of the chronosequence at 14.5 years post-fire. Between 1996 (the start of drainage) and the date of sampling (2011), all sites in the former MRP area experienced artificial lowering of the peat water table which exposed the upper 50 cm of peat (and often peat a greater depths) to conditions ideal for aerobic decomposition. The results presented in this chapter identify decomposition as the dominant process causing variation in the OM composition of peat samples and as fire-affected peat if given a minimum of 1.5 years to recover after burning the composition of the peat OM will be chemically similar to that of peat that has been drained for a period of 15 years.

The proportion of C, hydrogen and oxygen in peat sample pyrolysates from Sites 1-3 are presented as a ternary plot (Fig.39). These data further support the previous findings in this thesis that the undisturbed peat at Site 1 has a relatively high oxygen content compared to all other samples from Sites 2 and 3 that had been exposed to both drainage and burning.

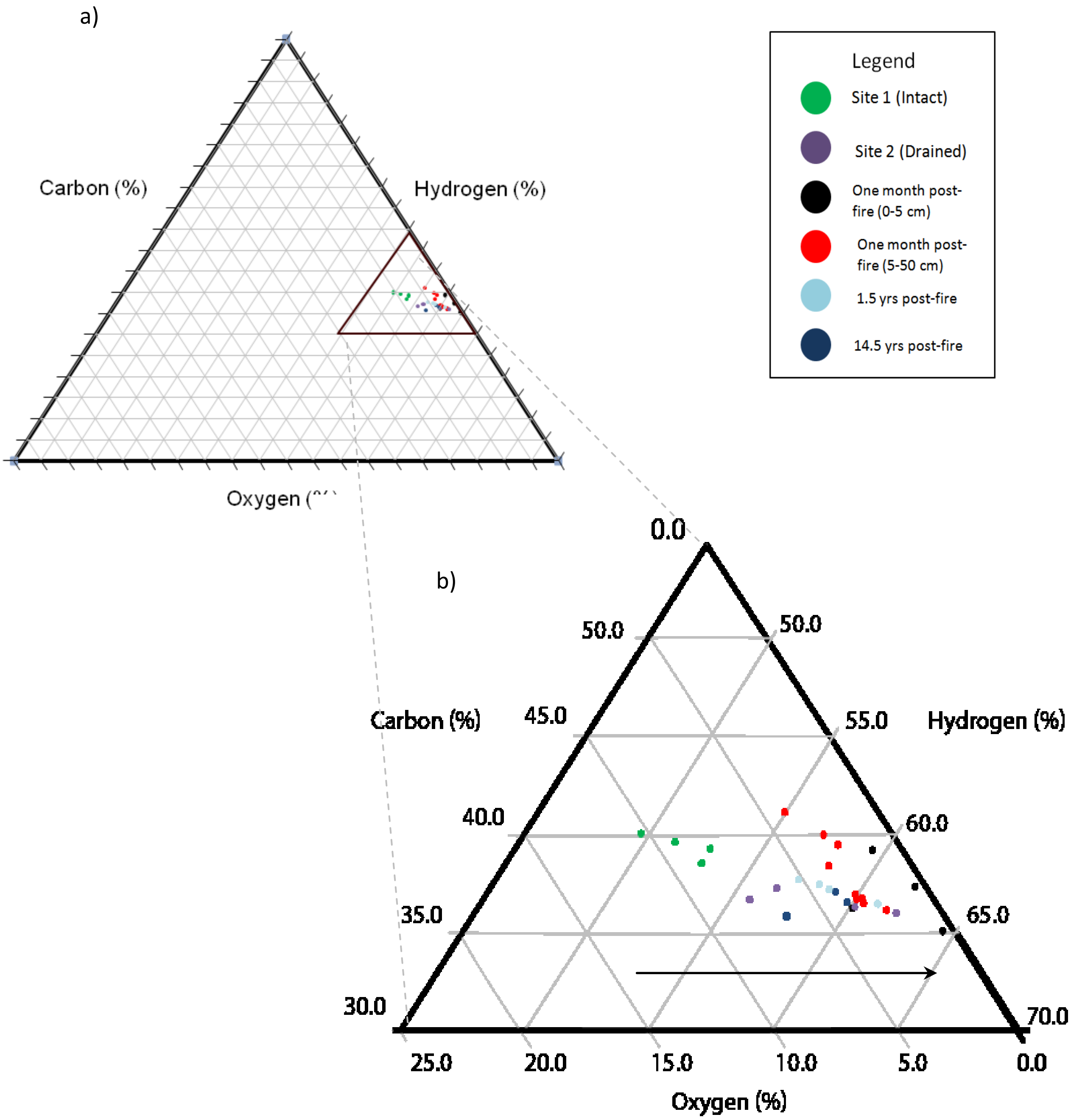


Fig 39: Three dimensional ternary plots of relative C, hydrogen and oxygen content in sample pyrolysates along a fire chronosequence. a) Full ternary diagram b) Sub-section of the full ternary diagram. Relative proportions of elements were calculated from the proportion within each identified pyrolysis product multiplied by the relative concentration found in each sample. The sum of each element (C, H, O) measured in each sample has been plotted. The relative proportion of nitrogen in samples

pyrolysates is not included in this figure as it does not significantly vary between samples. Arrow symbol represents the reduction in relative oxygen content in peat sample pyrolysates.

The oxygen content of peat sample pyrolysates is significantly depleted, i.e. the compounds are chemically reduced, when the peat has been degraded, either solely by drainage or a combination of drainage and burning (Fig 39). Pyrolysates of peat samples from the inundated, intact peat swamp forest (Site 1) have an average oxygen content of 9.2 ± 1.4 % whereas samples of drained peat (from Site 2) contain on average just 4.7 % ± 2.5 % oxygen molecules. There is also a significant difference in the oxygen content of the peat pyrolysates between the upper 15 cm of peat and peat between 15 and 50 cm below the surface at the drainage-affected site (Site 2). This suggests that below a depth of 15 cm the peat is more decomposed than in the upper 15 cm as the most labile compounds containing oxygen molecules are decomposed more readily. The oxygen content of surface peat pyrolysates collected one month after burning were further reduced to 0.75 ± 0.36 %. A reduction in oxygen containing functional groups from larger soil OM macromolecules is commonly reported as an effect of fire on OM (Almendros, 1992).

The hydrogen content of peat pyrolysates varies between the intact and the degraded (drained/burnt) sites; pyrolysates from drained peat (58.7 ± 3.2 %) contain proportionally more hydrogen molecules than those from intact peat (51.2 ± 1.2 %). At one month post-fire, the hydrogen content of peat sample pyrolysates is significantly greater (61.8 ± 2.6 % than in pyrolysates from peat samples that have been exposed to either drainage (Site 2) or inundation (Site 1). The higher proportion of hydrogen molecules in peat sample pyrolysates form the recently burnt site can be explained because of the reduced chemical functionality of pyrolysates of peat samples collected one month post-fire, which provides increased availability for bonding of hydrogen to C atoms. The hydrogen concentration of peat sample pyrolysates is greatest one month post-fire, and a relative reduction in hydrogen content is observed 1.5 years post-fire (57.7 ± 3.1 %). Hydrogen concentrations 1.5 years post-fire are similar to those determined in unburnt (drained) peat sample pyrolysates from Site 2. Hydrogen content does not significantly change between 1.5 and 14.5 years post-fire, which is in line with previous data presented in this chapter, confirming that fire does not have a significant medium or long term effect on the OM composition. Drainage has, however, reduced the proportion of oxygen containing molecules and decreased the proportion of hydrogen molecules observable 15 years after the water table was lowered.

The Py-GC/MS data have revealed that immediately post-fire the pyrolysates from the upper 5 cm of peat are dominated by the most condensed forms of C, including PAHs; this is also reflected in the carbon to oxygen ratio (C:O). At one month post-fire, the C:O ratio is relatively high at 49.6, but 1.5 years later the peat pyrolysates have a greatly reduced C:O ratio of 9.5. Aromatisation is likely to have caused the loss of oxygen containing functional groups.

Elemental Analysis

Elemental analysis for total organic carbon (TOC) and total nitrogen (TN) was conducted using a SerCon ANCA GSL elemental analyser. All analyses were carried out in triplicate and standard deviations were equal or less than 0.05 ‰. Samples from all three sites were analysed as per the fire chronosequence analysis (Table 9) and three samples from each of the sampled depth intervals (0-5, 5-15, 15-30, and 30-50 cm) were analysed in order to obtain an average for each plot.

The total C and N contents of peat samples vary considerably, particularly in the upper 5 cm, and there is a notable effect of fire history. Total C contents of the upper 5 cm of peat are greater in samples from Site 2 than Site 1 (Site 2, 52.4 ± 0.0 %, Site 1, 47.8 ± 0.0 %). One month post-fire there is a significant increase in C content (Site 3, 79.0 ± 0.5 %). There is, however, a decrease in total C content with time post-fire; at 1.5 years post-fire, the total C content of the upper 5 cm of peat was 59.9 ± 0.1 % and at 14.5 years post-fire, it was 56.85 ± 0.22 %. It is notable that at 14.5 years post-fire that the surface C content of the peat remains greater than pre-fire. Burning was not shown to have had any effect on the total C content of the peat at depths greater than 5 cm below the surface; the C contents of peat at all locations at Site 3 remained relatively unchanged from values determined in the drained peat samples from Site 2.

The total N content of the upper 5 cm of peat is also greater when the peat is drained (Site 1, 1.20 ± 0.02 %; Site 2, 1.65 ± 0.02 %) but one month post-fire there is a notable decrease to 0.73 ± 0.01 %. The N content of the peats recovers at 1.5 years post-fire (1.18 ± 0.02 %), but remains at below pre-fire levels even 14.5 years post-fire (1.12 ± 0.02 %). Below 5 cm from the peat surface, drainage led to a decrease in the N contents of peat samples (Fig.41). Burning also had a significant effect on the N content of peat below 5 cm from the peat surface, but the N contents of peat samples from burnt sites remained relatively unchanged from values determined for peat samples from the drained site.

The ratio of C to N content in peat samples decreased in the upper 5 cm of peat at the drained site (C:N ratios of 39.9 – 31.9 for Site 2) but in surface peat samples from the recently burnt site there was a considerable increase to 107.7. The C:N ratio remained greater than pre-fire levels at 1.5 years (50.3) and up to 14.5 years post-fire (50.9). Below 5 cm from the peat surface drainage led to an increase in the C:N ratio (Fig.40), while burning had no significant effect at this depth and the C:N ratio remained relatively unchanged from the values determined for the drained peat samples

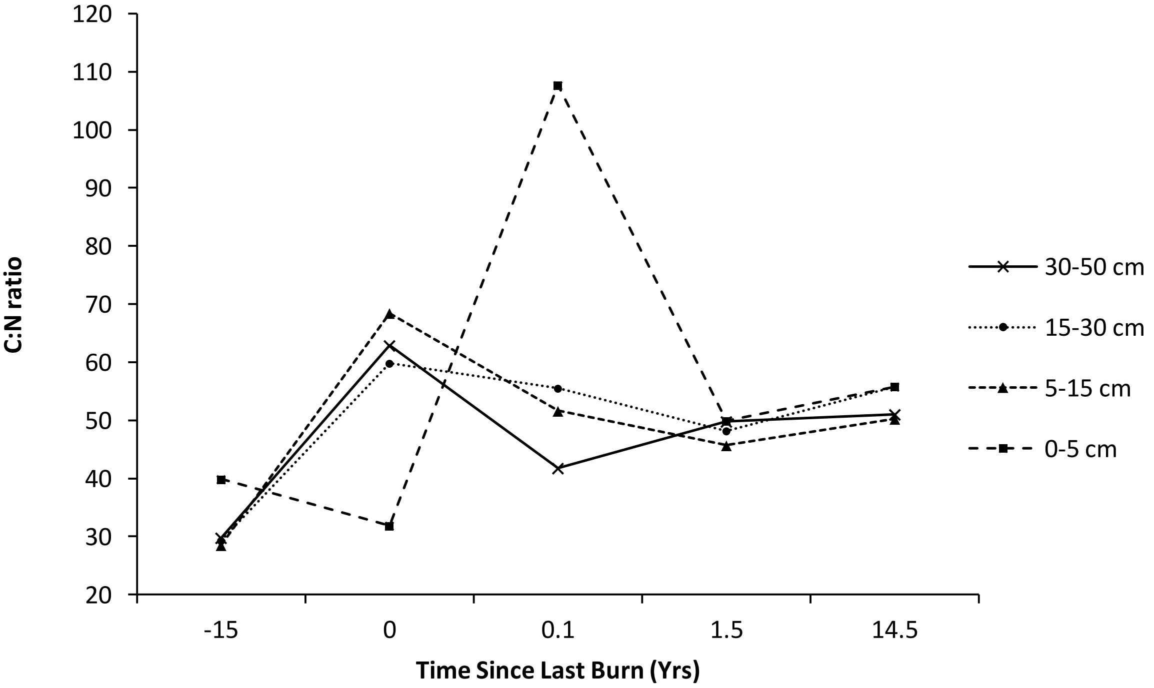


Fig. 40: Carbon nitrogen (C:N) ratio of peat samples along a pre (drainage only) and post-fire chronosequence (1997-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling.

The results from the elemental analysis support the pyrolysis data because the chemical changes are only significant in the upper 5 cm of the peat. Evidence, including the total C and N and calculation of the C:N ratios, suggest that fire has a significant short term effect but that at 1.5 years after a fire, the peat is chemically similar to that which has only experienced drainage.

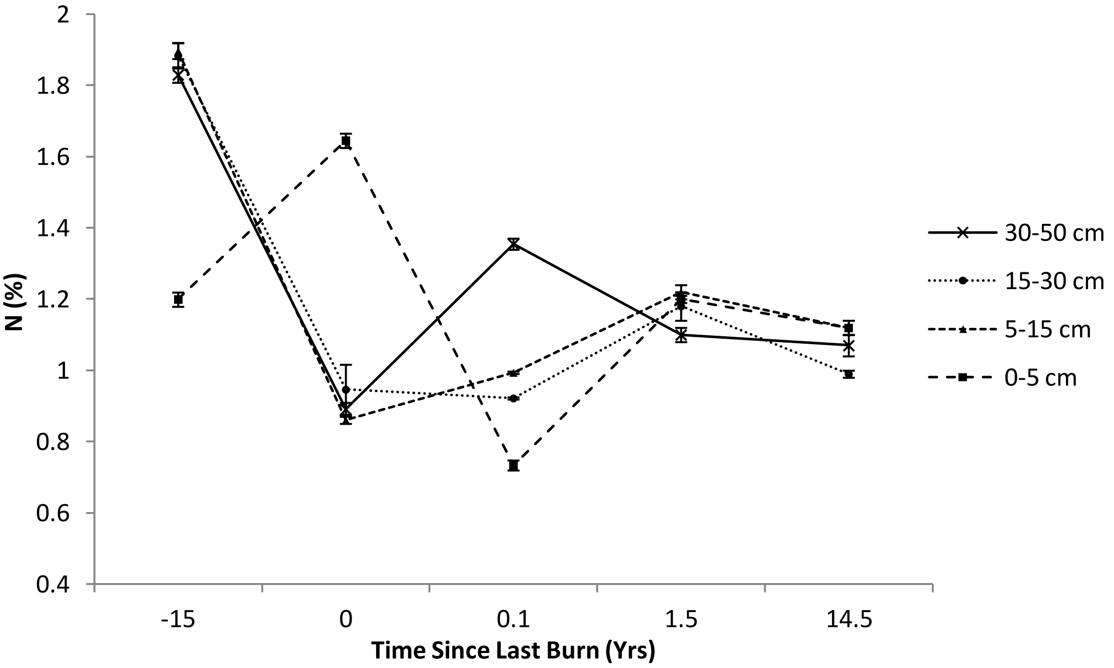


Fig. 41: Total nitrogen content (%) of peat samples along a pre (drainage only) and post-fire chronosequence (1996-2011) at a range of depth intervals between 0 and 50 cm from the surface. Negative years represent time between initiation of drainage and collection of sample. Year '0' represents the time of sampling. Error bars represent one standard deviation of the mean.

5.4 Fire Frequency

Previous research has shown that some areas in the former MRP area that were exposed to a single fire were able to undergo subsequent rapid succession and develop a vegetation cover representing an advanced stage of regeneration, i.e. closed canopy forest (Hoscilo, 2011). Multiple fire sites showed a far less advanced regeneration, with non woody biomass dominating these sites, typically comprising one or two fern species (*Stenochlaena palustris* and *Blechnum indicum*). There is very slow or no recovery of woody biomass at these sites, with the exception of occasional pioneer tree species, notably *Combretocarpus rotundatus* and *Cratoxylon glaucum*. Thus, the above-ground biomass is significantly lower in at sites affected by multiple fires compared to single fire sites and these differences in vegetation cover may be reflected in the peat OM composition, in addition to the effects that may be caused by repeated thermal alteration of the peat OM. It is therefore hypothesised that sites which have experienced a multiple fire regime will have a different OM composition from those that have been exposed to only a single fire.

5.4.1 Sample Collection

In order to assess the effect of fire frequency on the composition of peat OM, fire frequency maps (see Chapter 3) were used to select a range of sampling locations within Site 3 that were burnt under a multiple fire regime. There are areas within the former Mega Rice Project area that have been burnt up to four times and small areas up to six times. A variety of peat samples were collected as per the method outlined in Chapter 3 (Section 3.2.2.) under a range of fire frequencies (from once and up to four times burnt). Each plot used in this analysis was sampled 1.5 years post-fire. Samples were stored and analysed as described in Chapter 3 (Section 3.2.2) using Py-GC/MS. Table 9 presents a list of samples and the relevant fire frequency data.

5.4.1 Fire Frequency (PCA)

Overview

There are contributions from all selected compound classes in pyrolysates from both single and multiple fire sites. General observations from this data are: (i) all pyrolysates are dominated by the aliphatic compound class regardless of the fire frequency; (ii) PAHs are present in all pyrolysates which are indicative charred material formed during burning event/s; (iii) there are no significant differences between single and multiple fire sites with respect to any of the compound classes; (iv) at the single fire site, polysaccharides, lignins and phenols all increase with depth, while aromatics, nitrogen-containing compounds, polyaromatics and aliphatics all decrease with depth; (vi) there are no consistent trends with depth at the multiple fire sites. Relative contributions of each compound class are variable within the 50 cm analysed depth range.

Table 9: Relative contributions of all identified pyrolysis compound classes. Results are displayed as a percentage of the total identified pyrolysis products. Al, Aliphatics, Ph, Phenols, PAH, Polyaromatic hydrocarbons, N, Nitrogen-containing compounds, Lg, Lignins, Ar, Aromatics, Ps, Polysaccharides.

Fire Frequency	**Sample No**	**Ps**	**Lg**	**Ar**	**Ph**	**N**	**PAH**	**Al**
Single Fire	1d	4.6	8.8	5.9	12.1	4.0	1.7	62.9
1 x Burnt	1c	5.6	9.8	5.5	12.4	5.3	1.3	60.1
(2009)	1b	4.2	12.3	4.7	12.4	3.7	1.2	61.6
	1a	6.0	17.6	4.8	19.8	2.6	1.4	47.9
Multiple Fire	2d	12.2	11.0	5.8	10.0	4.6	1.5	53.3
2 x Burnt	2c	11.4	10.1	5.6	9.0	5.0	1.9	55.6
(2009,1997)	2b	5.0	6.6	6.5	10.4	5.5	2.4	65.2
	2a	11.8	7.9	7.2	11.6	4.9	1.1	57.2
Multiple Fire	3d	6.1	11.3	4.8	10.6	4.1	1.9	61.2
3 x Burnt	3c	10.2	12.1	5.5	15.3	3.5	1.9	51.6
(2009,2006,1997)	3b	6.6	9.6	6.8	15.0	3.6	1.4	57.1
	3a	7.7	11.5	5.3	12.2	4.6	1.9	56.6
Multiple Fire	4d	3.2	9.7	5.3	11.3	4.4	1.7	64.4
4 x Burnt	4c	6.3	18.3	5.6	10.4	3.5	1.5	54.4
(2009,2006,2002,1997)	4b	15.5	28.9	5.6	9.9	2.3	2.4	35.3
	4a	7.5	18.9	6.3	10.4	4.7	2.4	49.7

Factors 1 and 2 explain 41.16 % of the variation and 3 factors explain 50.01 % of the total variation. Up to 78.6 % of the total variation is explained by 12 factors. The loadings of samples on factors 1 and 2 are shown in Fig.42. As was the case in the previous analysis (Chapter 4) a highly complex dataset such as this has resulted in a large number of factors explaining the total variance in the dataset. Plots of variables are presented in Fig.43. The loadings of the cases (samples) and their corresponding variables allow deductions to be made regarding the differences in OM composition between samples.

Factor 1

Factor 1 explains the greatest proportion of the total variation in pyrolysates (28%). As with the previous analysis of 'time since last burn', Factor 1 can be attributed to differences in peat OM composition caused by enhanced aerobic decomposition caused by drainage that has affected all of the burnt areas prior to fire.

Both single and multiple burnt sites have positive loadings on Factor 1 (plots 3-8) suggesting that aerobic decomposition has modified the original intact (Site 1) composition of these pyrolysates. Pyrolysates of surface peat that had been burnt on three or four occasions (3d & 4d) have a greater positive loading on Factor 1 than those samples burnt once or twice (1d & 2d). This result suggests that peat that was burnt more than twice is relatively more decomposed and therefore more recalcitrant than peat that has experienced either one or two fires. In contrast, subsurface sample pyrolysates do not display any consistent trends with respect to fire frequency regime. Cases with positive scores on Factor 1 correspond to loadings of the majority of aliphatic pyrolysis products such as mid-length alkene/alkanes (Fig.43).

The compound loadings presented in Fig 43. reveal a similar trend to that observed in the analysis of fire chronosequence, namely that recalcitrant compounds plot positively on Factors 1 and 2 (e.g. aliphatics and aromatics) and labile compounds plot negatively on Factor 1 (e.g. polysaccharides and lignins). The compounds which load most positively on Factor 1 are: Al18 (0.79), Al15 (0.77), Al20 (0.77) and Al35 (0.76). These alkene and alkane pyrolysis products may indicate microbial biodegradation in all burnt samples regardless of the fire frequency. The compounds loading most negatively on Factor 1 include: Lg16 (-0.87), Ps11 (-0.86), Ps7 (-0.82), Lg5 (-0.81) and Ps3 (-0.81). In agreement with analysis presented earlier in this chapter and in Chapter 4, labile compounds such as lignin and polysaccharide pyrolysis products are most closely associated with the loadings of the peat samples from Site 1.

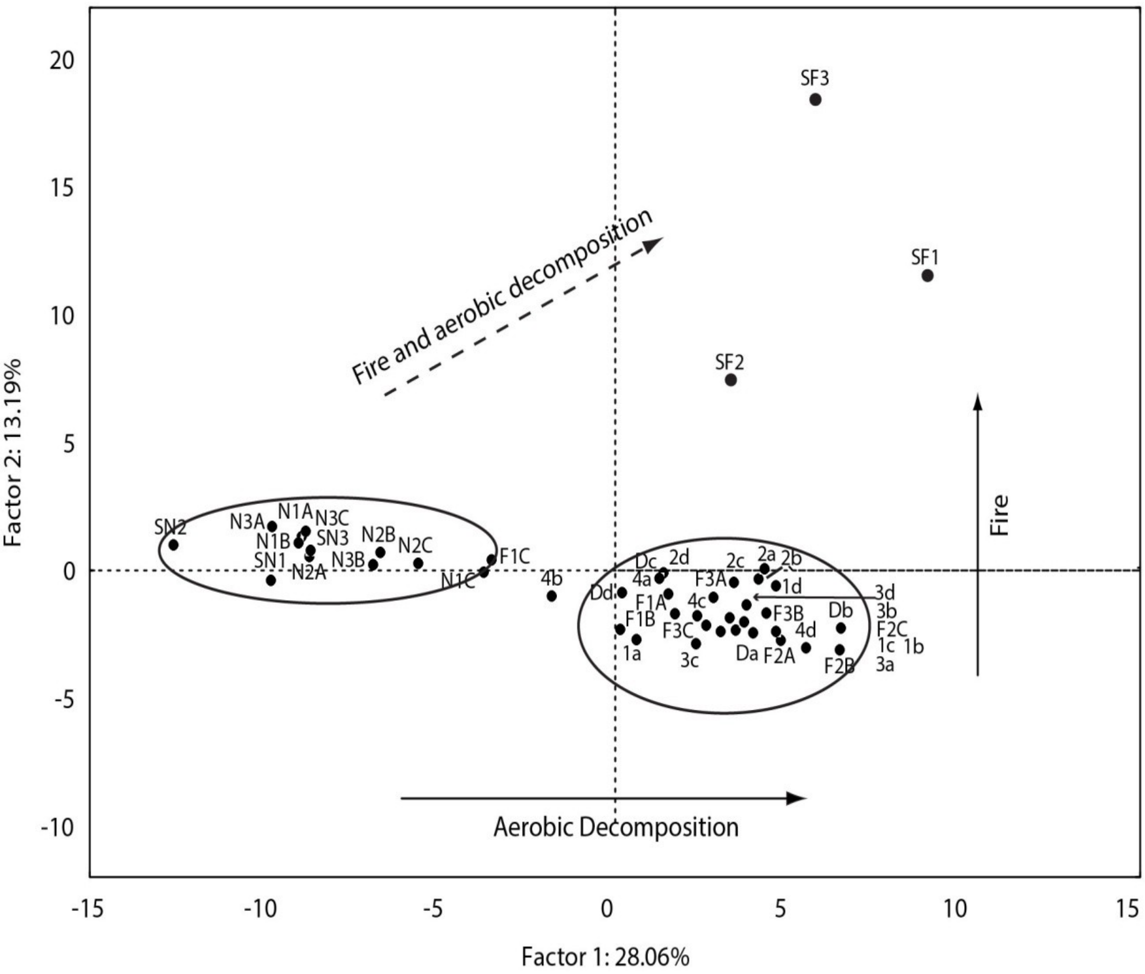


Fig. 42: Plot of cases (samples) in factor space. Loadings based on factors 1 and 2 which explain 41.16 % of the total variation combined. Circled areas highlight separation between intact, drained and burned pyrolysates.

Factor 2

With the exception of the recently burnt surface samples (SF1, SF2 and SF3) all other single and multiple fire sample pyrolysates do not significantly vary with respect to

Factor 2. There are also no consistent trends between sites exposed to different fire frequency regimes with respect to this factor. The compounds which load most positively on Factor 2 are: PAH1 (0.78), PAH3 (0.76), Ar7 (0.72) and Al55 (0.71). Compounds loading most negatively on Factor 2 are: Al22 (-0.79), Al24 (-0.77), Al26 (-0.74) and Al30 (-0.72). Positive loading of PAH pyrolysis products such as PAH1 (naphthalene) and PAH3 (biphenyl) is in agreement with the previous analysis (Fig.38). The key conclusion of this PCA analysis is that because there are no significant statistical differences between sites burnt under different 'fire frequencies' the thermal alteration of peat OM caused by the initial fire is the most substantial and any further burning does not lead to any significant additive effects.

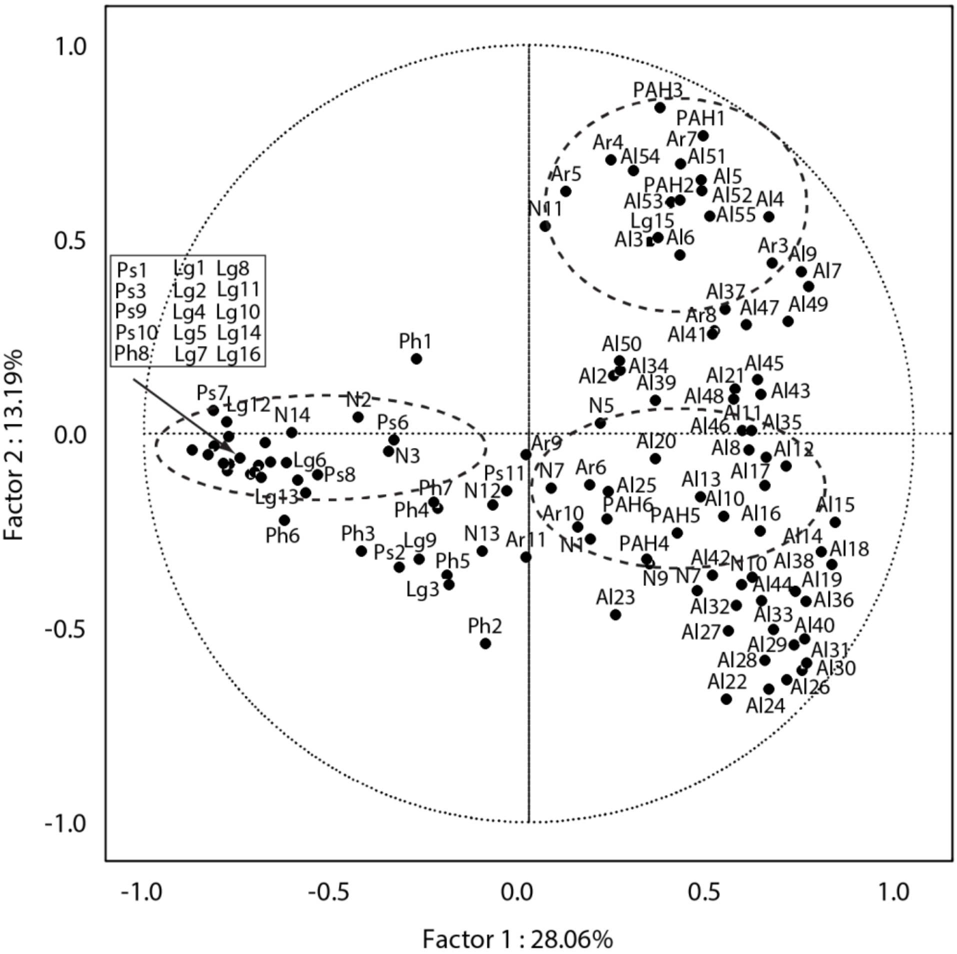


Fig. 43: Plot of variables (pyrolysis products) from fire frequency analysis in PC factor space. Loadings based on factors 1 and 2 which explain 41.25 % of the total variation

combined. Circled areas highlight separation between intact, drained and burned (single and multiple burn) pyrolysates.

5.5 Discussion

Assessing post-fire recovery of peat OM composition

Medium term effects of fire (1.5 – 4.5 years post-fire)

Investigating peat OM alteration has a practical purpose as the molecular composition can used to assess the initial impact as well as the medium and longer term effects of fire, thus indicating the potential recovery of fire-affected peat in terms of its biogeochemistry. Improved understanding of how regime variables such as fire frequency impact on peat OM composition is of importance as the frequency of fires on the tropical peatlands of Southeast Asia is expected to increase with future regional climatic change (Page *et al.*, 2009).

There are significant differences in OM composition between recently burnt peat and peat collected approximately 1.5 years post-fire; however these differences were only significant between surface samples (0 – 5 cm). For samples collected lower in the peat column (between 5 and 50 cm), the peat OM composition does not significantly vary. One month post-fire (November 2009), sample pyrolysates of the upper 5 cm of peat are significantly different from those collected approximately 1.5 years later (April 2011). Initially, burning transforms the peat OM composition so that it becomes highly aliphatic, with relative contributions of these compounds increasing from 41.0 % in drained, unburnt peat pyrolysates to 71.3 ± 12.9 % in the pyrolysates from peat collected one month post-fire. At 1.5 years post-fire, the aliphatic contributions remain significantly greater than pre-fire contributions (56.3 %). In addition, at one month post-fire the peat pyrolysates contain considerable contributions from aromatic compounds as well as pyrolysis products which are thought to indicate the presence of charcoal, e.g. naphthalene. Dimethylnaphthalene (PAH4) and trimethylnaphthalene (PAH5) both plot in similar factor space when assessing variance using PCA and the presence of PAHs at 1.5 years post-fire suggests charred OM is still present, although less dominant than in those samples analysed shortly after the fire was extinguished.

The overall OM diversity has increased 1.5 years post-fire (i.e. number of pyrolysis products identified has increased, from 72-75 to 111), and there is evidence that there are more labile compounds in the peat OM such as cellulose (as indicated by levoglucosan) and furans which were not detected in the pyrolysates at one month post-fire. The proportion of oxygen in surface sample pyrolysates also increases during the 1.5 year recovery period (3.9 % vs. 0.75 ± 0.36 %) which is due to the increased abundance of oxygen-containing functional groups which are typically part of the structure of polysaccharide- and lignin-derived compounds. Surface peat pyrolysates from Site 2 (drained peat) have a higher oxygen contribution of 7.5 % suggesting that 1.5 years after fire the peat OM is not as labile as it was prior to being burnt and thus has not fully recovered to its pre-fire composition, despite the OM compound diversity increasing.

There are a number of explanations for this short-term increase in OM diversity following fire, particularly in terms of labile pyrolysis product diversity. There may have been addition of new organic material deposited onto the peat surface from new growth of vegetation that established in the 1.5 years since the fire occurred. It is plausible that greater contributions of polysaccharide (4.6 % vs. 0.1 ± 0.1 %) and lignin (8.8 % vs. 0.8 ± 1.2 %) compounds detected in the pyrolysates of surface peat samples 1.5 years post-fire are due to the addition of labile OM from renewed growth of vegetation. An increase in OM compound diversity through the addition of litter would be an indication that the peatland was recovering from a fire event. A further explanation could be that the upper 5 cm of peat have been lost laterally through erosion by rainfall and that this erosion has exposed a formerly deeper peat layer at the surface that had not been so significantly affected by fire.

The most convincing explanation, in my view, is the latter – i.e. that there has been lateral loss of organic material by erosion. Burning often destabilises soils by consuming the aboveground vegetation (Larsen *et al.*, 2009) and at very high temperatures (270-300 ^{o}C) hydrophobicity of soils can be destroyed (DeBano, 2000;

Doerr *et al.*, 2000), both of which can lead to soil erosion. Destabilisation and possible destruction of hydrophobicity may suggest a loss of the upper 5 cm charred layer of peat. High precipitation during the wet season coupled with a lack of stabilisation of the peat by vegetation were the reasons given to explain the high dissolved and particulate organic C (DOC & POC) content measured in drainage canals in the MRP area shortly after the 2009 fire (Moore *et al.*, 2011). In addition, previous analysis (presented in Chapter 4) has shown that at depth (5-50 cm) the composition of the peat OM is not statistically significantly different from that of the peat that has been only drained. This further substantiates the theory that at between 1 and 18 months post-fire a considerable proportion of the upper 5 cm of peat at the burnt site had been lost through erosion and transport into waterways. Therefore the current peat surface is not necessarily showing signs of post-fire recovery but simply exposure of a lower layer of peat.

Long-term effects of fire (up to 14.5 years post-fire)

Between 1.5 and 14.5 years post-fire, the peat OM composition does not significantly change. This suggests that although the effects of burning on peat OM composition are substantial in the short-term, fire has not had any significant influence on the peat OM composition in the longer-term. There are no other published results on the medium or longer term effects of fire on tropical peat OM composition, however results from this study imply that burning in the former MRP area has not had a significant longer term effect. Evidence for this is provided by the peat pyrolysate data which are chemically similar regardless of whether the sampled plot had experienced 4.5, 8.5 or 14.5 years without further burning.

Thus, the results indicate that burning of tropical peat has no significant long-term effect on the overall soil OM composition. In support of this finding, long term effects of fire were not significant in burnt soils from the Alcante region in east Spain, although it was thought that the recovery of the vegetation and additional litter inputs to the soil may have masked some of the effects that were determined immediately post-fire (Duguy and Rovira, 2010). The finding that the contribution of oxygen-containing functional groups was depleted by fire has also been observed in other environments (Almendros *et al.*, 2003, González-Pérez *et al.*, 2004) and, in the longer term, o-alkyl forms, often attributed to polysaccharides and lignins, can dominate the OM of soils (Santin *et al.*, 2008, Duguy and Rovira, 2010).

In the short-term peat OM was severely depleted in the most labile OM but, in the longer term, labile compounds such as polysaccharides and lignins recovered slightly and aliphatic derived compounds became more dominant, thus the peat was more recalcitrant than before fire. This result supports other findings from wildfire research, e.g. soils burnt in NW Spain were depleted in carbohydrates primarily in the short-term (immediately post-fire) but in the longer term (9 years post-fire) aliphatic compounds were abundant (Rovira *et al.*, 2012).

Both PAH and aromatic compounds are not significantly different between unburnt and samples burnt 14.5 years before, suggesting that the presence of charred materials that are often indicated by these types of compounds are no longer present. It is likely that many of the characteristic molecules that would signify that burning had taken place were lost over the 14.5 years since burning due to post-fire erosion processes (Santin *et al.*, 2008) and biological degradation of charred matter (Bird *et al.*, 1999). In some environments, charred OM or charcoal is thought to be a method of C sequestration in soils (Schmidt *et al.*, 2002), however other authors have reported relatively rapid rates of degradation of these materials (Bird *et al.*, 1999, Zimmerman *et al.*, 2012). The results from my analysis of the longer-term effects of fire suggest that any charred material that was formed during burning was no longer present in any significant quantities after 14.5 years post-fire.

Although the chemical composition of burnt sample pyrolysates were not statistically different in either the medium or longer-term (as shown by the PCA), there are differences in some components of the OM that provide evidence that fire has had a long term impact. 14.5 years after fire the contribution of oxygen (3.84 %) in surface sample pyrolysates is similar to contributions measured just 1.5 years after fire (3.86 %). The contribution of oxygen containing pyrolysis products remains lower than in the peat that was inundated (10.61 %) and drained (7.74 %) suggesting that this change had been chemically reduced. Therefore the peat OM composition has not been significantly modified over increasing time post-fire. It must be noted that although the samples that were analysed experienced different recovery periods the time the peat had been exposed to drainage remained equal. As there was no statistical difference in these sample pyrolysates from subsurface (15-50 cm) drainage-affected peat, it is concluded that aerobic decomposition remains the greatest contributing factor to the modification of the peat OM composition.

Fire has led to an increase in the total C content of the peat; 14.5 years post-fire peat C content is 4.5 % greater than pre-fire. A similar result was obtained by Johnson and Curtis (2001) who showed an 8% increase in soil C content in the A horizon of mineral soils that had burnt more than 10 years before. Increase in total C was more significant one month post-fire (+ 26.6 %) implying that both the short and long-term increase in C have been caused partly by the heat induced transformations of the peat OM that have converted the fresh OM to more recalcitrant forms, that do not contain oxygen or nitrogen molecules such as charcoal. Evidence of increased recalcitrance following fire was also obtained from pyrolysate data.

C:N ratios have widened significantly as a consequence of fire and have remained wider than pre-fire levels when measured 14.5 years post-fire. This result is explained by the significant reduction in nitrogen due to volatilisation during burning coupled with an increase in C content through transformation of the OM to more condensed C structures. This result is in contrast to other studies of the long term effects of fire on soil OM that found the C:N were lower after burning due to the formation of recalcitrant forms of organic nitrogen in charred materials (Almendros *et al.*, 2003, Knicker *et al.*, 2005b).

Drainage and inevitable decomposition of peat makes these huge terrestrial stores of C available for decomposition. In the long term this may be of greater concern than the direct damage caused by fire because burning has had no significant medium or long term effects on peat OM composition. Drainage however is having a long-term detrimental effect on the diversity and hence quality of the peat OM.

Effect of fire frequency on peat OM composition

Samples 1-4 were collected approximately 1.5 years after being burnt during the dry season of 2009. Peat sample pyrolysates from sites experiencing single and multiple (2, 3 and 4 fires) fires displayed no significant variance. Samples 1-4, across all measured depths, plot in the lower right quadrant in Fig.41 with a positive loading on Factor 1 and a negative loading on Factor 2. This result suggests that the initial burning of an area of peatland has significant implications for peat OM composition but any subsequent burning does not lead to any further alteration of peat OM at 1.5 years post-fire. Wildfires are predicted to become more frequent in both boreal and tropical peatlands with predicted future climatic change (Flannigan *et al.*, 2010, Page *et al.*, 2009). Thus the results in this chapter are significant because despite many areas of peatland in the former MRP area being subjected to multiple burning events the results presented in this thesis indicate that there is no further alteration to the peat OM composition during subsequent fires.

Fire frequency has affected the vegetation composition in burnt areas of the MRP, with multiple fires typically leading to a dominance of non woody biomass dominated by two fern species; *Stenochlaena palustris* and *Blechnum indicum.* Under a single fire regime, the peatland can, however, recover back to closed canopy, secondary forest (Hoscilo, 2009). It was thus hypothesised that the variable aboveground vegetation cover between areas with different fire frequencies would be linked to differences in the OM composition. The results of this study suggest, however, that above-ground vegetation (at least at its current stage of succession) has no significant influence on peat OM composition once it has been burnt. Although there are no comparable studies of fire frequency and OM composition in tropical peatland environments, several studies have commented on how the proportion of woody vegetation decreases significantly the greater the fire frequency. Studies in other environments have reported that the chemistry of many soils types is not influenced by fire frequency (Shackleton and Scholes, 2000; Duguy and Rovira, 2010; Rovira *et al.*, 2012). Chemical composition of OM soils from the Alcante region, Spain were not affected by repeated fires. Chemical analysis of the OM revealed that soil that had burnt twice was chemically no different from soil burnt only once (Duguy & Rovira, 2010). Furthermore, results from a soil nutrient analysis from burnt soils in the Kruger National Park, South Africa revealed that fire frequency had no significant effect on the concentrations of any of the analysed nutrients including organic C, however organic C contents were significantly higher in fire exclusion areas compared to burnt areas (Shackleton and Scholes, 2000). There are few studies that have assessed the link between post-fire vegetation change and changes to the soil OM. The results within this chapter do however imply that there is no clear link between post-fire vegetation and the OM composition of peat in burnt peatlands.

5.6 Conclusion

The key findings from this analysis can be summarised as;

- The effects of fire on peat OM are short-lived (up to 1.5 years post-fire) and evidence implys that peat OM composition recovers when left 1.5 years without further burning.

- Fire frequency has no significant influence on the composition of burnt peat OM as thermal alteration takes place during the initial fire.

Figs.30 36 (line graphs) show that there is some variation between sites and within the 50 cm depth profile, i.e. a peak in PAH's contributions measured in the 30-50 cm pyrolysate (Fig.32) and a peak in polysaccharide content 14.5 years post-fire (Fig.36). This variation, albeit insignificant, could be due to a range of other fire regime and ecological variables that are difficult to exclude when working in any natural environment. Information regarding many these variables could not be obtained as in-situ measurements would be required immediately prior and during the fire. The following variables may explain the observed differences in OM composition:

1) The **temperature of burning** may vary spatially, between sites and temporally, between each fire event. It is known that modification of soil OM is dependent on the temperature to which it is heated (González-Pérez, 2004). The peak temperature will also be related to the initial soil moisture content, a further

variable to consider. A challenge therefore remains when interpreting this data set as it is not possible to retrospectively estimate the average nor the range of temperatures within the peat during each particular fire. The sampling strategy was designed to mitigate against variation caused by small scale spatial variations in temperature. Samples taken one month post-fire (SF1, SF2.SF3) are slightly different from each other chemically and this is likely due difference in burning temperature.

2) The **duration of burning** may also vary between sites and fire events. The OM composition will likely be affected by the time it is exposed to a specific temperature i.e. peat heated to 200 °C for 1 hour may be different from peat heated to 200 °C for 24 hours.
3) The **quantity and quality of available fuel** will affect temperature and duration of burning. Burning of forest vegetation will provide a higher quality fuel source compared with multiple-burn sites which are dominated by ferns, with a much lower fuel load. Deeper rooting systems from trees may allow transfer of heat deeper in the peat profile.

Conclusions from this analysis of the effects of fire regimes suggest that aerobic decomposition as opposed to burning remains the dominant factor influencing OM composition.

Chapter 6- Fire modified peat OM: Implications for charcoal content and water repellence.

6.0 Introduction

The previous two chapters have demonstrated that shortly after fire (one month), the upper 5 cm of peat is thermally altered and aromatic compounds become relatively more abundant. This increased aromaticity, which is observed only in the upper 5 cm of the peat pyrolysates rather than at greater depth, is an indication that the OM has been charred, perhaps to the extent that charcoal has been formed. The most condensed aromatic compounds (PAHs) were detected in higher relative concentrations one month post-fire than pre-fire, further indicating that fire had likely led to charring of the peat. It was also observed that the aliphatic contributions in pyrolysates from the upper 50 cm of the peat column were also relatively greater when the peat had been drained, suggesting that aerobic decomposition through aeration of the peat also leads to a highly aliphatic OM.

In summary, drainage and fire have caused chemical alteration of the peat OM that indicate the following short-term physical changes have probably occurred: (1) charcoal is deposited or formed when peat is burnt, as indicated by the increased aromatic content of pyrolysates; (2) the water repellence of the peat is enhanced, as indicated by the highly aliphatic pyrolysates.

6.1 Charcoal and peat

Charcoal is encompassed within the black carbon spectrum which also includes graphite, soot and charred particles (Hammes, 2006). Charcoal is defined by Emrich (1985) as the 'residue of solid non-agglomerating OM, of vegetable or animal origin, that results from the carbonisation of by heat in the absence of air at a temperature above 300 °C'. Many studies suggest that black carbon, including charcoal, has the potential to be a sink of C in the slow cycling geological reservoir (Glaser *et al.*, 2000; Schmidt *et al.*, 2000; Bird *et al.*, 1999), thereby mitigating against climatic change. In order for climate models to accurately predict climatic change they must include information regarding the response of different C pools to warming. Some C pools, including black carbon, may have a slower decomposition rate than others thus altering the temperature sensitivity of soils (Lehmann *et al.*, 2008). *Terra preta* soils are evidence that black carbon is preserved over long time periods (centuries and millennia) in some environments (Cheng *et al.*, 2008, Glaser *et al.*, 2001). However the stability of black carbon in soils has long been debated in the literature (Shneour, 1966). A recent study using laboratory incubation suggests that black carbon may not as stable as initially thought (Zimmermann *et al.*, 2012), and can also be readily decomposed in some environments, for example, Bird *et al.* (1999) found that black carbon in savannah soils degraded over the order of decades. Environmental conditions, such as temperature, may influence the preservation of black carbon (Cheng *et al.*, 2008), with higher temperatures likely to favour black carbon mineralization.

In addition to C sequestration, there are many other reported benefits of charcoal addition to soil. When charcoal is incorporated into soils it often improves fertility and therefore the productivity of the soil (Wardle *et al.*, 1998). *Terra preta* soils are anthopogenic (anthrosols) dark earths that are typically very fertile and have a high charcoal content (Glaser *et al.*, 2012). *Terra preta* soils in Central Amazonia contain significant quantities of black carbon including charcoal, enhancing the fertility of these soils (Smith *et al.*, 1980, Glaser *et al.*, 2001). Due to the chemical (alkaline, negatively charged functional groups on surface) and physical (large surface area, highly porous) structure of charcoal, many soil properties, including pH, porosity and bulk density, can be altered (Major *et al.*, 2010). Leaching of nutrients can be inhibited as cations are readily adsorbed onto the charcoal surface (Lehmann *et al.*, 2008), improving soil fertility and enhancing seedling germination (Keeley *et al.*, 1985). Nutrient availability can be enhanced, including that of nitrogen, phosphorus and calcium, when charcoal is produced and incorporated into soils following a wildfire (Glaser *et al.*, 2001). Nitrogen cycling may be particularly affected; previous research has found the addition of charcoal increases mineralization and nitrification potential in forest soils (Wardle *et al.*, 1998, DeLuca *et al.*, 2006). Biochar is distinguished from charcoal by its use as a soil amendment; however, many of the reported benefits of charcoal addition from wildfires are similar to those reported for biochar amendments. Biochar is produced through burning of OM at high temperatures (between 300 °C and

500 °C) and under the partial exclusion of oxygen (Antal & Gronli, 2003). Biochar is often added to soils to improve soil fertility and quality (Liang *et al.*, 2006), ultimately increasing crop yields (Lehmann *et al.*, 2003a).

Despite the potential ecological benefits that charcoal addition to the soil can have in a range of environments, there remain challenges in developing a sound method for quantification of charcoal in soils (Hammes *et al.*, 2007). There are many chemical, optical and thermal methods that have previously been used; however, most do not differentiate between the different components of black carbon e.g. soot or charcoal (Simpson and Hatcher, 2004). Estimates of black carbon content in soils are as great as 30-45 % of soil organic C (Skjemstad *et al.*, 1999; Glaser *et al.*, 2000) in both Australian grasslands and *Terra Preta* soils of the Brazilian Amazon. There are no comparable values for tropical peatland environments, however a study of upland peats in the Peak District, UK estimated black carbon production of 6.35 g C m^{-2}, which was equivalent to 4.3 % of the total C consumed during a three day fire event in 2008 (Clay & Worrall, 2011).

Previous chapters of this thesis have highlighted how the chemical composition of burnt peat pyrolysates indicate the presence of charcoal through the identification of enhanced contributions of aromatic and polyaromatic pyrolysis products. Combustion in tropical peatlands can be in the form of flaming surface vegetation fires or smouldering subterranean fires (Siegert *et al.*, 2004; Usup *et al.*, 2004). Smouldering within the peat substrate would propagate under a limited supply of oxygen therefore it is expected that charcoal would accumulate, thereby sequestering C (Mooney *et al.*, 2011). It is therefore hypothesised that charcoal is formed during a tropical peat fire and is present within the peat. To date there are no studies that have investigated charcoal content following contemporary tropical peatland fires, therefore this chapter proposes to address this gap in scientific understanding by quantifying the peat charcoal content following fire. If peat burning does generate significant quantities of charcoal this could have implications for C cycling in tropical peatlands prone to fires. In this chapter, the charcoal content of the peat is quantified using a method developed by Kurth *et al.*, (2006).The method is based on a chemical oxidation, which aims to remove non-charred organics, thus any remaining material is assumed to be resistant or charred OM. This method is used in combination with Py-GC/MS to confirm the suitability of this relatively new technique for charcoal analysis of peat soils. It is hypothesised that any samples containing significant contributions of aromatics and PAHs in their pyrolysates will also contain charcoal.

6.2 Water repellence and peat

In Chapter 4 it was shown that there were no significant differences in the composition of peat pyrolysates between subsurface samples of burnt and unburnt, drained peat. This suggests that during a peat fire, temperatures belowground are relatively low. This may in part be explained by the fact that dry peat is a poor conductor of heat (Robichaud *et al.*, 2000), thus only the upper layers are thermally altered. As tropical peat decomposes its OM composition becomes increasingly aliphatic. This aliphatic component predominately consists of hydrocarbon chains of alkene/alkane doublets. Such aliphatic molecules are often described as 'hydrophobic' due to their multitude of C-H bonds and absence of polar functional groups (Capriel *et al.*, 1997). An aliphatic OM composition may therefore suggest a peat or soil that is more hydrophobic than one with high concentrations of apolar molecules. Heating has long been thought to be induced by the polymerisation of organic molecules into more hydrophobic ones (Giovannini & Lucchesi, 1983). A study of heat induced water repellence in mineral soils revealed that water repellence was associated with a loss of hydrophilic compounds such as sugars, aromatic acids and short chain low molecular weight compounds. Water repellent soils have been shown to contain monocarboxylic acids <C12 and other polar compounds in the dichloromethane (DCM) soluble fraction (Atanassova & Doerr, 2011).

Water repellence in soils has various implications for ecosystem processes including; soil erosion, reduced infiltration, and preferential flows in hydrophilic areas of soil leading to leaching of nutrients (Andrieu *et al.*, 1996, Certini, 2005). Overall enhanced water repellence may lead to reduced availability of water and nutrients that are required for plant growth. Water repellence is often a short-lived phenomena, as heavy rainfall will penetrate even the most hydrophobic of soils (Wondzell & King, 2003), however during dry periods, e.g. shortly after a fire, it could have considerable effect on peat erosion and thus the fluvial C loss into drainage systems, i.e. there will be an enhanced surface water flow from hydrophobic peats.

There are many studies that report on the difficulty of re-wetting peat once it becomes dry (Andriesse, 1988, Robichaud & Hungerford, 1999). Similar to water repellence in soils, irreversible-drying of peat also leads to water molecules being repelled from the soil surface. Irreversible-drying is a term used to describe a peat that does not become wetted easily after intense drying. It is not currently understood how a peat soil that is already water repellent due to intense drying is further altered by burning. Results presented in Chapter 4 show that highly aliphatic OM observed in the 5-50 cm depth interval (as opposed to aromatic OM), suggesting that relatively low temperatures are reached at depth compared to the upper 5 cm, and therefore at this depth the peat may be more water repellent than at the surface. A study of peat fire temperatures in Kalimantan found that at the surface maximal temperatures were 350- 450 °C while in the subsurface they were between 50–100 °C (Hamada *et al.*, 2012). It is hypothesised that dry peat, i.e. peat in drained areas and particularly during the dry season, becomes water repellent. Water repellence will further be altered by fire, although this will be dependent on temperatures reached at different depths within the peat column. It is currently unknown if tropical peat, either intact, drained or burnt, is water repellent, therefore the results in this chapter also include data from an experiment to test the ‘potential water repellence’ status of a range of peat samples from within the chosen study area. ‘Potential water repellence’ as opposed to ‘actual water repellence’ measures the water repellence of dry peat under laboratory conditions rather than ‘in-situ’.

By investigating the water repellence of a range of intact, drained and burnt peat soil samples the aim of this investigation will be to determine if fire affects the degree of water repellence of tropical peat.

6.3 Methods: Quantifying charcoal in peat

The charcoal content in peat samples was quantified using a method adapted from that of Kurth *et al*. (2006) which was originally developed for forest mineral soils. As peat soils typically have a far greater organic content than mineral soils the method has been adapted in order to be more appropriate for peat soil (Section 6.3.1). The chosen method provides a relatively quick and cost-effective way to isolate charcoal from soils and involves strong oxidation of samples to remove non-charred material. Chemical digestion with a solution of hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) was conducted to extract charcoal from all other organic material.

6.3.1 Charcoal Extraction

Peat samples were freeze dried for 24 hours prior to analysis and ground with a pestle and mortar. Samples were then sieved through a 200µm sieve to remove any larger components of the peat such as leaves or woody fragments. 2g of sample was placed into a round bottom flask with known mass of boiling chips (≈ 0.2g). The exact mass of boiling chips was recorded in order to calculate a mass balance before and after the chemical digestion.

Each 2g peat sample was pre-digested in a round bottom flask with 40 ml of 30% w/v H_2O_2 (laboratory grade) and then gently boiled under reflux in a soxhlet extractor for 24 hours*. 20 ml of 1M HNO_3 was then added to the peat mixture before being returned to the soxhlet and heated for a further 16 hours. The solution was observed for effervescence. After 40 hours and the reaction had ceased the solution was left to cool. Any remaining residue was washed with distilled water by centrifuge and the solution was decanted until a neutral pH balance was achieved. The samples were left to air dry before recording their final mass. The mass of the boiling chips remaining in the sample was accounted for by difference. Any residual material remaining after chemical oxidation was considered to be charcoal. Values are initially reported as percentage of dry weight of peat. Table 14 includes a conversion to grams per kilogram of dry peat.

* The original method by Kurth *et al*. (2006) does not include a 24 hour pre-digest with H_2O_2. A longer digestion period was used due to the greater organic content of the samples compared to mineral soils.

6.3.2 Controls

In order to test the suitability of the method for analysis of charcoal a number of controls from an unburnt site were initially tested. A series of unburnt peat samples (Site 1), that were considered to not contain any charcoal, were mixed with varying proportions of charcoal standard (charcoal wood powder – Fisher CAS - 7440-44-0). Peat collected from Site 1 (Intact peat swamp forest) was used for the control experiment as it was assumed that peat from this location would not contain any charcoal. Peat/charcoal composites were subjected to chemical oxidation with HNO_3 and H_2O_2 (as per above method in 6.3.1). The difference between the mass of recovered material and the initial charcoal added was used to determine the systematic error and thus the accuracy of the method (Fig.45).

Table 10: Sample information for charcoal isolation control experiment. Three (2g) samples of varying proportions of peat and charcoal standard were mixed for each of the listed controls.

Control ID	Charcoal Standard (g)	Peat (g)	% Charcoal Standard
1	2.000	0.000	100
2	1.000	1.000	50
3	0.500	1.500	25
4	0.200	1.800	10
5	0.100	1.900	5
6	0.050	1.950	2.5
7	0.000	2.000	0

The charcoal contents of a range of peat samples from sites 1-3 were also quantified including a range of intact, drained and fire-affected areas. Table 11 lists the samples that were analysed for charcoal content. All samples were analysed in triplicate and means are presented with error bars representing one standard deviation of the mean.

Table 11: Sample details used in the charcoal analysis. In samples 1-4 D represents the 0-5 cm interval (surface) and B represents the 15-30 cm interval (subsurface).

Sample ID	**Site**	**Depth (cm)**	**Time Since Last Burn (yrs)**	**Fire Frequency**
SN	1	0-5	n/a	n/a
NC		5-15		
NB		15-30		
NA		30-50		
SF	3	0-5	1 month	1
FC		5-15		
FB		15-30		
FA		30-50		
1d	3	0-5	1.5 years	1
1b		15-30		
2d	3	0-5	4.5	1
2b		15-30		
3d	3	0-5	8.5	1
3b		15-30		
4d	3	0-5	14.5	1
4b		15-30		

6.3.3 Statistical Analysis

Linear regression was used to determine the significance of the relationship between charcoal standard added and percentage of material recovered after reaction with H_2O_2 and HNO_3. Three replicates were used for each sample and the mean values are presented. Error bars represent one standard deviation. One way and repeated measures ANOVA followed by Tukey's post hoc test was used to analyse any significance between sample means. Statistical tests were completed using Excel and Statistica ™ software.

6.4 Results

6.4.1 Charcoal recovery from peat and charcoal standard composites

There is a positive relationship between the mass of charcoal standard added to the control and the mass of material recovered after chemical oxidation. The percentage of recovered material increases with increasing addition of charcoal standard (Fig.44), however at all tested charcoal concentrations between 0 and 50 % the mass recovered was greater than the initial mass of added charcoal standard. Only the 100 % charcoal control resulted in a negative residual mass.

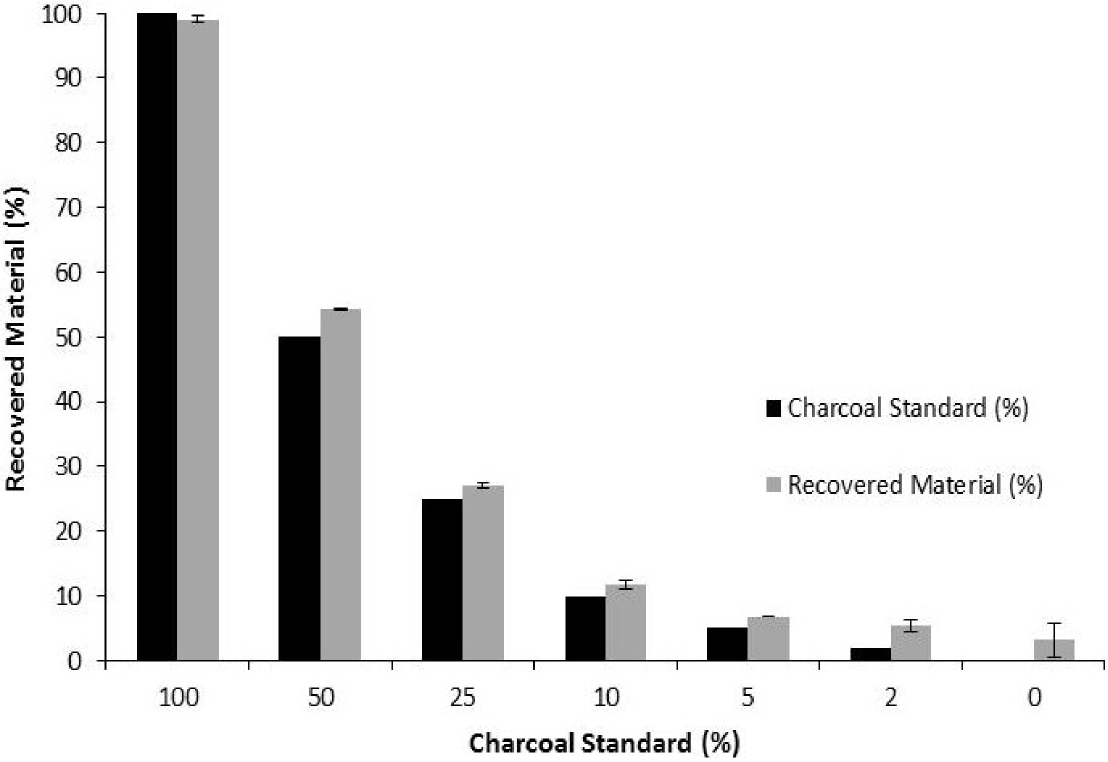


Fig.44: Mean charcoal recovered after chemical oxidation. 'Charcoal standard'

represents the starting percentage of charcoal. 'Recovered material' is the mean (n =3) recovery after chemical oxidation. Error bars represent one standard deviation of the mean (± s.d.)

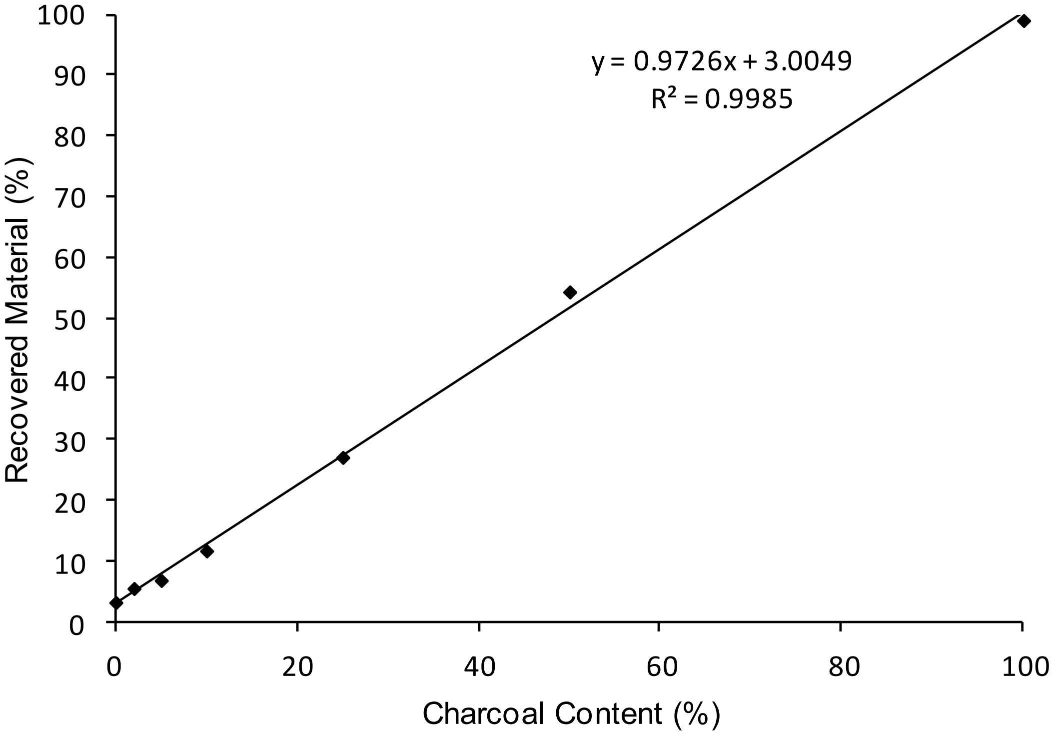


Fig.45: Linear regression analysis of results from control experiment, recovered material vs. charcoal standard concentrations.

There is a strong statistical relationship ($r^2 = 0.99$ $p < 0.05$) between the charcoal added to each peat sample and material recovered after chemical oxidation (Fig.45). However, at the lowest tested charcoal amendment this relationship is less convincing; i.e. for peat combined with between 0 and 10 % charcoal ($r^2 = 0.48$ $p > 0.05$). With the exception of the 100 % charcoal standard there was a consistent overestimation of charcoal content, ranging between + 1.25 to + 4.68 % of the known charcoal standard content. At high charcoal concentrations (≥ 25 %) the over estimation of charcoal was relatively low (< 9 % of original starting material), although at lower concentrations (≤ 2 %), the overestimation was more significant (Table 12). These results suggest that this method is most suitable for measuring peat containing high concentrations of charcoal. In samples that contained no charcoal there was a mean recovery of 3.19 (±

2.64) % of the original starting material. Overestimation of charcoal content at low or no charcoal amendments suggests that the method does not remove all non-charred organics. Therefore this uncertainty is taken into consideration when reporting charcoal concentrations in the remainder of this results section.

Table 12: Percentage of charcoal recovered from control samples amended with a range of charcoal standard. All masses are accurate to 3 decimal places.

Control (% Charcoal)	Run 1	Run 2	Run 3	Mean	S.D	Mean Difference	% Difference
100	98.80	99.70	98.80	99.10	0.520	-0.90	-0.90
50	54.35	54.54	54.21	54.37	0.166	4.367	8.73
25	26.810	27.04	27.46	27.10	0.330	2.103	8.41
10	11.980	10.88	12.21	11.69	0.711	1.690	16.90
5	6.805	6.758	6.910	6.82	0.078	1.824	36.49
2	5.885	4.435	6.185	5.502	0.936	3.502	175.08
0	0.150	4.920	4.500	3.19	2.641	3.190	319

The result of the control experiment revealed that charcoal content in peat is overestimated using this particular method. Although the samples were subject to strong oxidising conditions there is on average 3.19 % of the peat that is not removed from samples (not amended with charcoal) during the digest. It is likely that these samples contain the equivalent quantities of highly resistant OM, perhaps derived from cuticular waxes. Due to this systematic error introduced by the method the remainder of the data presented in this section will report the charcoal concentrations but the ~ 3.19 % resistant OM will be taken into consideration in order to not overestimate charcoal concentrations. Samples resulting in high reported values (> 25 %) of recovered material can be assumed to be mainly charcoal as at or above this value the overestimation is relatively low. At lower values (< 25 %), careful consideration is taken when reporting values that are a likely overestimation of charcoal contents which, nevertheless, indicate a proportion of highly resistant of OM. For the remainder of this chapter this chemically resistant fraction of peat OM will be referred to as charcoal, whilst it is recognised that part (~ 3.19 %) will be resistant OM rather than charcoal.

6.4.2 Charcoal estimates for recently burnt peat

Peat samples collected one month post-fire contained 64.94 (± 1.51) % charcoal in the upper 5 cm. Evidence from the control samples suggests that this material was predominately composed of charcoal although it is likely that ~ 3.19 % of the total peat sample is not charcoal but highly resistant OM. Thus one month post-fire, the peat contained ~ 61.75 % charcoal. In all subsurface peat samples (5 to 50 cm below the peat surface), concentrations of charcoal were significantly lower than the upper 5 cm of the peat column, ranging from 4.30 (± 2.081) to 4.67 (± 0.529) % and there was no significant difference between any of the recently burnt subsurface samples (ANOVA $p > 0.05$). Most of the material that was resistant to chemical oxidation at depth within the peat column not attributable to charcoal but to highly resistant forms of OM.

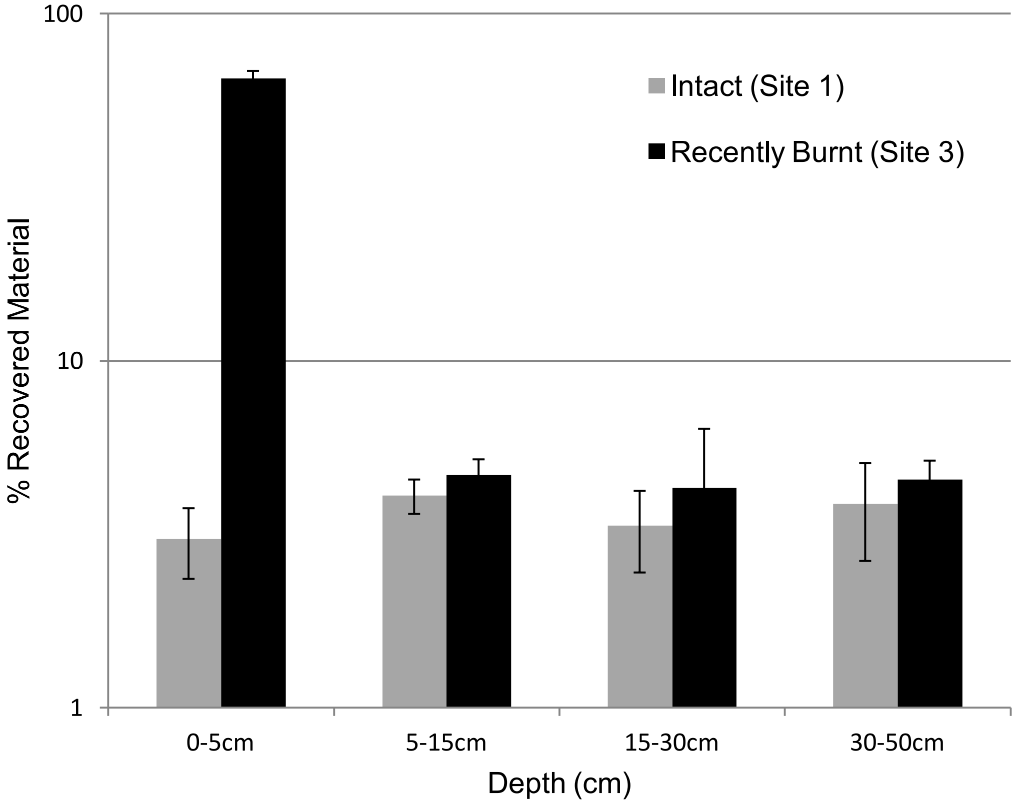


Fig. 46: Plot of intact and recently burnt (2009) peat samples. Mean (%) resistant material remaining after chemical oxidation is presented (charcoal and other resistant OM). Error bars represent one standard error of the mean. Please note vertical axis is a logarithmic scale axis.

The presence of charcoal in just the upper 5 cm of peat supports ideas discussed in Chapter 4, i.e. the Py-GC/MS data showed that the peat OM was not significantly altered beneath 5 cm but the upper 5 cm is considerably modified from its pre-fire composition. One month post-fire the pyrolysates of surface peat contained many chemical markers that indicated the presence of charcoal e.g. naphthalene, methyl naphthalene and biphenyl. Enhanced contributions of PAHs in burned compared with unburned peat samples further support the high charcoal estimates determined in the recently burnt surface peat.

Approximately 1.5 years after the 2009 fire (March, 2011), 5.42 % (± 0.49) of the surface peat was attributable to a combination of charcoal and resistant OM compared to and 6.82 % (± 1.83) in the subsurface peat (15-30 cm) (Fig.47). There was, therefore, a significant reduction in the concentration of recovered material between one month (64.94 ± 1.51 %) and 1.5 years post-fire (5.42 ± 0.27 %) ($p < 0.05$). There was no significant change in concentrations of charcoal and resistant OM in subsurface peat during the equivalent period. Between 1.5 and 14.5 years post-fire concentrations did not significantly vary in either the surface or subsurface peat samples. At 14.5 years post-fire, concentrations of 4.03 % (± 0.34) and 4.46 % (± 0.65) were determined in the surface and subsurface peat samples respectively. It can be concluded that one month after fire, the upper 5 cm of peat contained significant contributions of fire-deposited charcoal. No significant amounts of charcoal were deposited or formed in subsurface peat layers. At 1.5 years after the 2009 fire none of the initial deposited charcoal was detected in the upper 50 cm of peat, thus the presence of charcoal appears to be a transitory phenomenon.

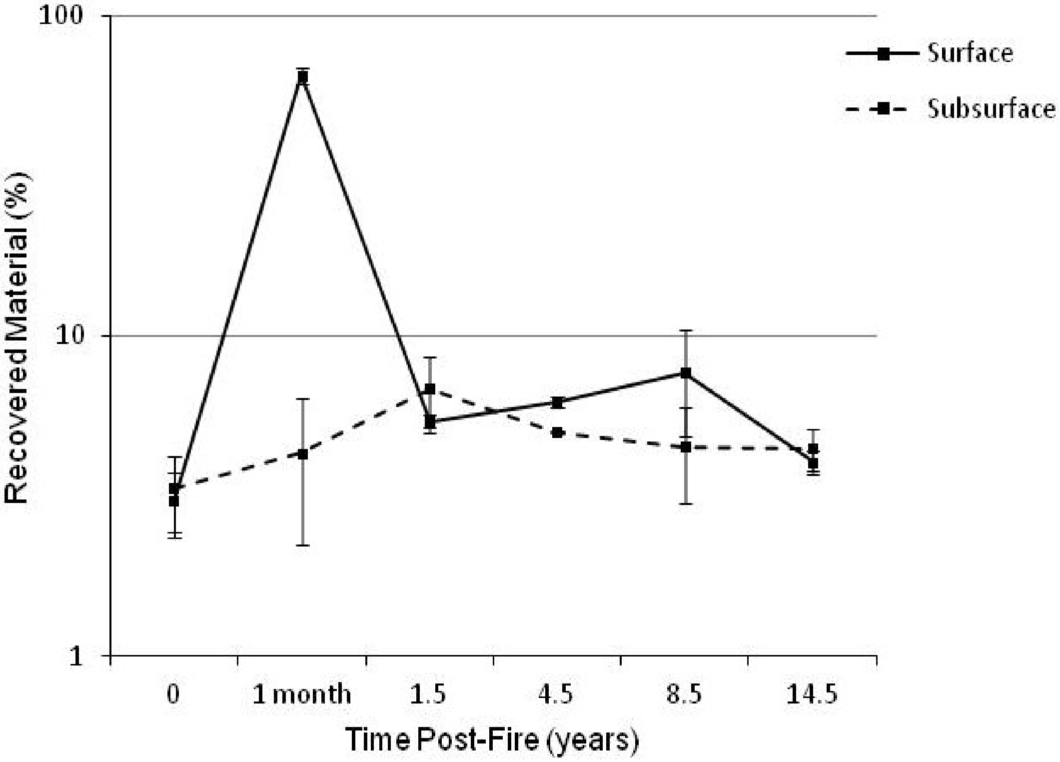


Fig. 47: Plot of mean recovered material (n=3) (%) against 'Time Since last burn'. '0' years represents peat from the intact PSF site (Site 1) that has not been burnt. Surface data represent the 0-5 cm depth interval. Subsurface data represent the 15-30 cm

depth interval. Error bars represent 1 standard deviation. Please note vertical axis is a logarithmic scale.

6.4.3 Chemical analysis of ‘resistant OM’

Py-GC/MS analysis of peat samples before and after chemical oxidation with H_2O_2 and HNO_3 reveals information firstly, about the composition of the peat OM after the reaction and, secondly, the differences between the results reveal the types of compounds that are resistant/non-resistant to such chemical treatment (Fig.48).

The material remaining after chemical oxidation was significantly different in its chemical composition. Even the burnt peat contained notable contributions of a variety of pyrolysis compounds including those derived from lignins, polysaccharides, aliphatics and aromatics. However, digesting these samples under strongly oxidising conditions removed most of the OM diversity and the material was dominated by aliphatics, namely alkenes and alkanes (Fig.48)

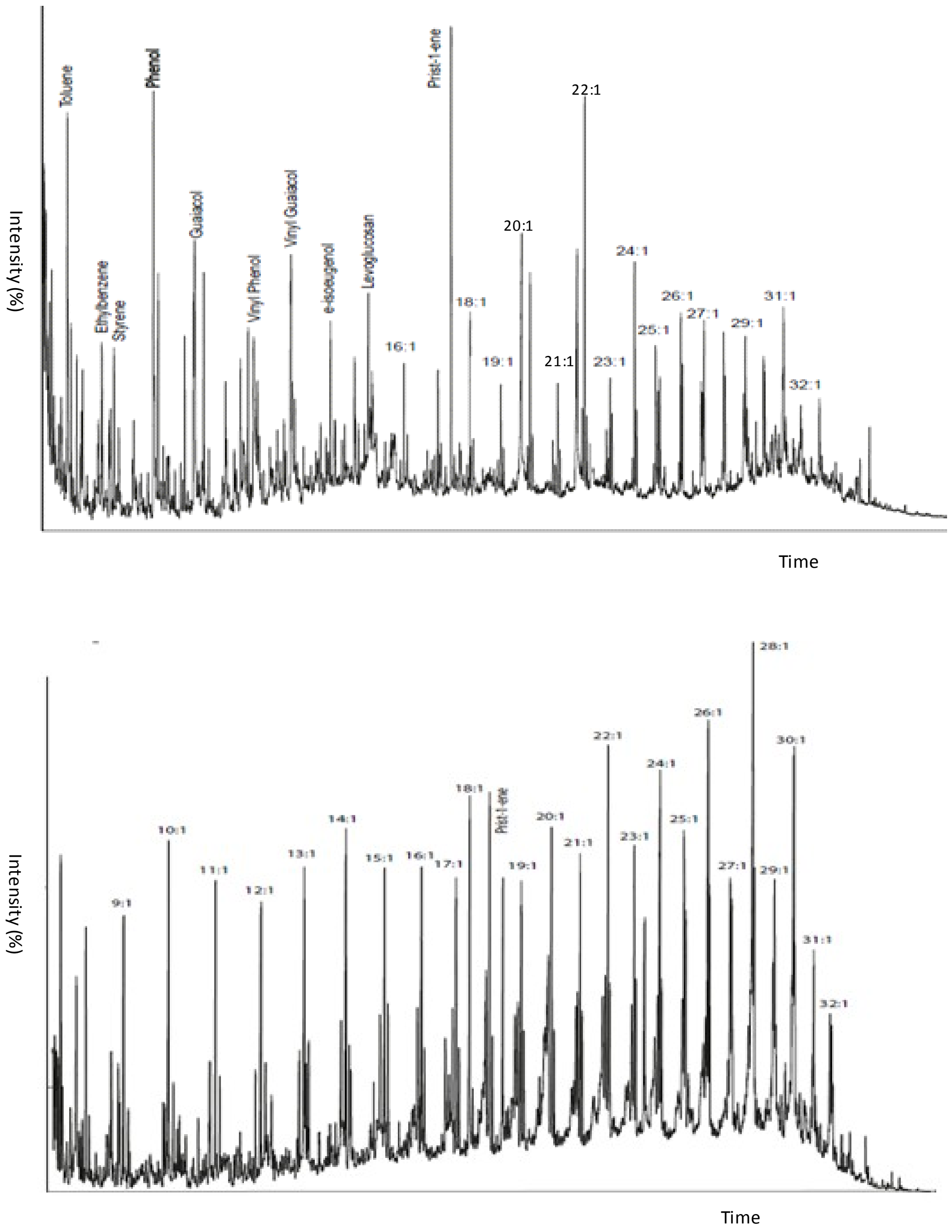


Fig. 48: Pyrograms of peat OM before (a) and after (b) treatment with nitric acid and hydrogen peroxide. This sample from Site 3 experienced burning 1.5 years prior to collection and had been burnt on four separate occasions.

Soil charcoal contents are typically expressed as units of either % of soil organic carbon (SOC) or kg/ha. By converting to units of mass per unit area the bulk density of the sampled soil can be considered. Bulk density varies between intact and degraded peatlands; therefore, any charcoal content should reflect this variation. Bulk density is higher in degraded peatlands than intact in peat swamp forest as peat is typically compacted when it is drained and deforested. Bulk density values were not obtained in this study but values have been taken from a recent study in the same study area and are presented in the table below (Jauhiainen *et al.*, 2012 *b*).

The following equation has been used to calculate 'resistant OM (kg/ha)':

Equation 2: Resistant OM (kg/ha):

$$Resistant\ OM\ (\mathrm{kg/ha}) = \mathrm{SChar} \times \mathrm{BD} \times \left(\frac{d}{10}\right)$$

Resistant OM (kg/ha) *= total charcoal and other highly resistant organic material*

SChar *= Soil charcoal*

BD *= Bulk density (values taken from published data Jauhiainen et al., 2012b).*

d *= Depth of soil (cm)*

Resistant OM in the upper 5 cm of peat is significantly greater one month after fire (64,615 kg/ha) than prior to fire (2,017 kg/ha) (Table 13). The bulk density of peat at burnt sites is higher than that of unburnt peat leading to a more concentrated amount of resistant OM detected shortly after fire compared with intact sites. One month after fire the total C (%) content also increases significantly in the upper 5cm from 47.81 % to 79.03 % suggesting that burning has removed significant quantities of other molecules such as oxygen and nitrogen from the OM. Charcoal C content can vary depending on the age and type of charcoal that is measured. Typically charcoal has a high C content e.g. 67 % (Abvien *et al.*, 2011) to 82 % (Olhsen *et al.*, 2009). High C content (79.03 ± 0.48 %) of recently burnt peat in itself further supports the finding that at one month post-fire the upper 5 cm of peat contains a significant quantity of charcoal. Approximately 8% of the SOC in the subsurface burnt peat was determined as 'Resistant OM'; this is not significantly different from the equivalent value for subsurface peat at intact sites (~ 6-7 %). This result suggests that no charcoal was detected in the subsurface peat layers.

Table 13: Results of conversion of percentage charcoal to quantities per unit area (kg/ha).* [*] *From Jauhaiainen et al., (2012b) * Material including charcoal and other material resistant to chemical oxidation using the described method.*

Sample	Depth Interval (cm)	Site	Total C (%)	BD (g/cm^3) [*]	Charcoal (%)	Charcoal (% of SOC)	Charcoal (kg/ha)
SN	5	Intact	47.81	0.132	3.057	6.39	2,017
NC	10		54.1	0.141	4.087	7.55	5,762
NB	12		55.24	0.141	3.340	6.05	7,064
NA	20		54.51	0.141	3.860	7.08	10,885
SF	5	Burnt	79.03	0.199	64.940	82.17	64,615
FC	10		56.28	0.151	4.673	8.30	7,056
FB	15		51.2	0.151	4.296	8.39	9,730
FA	20		56.61	0.151	4.544	8.03	13,722

6.5 Water Repellence: Methods

There are two well established methods currently in use to test the degree of water repellence of soils. These are, the ‘Water Drop Penetration Test’ (WDPT) and the ‘Molarity of an Ethanol Drop Test’ (MED). The MED test is more suitable for soils that have background levels of hydrophobicity as they provide data rapidly compared to the WDPT, therefore the MED test was selected on the basis that peat can be very hydrophobic when dry (Andriesse, 1988).

The MED test involved making up a series of ten ethanol solutions, with distilled water, of varying concentrations from 0 to 36 % ethanol (Table 14). Peat samples were freeze dried and ground using a pestle and mortar. A level 1 cm layer of peat was then placed into a petri dish. Using a dropping pipette three drops of the (weakest) ethanol solution were placed onto the surface of the peat sample. The drops were observed for any change in shape or infiltration for up to 5 seconds. If infiltration occurred within five seconds the process was repeated with the next most concentrated ethanol solution. This process was repeated with increasingly concentrated ethanol solutions until no infiltration was observed. The lowest ethanol concentration permitting droplet penetration by each sample was recorded and from this the degree of hydrophobicity was implyed. Previously published studies have utilised MED groupings to determine the water repellence of a soil and the categories constructed by Doerr *et al*. (1998) are used when presenting the following results (Table 14). These categories have previously been used in a range of key literature addressing the measurement of the water repellence of soils (Doerr *et al*., 1998, Letey *et al*., 2000, Roy and McGill, 2000)

*Table 14: MED categories. Adapted from Doerr et al., (1998) * Extra ethanol solutions in addition to those included in original study by Doerr et al., (1998).*

Class	% Ethanol	Hydrophobicity Class
1	0	Very hydrophilic
2	3	Hydrophilic
3	5	Slightly hydrophobic
4	8.5	Moderately hydrophobic
5	13	Strongly hydrophobic
	18*	
	21*	
6	24	Very strongly hydrophobic
	27*	
	30*	
7	36	Extremely hydrophobic

6.5.1 Results

The results presented are the ‘potential water repellence’ of dried samples. ‘Actual water repellence’ can only be determined using in situ field measurements.

Unburned peat (Site 1) was found to be water repellent at all tested depth intervals between 0 and 50 cm. (Fig.49). Corresponding hydrophobicity classes ranged between 5 and 6, equivalent to 18 and 21 % ethanol concentration. Peat from Site 1 can therefore be classified as ‘Strongly hydrophobic’ at the 0-5 cm interval and ‘Very strongly hydrophobic’ at the 5-15 cm, 15-30 cm and 30-50 cm intervals (Table 14). One month post-fire, the results showed that all background water repellence had been destroyed in the upper 5cm; this sample was classified as ‘Very hydrophilic’ (0 % ethanol). However, all subsurface (5-50 cm) peat samples were water repellent (Fig.48), particularly at the 30-50 cm interval, and were classified as ‘Very strongly hydrophobic’. MED values increase from 18 % before burning to 24 % one month after burning in the samples collected from 30-50 cm depth. Recently burnt subsurface samples have an enhanced water repellence compared to unburned samples, however this result was significant only at the 30-50 cm interval.

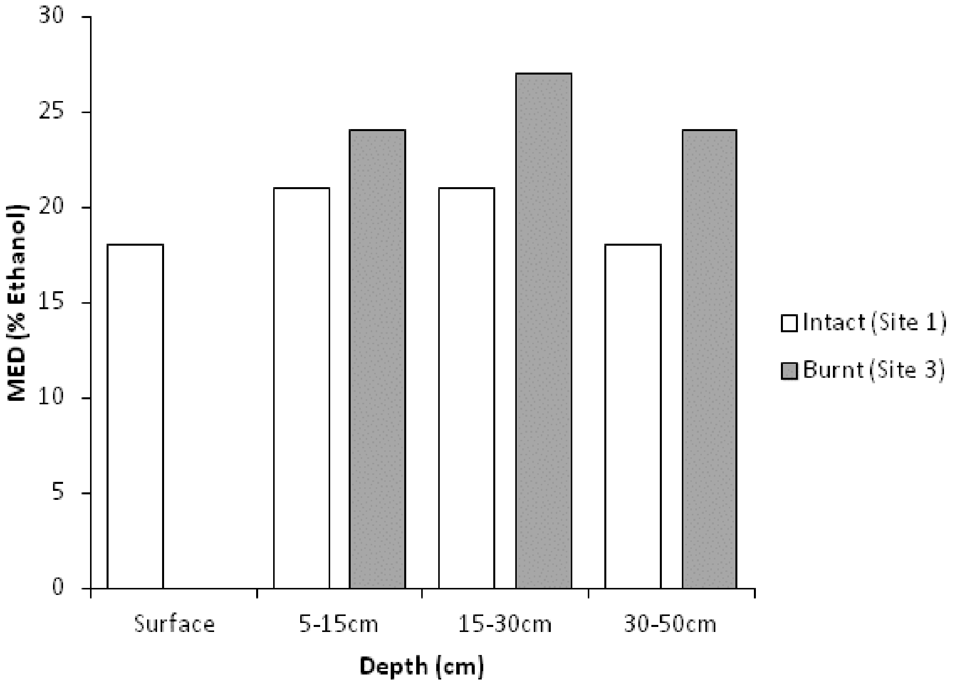


Fig. 49: Results of MED test of intact (Site 1) and recently burnt (Site 3) peat from the upper 50 cm of peat.

Drained peat was found to be more water repellent than inundated, i.e. intact peat, at all tested depth intervals (Fig.49) suggesting that drainage enhances water repellence. Although water repellence is destroyed in the upper 5 cm of peat when tested one month post-fire this is not sustained 1.5 years post-fire because the upper 5 cm of peat regains its water repellence character (Fig.50). The upper 5 cm of peat was classified as 'very strongly hydrophobic' 1.5 years after being burnt.

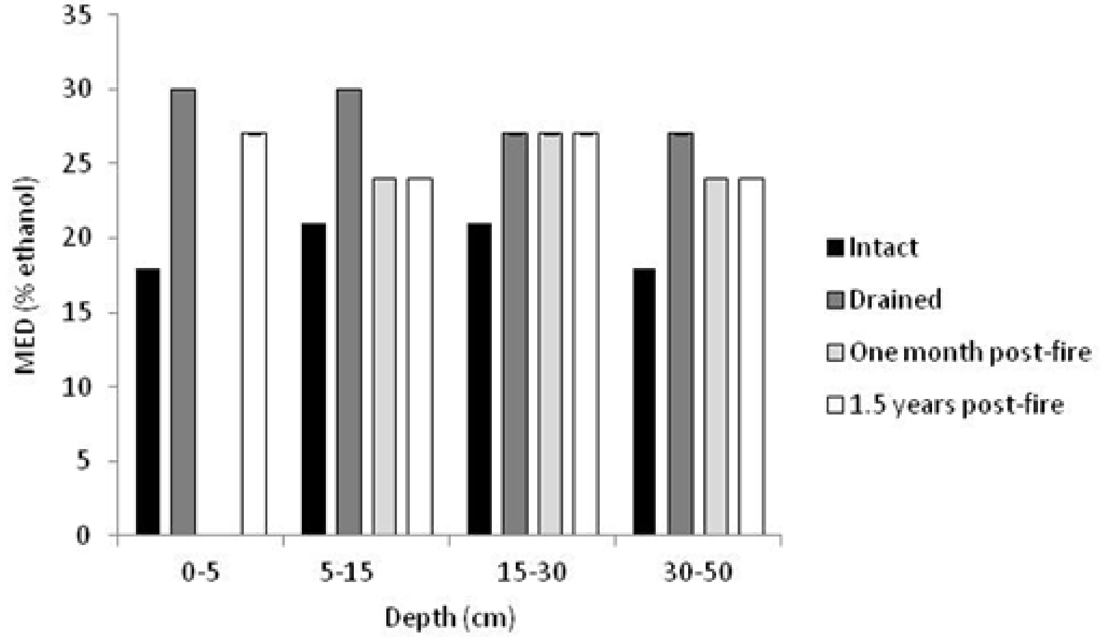


Fig. 50: Results of MED test from a range of samples collected in intact, drained and burnt sites. Each bar represents results in triplicates and errors bars represent one s.d of the mean.

MED values do not vary with regard to subsurface (5-50 cm) peat samples either one month or 1.5 years post-fire (Fig.50). Results from this analysis suggest that destruction of water repellence is a short-lived phenomenon observed at one month post-fire but after 1.5 years post-fire water repellence has returned to pre-fire levels. ‘Potential water repellence’ gives an indication of the water repellence status of peat, however ‘in situ’ measurements of ‘actual water repellence’ are likely to vary due to variable peat moisture contents. ‘Potential water repellence’ measures the difference in water repellence at different sites and reveals the water repellence status when the peat is dry. In situ measurements would be of little use for comparison between sites as samples have different water contents which will also vary according to time of year. Peat water content fluctuates between wet and dry seasons in tropical peatlands hence the decision to measure ‘potential water repellence’ rather than ‘actual water repellence’ was made to ensure comparability between samples.

6.6 Discussion

This chapter has presented results from charcoal and water repellence analyses. Both the concentration of charcoal and the degree of water repellence of peat samples have been affected by burning, findings that are supported by the changes observed in the peat OM composition following fire (reported in Chapters 4 and 5). Burning has led to formation of charcoal as well as elimination of hydrophobicity in the upper 5 cm of the peat, but between 5 and 50 cm in the peat column burning has not had these effects. Data presented in the previous two chapters indicate that fire has significantly altered the OM composition of the peat but only in the upper 5 cm, while of drainage has altered the OM composition in the upper 50 cm compared with peat OM from an inundated intact site.

6.6.1 Charcoal analysis (Critique of method and discussion of results)

Py-GC/MS data indicate that after burning peat OM may contain charcoal/black carbon; this was implyed from the presence of aromatics and PAHs which are commonly thought to be biomarkers of charred material (Kaal, 2009). Increased contributions of such organic molecules in peat pyrolysates one month after burning suggested that charcoal had been formed from woody material contained within the peat substrate. In this chapter, charcoal content was quantified using a previously established method formulated for mineral soils. However, the results revealed that this method does not fully remove all non-charred organics in tropical peat soils. H_2O_2 and HNO_3 appear to have a low removal efficiency of what can be regarded as the most chemically resistant OM (Fig.45), resulting in an overestimation of charcoal content (Table 12). This relatively low removal efficiency has been previously reported by other authors including Mikutta *et al*. (2005). Analysis of post-digest pyrolysates suggested this residual material was highly refractory OM (Fig.48). Plante *et al* (2005) also suggest that peroxide resistant soil OM is thermally more stable than the total soil OM and that this resistant material is therefore an inert pool of OM; this is an inherent property of charcoal. Thus although the results in this chapter do not provide a full quantification of peat charcoal content they do quantify the fraction of the peat that is highly refractory OM. The rationale for attempting to quantify the post-fire charcoal in peat soils was because of its relative resistance to biological degradation and its potential long term role as a store of terrestrial C. In this analysis the material that remained after chemical oxidation, the so called ‘resistant OM’, is a combination of both charcoal and the most refractory OM, both of which are likely to be a long term store of terrestrial C in tropical peats.

The method used in this analysis is reliable when measuring samples that have a high charcoal content, as was the case for the upper 5 cm of peat sampled one month post-fire. When testing the method on a range of samples with pre-determined charcoal concentrations a strong relationship was found between charcoal content and recovered material, i.e. when using samples amended with between 0 and 100 % charcoal standard (Fig.44). At low charcoal concentrations, however, there was a significant overestimation of charcoal content. The H_2O_2/HNO_3 solution did not fully remove all material from intact sites, so it is assumed that all of the samples contain a proportion (approx. 3.5 %) of refractory OM. This is not considered to be charcoal, but rather other ‘resistant OM’, and therefore the results presented here for charcoal content are semi-quantitative.

The precise nature of the ‘resistant OM’ material is not known, but it is clearly unaffected by strongly oxidising conditions. This is supported by the results from the py-GC/MS analysis that suggest only the most recalcitrant pyrolysis products are present in the peat OM following this chemical oxidation with H_2O_2/HNO_3 solution (Fig. 47). Combinations of charcoal and cuticular waxes such as cutin and suberin may be sources of such resistant OM. Cutin and suberin are ester bonded polymers composed of omega hydroxy acid units. Cutin comes from leaf cuticles (Boom *et al.*, 2005) and suberin from the periderm of barks and plant roots (Gardini *et al.*, 2006). Such lipids are known be resistant to acidic conditions and are highly stable (Derenne and Largeau, 2001, Köegel-Knaber *et al.*, 1992), but are readily saponified under alkaline conditions. Saponification breaks ester linked structures found in both cutin and suberin but does not depolymerise ether bonds in cutan. A selection of subsurface samples were saponified under reflux with 10% KOH for 2 hours. All samples were solubilised meaning that the resistant OM did not contain cutan but potentially both cutin and suberin were likely present. The presence of aliphatics such as the biopolymers cutin and suberin in peat soils may explain why ~ 3-4 % of the peat samples were not removed by strongly oxidising conditions presented by the H_2O_2/HNO_3 solution.

The higher concentrations of 'resistant OM' found in subsurface burnt peats, compared with subsurface intact peats, could be explained by differences in the proportions of these waxy biopolymers (cutin and suberin) rather than of charcoal. In other words, the differences, albeit not statistically significant, could be due to cutin and suberin being selectively preserved in decomposed peats. Upon observation is was clear this material was not of charcoal origin due to its pale appearance thus supporting the idea that this material is some other type of highly resistant OM.

The results of this analysis enable acceptance of the hypothesis that charcoal is formed during a tropical peat fire and that it is present within the peat. However, charcoal was only present in the upper 5 cm layer of the peat and was not formed in subsurface layers. High concentrations of 'resistant OM' (64.94 ± 1.51 %) were found in samples collected from the upper 5 cm of peat one month after a fire in 2009. It is assumed that this material was predominantly composed of charcoal. Below 5 cm there was no significant difference in resistant OM concentration between intact and burnt peat and therefore it is likely that no charcoal was formed at depths of between 5 and 50 cm. Relatively high temperatures (350- 450 °C) are typically reached during peat fires in the upper 10 cm of peat (Hamada *et al.*, 2012). Maximal temperatures of 275 °C were recorded in the surface layer of peat in an experimental plot during a fire in 2002 (Fig.51). At 10 cm depth the temperature peak was much lower at 90 °C and reached only 40 °C at 40 cm depth (Usup *et al.*, 2004). Charcoal typically forms as a product of incomplete combustion. Charcoal will form when belowground woody material is heated between 200 and 250 °C under oxygen limited conditions thus resulting in a pyrolysis reaction (Rein, 2009). Higher temperatures of >300 °C and a plentiful oxygen supply, as has been observed in surface peat fires (Hamada *et al.*, 2012, Usup *et al.*, 2004), results in an oxidation reaction and is less conducive to the formation of charcoal. This complete combustion is the main source of CO_2 and CO emissions from peat fires (Rein, 2009).

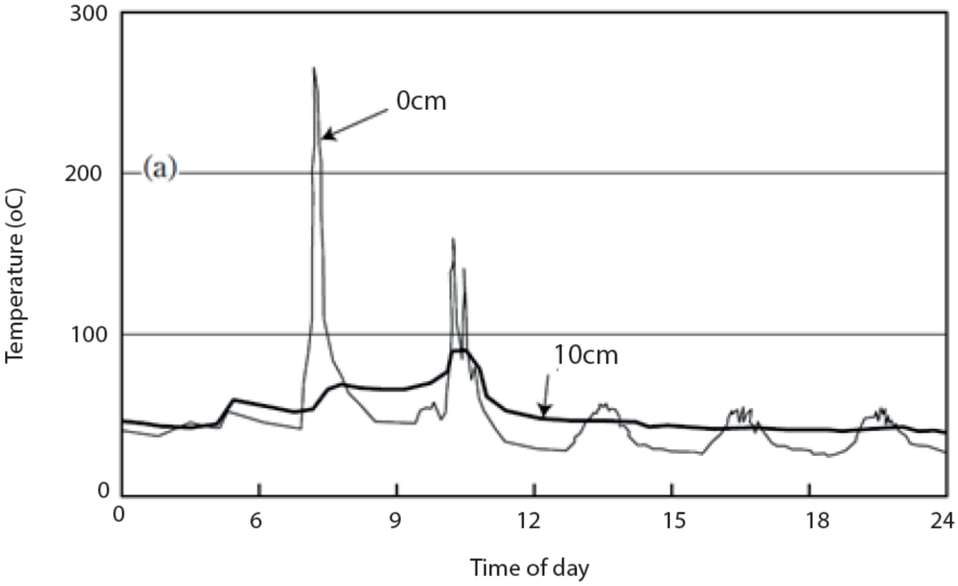


Fig. 51: The temperatures of peat layers during a fire event from 21st to 26th August 2002 in Kalampangan, Central Kalimantan, Indonesia. Data shows temperatures at the ground surface and 10cm depth on 22nd August 2002. Source: Usup et al., (2004).

Concentrated charcoal stocks detected in the upper 5 cm of peat that were formed during the 2009 fire, are no longer present 1.5 years post-fire. Almost all the charcoal that was detected one month post-fire had been lost from the site between one month and up to 1.5 years post-fire. Mechanisms that cause charcoal loss from peat are unclear. Traditionally black carbon including charcoal is believed to have long residence times in soils (Skjemstad *et al.*, 1996) which may be in the order of thousands of years (Lehmann *et al.*, 2008), although more recently it has been established that fire derived charcoal is not as stable as initially thought (Zimmerman *et al.*, 2010, Kuzyakov *et al.*, 2009). Biological degradation, physical fragmentation and chemical oxidation can all cause a loss of black carbon (Hammes *et al.*, 2008). It seems unlikely however that charcoal could be lost by such mechanisms over only a 1.5 year period. A more plausible explanation is that the charcoal has been lost by erosion facilitated by heavy and persistent rainfall during the wet season that followed the 2009 fire; a similar phenomenon has been observed in other environments (Johansen *et al.*, 2001, DeLuca and Aplet, 2008). This deduction is further supported by the results of the water repellence analysis; the upper 5 cm peat layer (charred layer) was classified as hydrophilic. All background hydrophobicity, a characteristic of unburned peats (Fig.48), was destroyed by the fire. High temperatures reached at the peat surface (> 300 °C) provide an explanation for the formation of this readily wettable, charred peat surface. Many studies have reported that hydrophobicity is destroyed above 280 °C (Doerr *et al.*, 2000) in mineral soils. Results indicate that this is also the case in peat soils (Fig. 51).

Reported charcoal concentrations are highly method-dependent (Preston and Scmidt, 2006). Quantification may be an order of magnitude different depending on the method that is used (Hammes *et al.*, 2007). Before comparing results of this analysis with those in the literature consideration of the method must be made. There are no comparable studies of black carbon or charcoal in tropical peatland environments, however a charcoal study from temperate upland peats in the UK Pennines reported values of 4.3 % black carbon/CC (CC= Carbon Consumed) or 6.35g C m^{-2} (Clay and Worrall, 2011). This is the equivalent of 635 kg C ha. However this result is expressed as a percentage of the total CC (from the above-ground vegetation only), during a fire (reporting of the BC/CC ratio is derived from a method first proposed by Forbes *et al* (2006)). Between 5 % and 3 % black carbon/CC is reported in African savannas fires. This method involves calculating the pre and post fire biomass and determining the proportion of the pre-fire biomass that is converted into charcoal and subsequently added to the soil surface during a fire. This method does not however consider below-ground concentrations; if the peat itself was to ignite then these charcoal estimates could be considerably higher. 3.2 % of the pre-fire vegetation was consumed during a fire in deciduous scrub-oak forest in Florida and it was estimated that 0.14 kg BC m^{-2} was contained within the upper 30 cm of soil (Alexis *et al.*, 2007). The results in this chapter do not consider the charcoal that is added to the peat from burning of the aboveground vegetation. It is likely that such charcoal addition would be highly dependent on the nature of the vegetation that is being burnt, i.e. woody vegetation would result in greater charcoal addition than non-woody vegetation.

Many studies report black carbon concentrations as a proportion of the SOC. For example, average black carbon concentrations from A-horizons in soils from Queensland, Australia ranged from 31.5 to 82 % of SOC. Sandy soils near to Darwin, Australia contained significantly less charcoal (13.6 % SOC) (Lehmann *et al.*, 2008). Chemical oxidation followed by ^{13}C NMR revealed mean black carbon concentrations of 31.3% of SOC in dry tropical forests of Costa Rica. (Lorenz *et al.*, 2010) However, use of a thermal oxidation method (CTO-375) revealed considerably lower black carbon concentrations of 3.7 % of SOC from the same site (Lorenz *et al.*, 2010). Conversely, black carbon concentrations may be reported in a number of other ways; per unit mass of dry soil, e.g. mg/g, or mass per unit area, i.e. kg/ha. Between 1,000 and 5,000 kg/ha black carbon was found in Sierra Nevada woodland, California (Mackenzie *et al.*, 2008).

It is useful to present results as a mass per unit area as concentrations are likely to differ significantly depending on the bulk density of a soil. Higher bulk density in drained and burnt peatlands compared to unburnt undrained sites results in higher concentrations of charcoal within the peat of the drained and burnt sites. The mass of charcoal per hectare is calculated and the published bulk density values for the unburnt undrained and burnt sites are included in this calculation. One month post-fire approximately 64,615 kg/ha of charcoal is present in the upper 5 cm of peat compared to 2,017 kg/ha in the unburnt, undrained site. When results are presented using bulk density values the differences between sites become more significant.

6.6.2 Water Repellence Analysis

All the peat samples that were tested, with the exception of the upper 5 cm of peat from Site 3b, were hydrophobic. Only the 0-5 cm peat samples collected one month post-fire were classified as 'hydrophilic'. Therefore, burning does not alter the water repellence status of tropical peat other than in the upper 5 cm where it is destroyed. High temperatures (>300 °C) were likely obtained in this upper layer of peat during the fire, causing destruction of any background water repellence. Water repellence in mineral soils has frequently been reported to be enhanced as a result of burning or heating (Doerr *et al.*, 2000), however such soils may not have been hydrophobic prior to burning as is the case with the peat samples used in this analysis. Hydrophobicity in peats is a well documented phenomenon and many authors describe the difficulties in re-wetting peats once they have become dry (Andriesse, 1998). Prior to this analysis it was not known if tropical peats would become more or less hydrophobic when subjected to heating during a fire. One month post-fire the peat surface (0-5 cm) was hydrophilic surface thus wettable and the peat at would become readily saturated by rainfall. It is hypothesised that the strongly hydrophobic subsurface would inhibit infiltration, thereby enhancing erosion of the peat surface (upper 5 cm). Fig.52 illustrates the changes in hydrophobicity when peat is drained and then burnt. High charcoal content in the upper 5cm of burnt peat is associated with hydrophilic material; therefore, any lateral erosion that does occur will lead to pyrogenic (highly stable) forms of C being lost to adjacent waterways. This may be reflected in the high dissolved and particulate organic C content recorded in canals draining peatlands in the MRP area immediately after the 2009 fire (Moore, 2011; Moore, unpublished data).

Background water repellence in drained peats is caused by changes to the OM structure that occur over a long period of drying, in particular an increase in apolar molecules such as hydrocarbons and amino acids relative to polar molecules (Giovannini and Lucchesi, 1983). An enhancement of apolar molecules relative to polar molecules was observed from the results of the Py-GC/MS analysis of peat samples from Site 2 (Chapter 4). Long term drying and subsequent decomposition of the peat depletes many of the polar molecules in the OM leaving behind the typically water repellent apolar compounds (aliphatics). Water repellence can be strongly correlated with OM content (Dekker and Ritsema, 1994) thus organic soils such as peats are typically highly water repellent. This further supports the result found in this analysis as the upper 5 cm of peat in Site 3 because this peat was likely burnt at relatively high temperature and long enough for the organic substances responsible for water repellency to be consumed by the combustion process (DeBano *et al.*, 2000) thus the peat became hydrophillic.

Critical soil moisture is defined as the point at which soils change from a wettable to a repellent state and *vice versa* (Dekker and Ritsema, 1994). Critical soil moisture contents vary considerable depending on the type of soil. In Portuguese sandy loam and loamy sand forest soils water repellence is absent when soil moisture content exceeds its critical soil moisture content of 28% (Doerr and Thomas, 2000). Critical moisture contents were found to be greater (34 – 38 %) in peat clay and clayey peat soils in the Netherlands, (Dekker and Ritsema, (1996). It is not currently known what the critical moisture content may be for Indonesian tropical peat, however, when air-dried all the samples used in my study were found to be hydrophobic. Water repellence is not a feature of the peat in inundated PSF sites as the peat remains very wet all year round, (likely exceeding the critical moisture content) due to the naturally high water table, therefore the peat is does not become dry and so water repellence has no hydrological or geomorphological significance. Further investigation is required to determine the critical peat moisture content of tropical peats so that the effects of water repellence in heavily drained peatlands can be better established.

There are a large number of studies that have been published on the degree of water repellence of burnt soils, most of which are from dryland environments. Most report an increase in water repellence shortly after burning, however this is a transient phenomenon. Ravi *et al* (2007) report 'Molarity of an Ethanol Drop test' values of 3 M (molarity) ethanol for prairie grasslands in Kansas, USA, but after 76 days, pre-fire levels were re-established. Burning does not always enhance soil water repellency. Doerr *et al*. (1998) found that forest soils (*Pinus pinaster*) in Portugal were stongly hydrophobic following fire (MED test, >24 %), however this was not siginificantly different from values for unburnt soils. Both burnt and unburned soils were found to be hydrophobic and fire had no affect. Few studies exist from tropical environments, however a study of Amazonian pastures (Johnson *et al*., 2005) states that the upper 1 cm of soil becomes strongly hydrophobic following burning but hydrophobicity rapidly declines with time post fire and at one year post-fire the soil had become hydrophillic.

As peat samples from the study area had a degree of background water repellence, as measured by potential water repellence, drainage and drying of the peat may have already had considerable hydrological and geomorphological impacts. When peats become dry and if hydrophocity persists, infiltration may be inhibited (Fig.52). This is likely to have implications for delivery of water and solutes needed for vegetation growth. Burning leads to the formation of a hydrophilic upper 5 cm of peat, observed one month post-fire, which could enhance surface erosion. The issue of the change in hydrophobicity in tropical peatland is probably only a concern during periods of very low rainfall in drained areas or shortly after a fire. During the wet season and when peat is inundated the critical soil moisture content is likely to be exceeded thus drained and burnt peats are would be readily wettable.

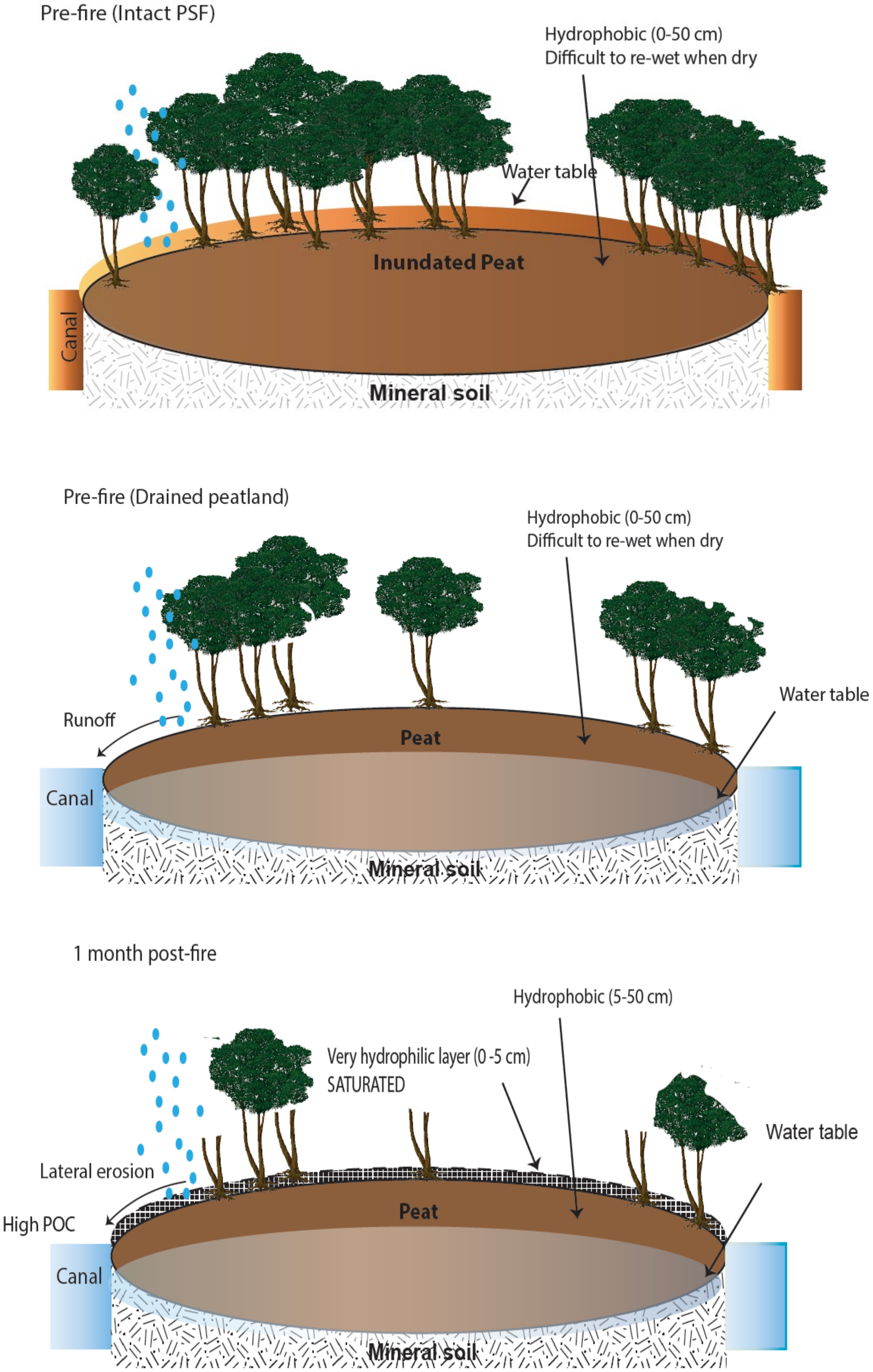


*Fig.52**:** Schematic diagram of a peat dome illustrating the changes in the degree of*

water repellence following drainage and fire in Site 3.

Summary

This chapter investigated the implications of a thermally altered OM composition for some physical properties of tropical peat soils. Charcoal content and water repellency were measured and in both sets of analyses the results were spatially and temporally variable. The key findings from this chapter are:

- Charcoal contents were very large one month post fire in the upper 5 cm of the peat (64.94 ± 1.51 %) column compared to peat samples from an unburnt site (3.19 ± 2.64 %)
- No significant quantities of charcoal were detected between 5 and 50 cm below the peat surface from either unburnt or burnt sites.
- Charcoal was not detected at 1.5 years post-fire throughout the upper 50 cm peat column.
- Approx (3.19 % ± 2.64 %) of the peat OM was comprised of a highly resistant form of organic material possibly indicating the presence of cutin.
- When air-dried, all peat samples from all sites displayed hydrophobic properties with the exception of the samples from the upper 5 cm of peat from the recently burnt site that were shown to be hydrophilic.
- Peat samples from Sites 2 (drained) and 3 (drained and burnt) were more strongly hydrophobic at 1.5. years post-fire than the peat samples from Site 1 (intact).
- At 1.5 years post-fire, the upper 5 cm samples at Site 3 were no longer readily wettable but 'very strongly hydrophobic'.

Chapter 7

7.0 Discussion and Synthesis

This study has demonstrated that burning modifies the OM composition of tropical peat although the extent of this modification varies dependent on depth within the peat profile and the time that has elapsed since burning. It is clear from the findings that fire and drainage are having a significant impact on the biogeochemical characteristics of the upper peat substrates within the study area.

This final thesis chapter provides a synthesis of all of the data and discussion points made in previous results chapters (4, 5 & 6) in order to address the research questions and contextualise the findings within the relevant literature. A discussion of the wider implications that the results could have for C cycling in tropical peatlands in the Southeast Asian region will also be provided. This project has provided an initial insight into the role that fire plays in determining the geochemistry of tropical peat but there still remain many unanswered questions, thus this thesis provides a platform for further research. Recommendations for future research directions are made in Section (7.5).

The overall aim of this research was to address the following research question:

How does fire affect the biogeochemical composition of tropical peat soils?

The general purpose was therefore to gain an initial understanding of how fires in an area of disturbed (drained and burnt) tropical peatland in Indonesia alter a range of biogeochemical characteristics of the peat soils and to explore the implications of the results for various ecosystem processes, including the tropical peatland C cycle. Due to the disproportionately large store of C in tropical peatlands in comparison with their land area, even a small alteration of C forms may have implications for the global C balance. Differences in OM composition between fire affected and unaffected sites could also potentially be used for monitoring the post-fire recovery of tropical peat.

This thesis presents some of the first biogeochemical data for fire-affected Southeast Asian peats and provides findings that are complementary with the wider scientific research that has previously been conducted in these environments.

The following specific research questions have been addressed within each of the results chapters:

1) ***What are the short-term effects of fire on tropical peat OM composition? (Chapters 4 & 6) (Discussed in Section 7.2).***
2) ***Do different fire regime variables, such as 'fire frequency' and 'time since last burn', influence the biogeochemistry of tropical peat soils? (Chapters 5 & 6) (Discussed in Section 7.3).***
3) ***To what extent is charcoal deposited and/or formed during a tropical peatland fire? (Chapter 6) (Discussed in Section 7.2 and 7.3).***
4) ***Does fire enhance water repellence in tropical peat soils? (Chapter 6) (Discussed in Section 7.2 and 7.3).***

As fires have become a more frequent form of ecosystem disturbance over recent decades in areas of tropical peatland (Siegert *et al*., 2004, Page *et al*., 2009, Hoscilo *et al*., 2011), it has become critical to determine the nature of such changes on belowground organic stores (peat OM). The biogeochemical composition of soils can influence physical, chemical and biological belowground processes, all of which, within the tropical peatland context, will influence the ability of disturbed peat swamp forest to regenerate following fire. In the study area, burning typically occurs in areas that have been subject to drainage since this provides a fuel load of dry, surface peat. In addition to increasing the risk of fire, drainage of the peat facilitates aerobic decomposition which also results in considerable chemical changes to the peat OM (Chapter 4). In the study area, areas of peatland that have been affected by burning have formerly undergone chemical change due to drainage. Consequently a further research question has been addressed by this thesis:

5) ***To what extent does drainage alter the OM composition of tropical peat? (Chapter 4) (Discussed in Section 7.1)***

Tropical peatlands are only at risk of fire if they have been first drained. Therefore the first section of discussion (7.1) reviews the findings from the drained unburnt site (Site

2) compared to the undrained unburnt site (Site 1). Following this (Section 7.2-7.4) a discussion of the effects of fire is presented, thus allowing the effects of drainage and fire to be differentiated from each other.

Py-GC/MS data allow inferences to be made regarding the composition of peat OM. This is a consequence of the GC amenable fragments that are produced from the thermal degradation of the original starting material and which are chemical markers for the original macromolecules. Use of such Py-GC/MS data, along with data from elemental analysis, allows deductions to be made about the chemical composition of the peat OM. There are no previous studies that have made use of Py-GC/MS as a tool to characterise tropical peat OM; in addition, the number of published studies on the impact of burning on soil OM is limited, although recently expanding (Neff *et al*., 2005; Buurman *et al*., 2006; Knicker *et al* 2007; Kaal *et al*., 2008; Schellekens *et al*., 2009; Campo *et al*., 2011; De La Rosa *et al* 2012). The benefits of Py-GC/MS are that it is a relatively rapid and reproducible technique that provides highly detailed chemical data at the molecular level. When samples from different sites are analysed inferences can be made about the composition of the original peat OM and thus variations between different sites can be described.

7.1 Effects of peat drainage.

In the study area, the peat has only burnt in areas that have previously been drained. Thus the chemical changes that are observed in peat OM, as indicated from peat sample pyrolysates, following fire are a consequence of both drainage and burning.

The water table in the former MRP area is considerably lower, (annual average water table depth between 2002 and 2009 was 53 ± 11 cm (Hirano *et al*., 2012)) than that of the undisturbed PSF (a maximum of 40 cm below the surface during the dry season but at or above the surface during the wet season (Takahasi *et al*., 2003)). Therefore, prior to burning, the upper 50 cm of peat in the MRP had been exposed to aerated conditions for more than a decade (since the area had been drained for the MRP), allowing aerobic decomposition to take place in the uppermost layers of peat. Thus the differences in OM composition that have been detected between the intact and the drained or drained and burnt peat samples, such as the reduction in polysaccharides, including levoglucosan, methylfurans and acetylfurans alongside enhanced concentrations of aliphatics, are a result of disturbance both by drainage and by fire. In order to differentiate between the chemical changes induced by these two events, peat samples from a drained but unburnt area were analysed. Analysis of pyrolysates from these samples enabled distinctions to be made about the chemical alterations induced solely by drainage.

Generally, drainage leads to a shift from peat with a highly diverse OM and a considerable presence of labile components, to peat with an accumulation of recalcitrant compounds such as aliphatics, and aromatics. An overall decline in polysaccharides has been suggested as a parameter that could be used to judge the degree of aerobic decomposition in peats (Schellekens *et al.*, 2009). The results presented in this thesis agree with this; polysaccharide content was reduced across all analysed samples from drainage-affected peat (30.8 – 22.6 % at 0-5 cm; 24.6 – 6.9 % at 30-50 cm), indicating that significant aerobic decomposition was taking place within the peat column.

Although lignin decomposition is generally regarded as an aerobic process (Kuder and Kruge, 1998), polysaccharides are more readily decomposed (in either aerobic or anaerobic conditions) than lignins (Beguin and Aubert, 1994, Leifield *et al.*, 2012). Anaerobic conditions therefore favour the preservation of lignin (typically classed as a relatively labile component of OM). This was confirmed by the results of the analysis of peat samples from the intact peat swamp forest (Site 1), where anoxic conditions exist in the upper peat for most of the year (Jauhiainen *et al.*, 2005) and where the proportions of lignins do not significantly differ in the upper 50 cm of the peat column (36.1 – 35.2 %). Lignin molecules have long been regarded as recalcitrant components of OM if the soil is in an anoxic state (Zaccone *et al.*, 2008), explaining why there are significant contributions of lignin in the samples extracted from Site 1. In addition, the continual addition of fresh organic material from aboveground vegetation is detected, in the form of high relative contributions of both lignins (36.1 ± 9.1) and polysaccharides (30.8 ± 6.7), in the upper 5 cm sample pyrolysates from this study location. Comparison with peat samples collected at a drained location in Block C (Site 2), demonstrated that when the peat water table is lowered (water table depth 1.57 ± 0.3 m) that enhanced aerobic decomposition is allowed to proceed and lignins are then rapidly decomposed. It should also be noted that the peat soils in the study area are highly acidic (an average pH of 3.0 ± 0.3 was measured in the upper 100 cm of peat from at Site 1 (Page *et al*., 1999)) which may also encourage the rapid degradation of lignin compounds (Buurman and Roscoe, 2011). As a consequence of enhanced drainage, a reduction in lignin contribution was observed in sample pyrolysates from the upper 5 cm of peat from drained locations (36.1 (± 9.1) – 10.1 %). This trend was also apparent in all analysed subsurface peat sample pyrolysates, at the 15-30 cm depth interval, with relative lignin contribution decreasing from 29.05 (± 4.1) % to 7.0 % following drainage. These results support the idea that lowering of the natural water table enhances the degree of aerobic decomposition in the upper 50 cm of peat accompanied by a reduction in the most labile components of the OM. Clear differences in pyrolysis products of saturated and unsatureated peats has also been found in boreal regions. Following thermally assisted hydrolysis and methylation of peat cores from the Ryggmossen peatland, Sweden there were clear differences in Spagnum acids observed in oxic compared to anoxic peat layers, (methylated 4-isopropenylphenol dominated samples from anoxic conditions) (Swain and Abbott, 2013).

Py-GC/MS data for samples from the drained forest site indicates that lowering of the natural water table has significant effects on peat OM composition. The reduction in relative contributions of both polysaccharide and lignin-derived pyrolysis products coupled with an increase in relative contributions of aliphatic (54.9 ± 14.1 %), aromatic (5.6 ± 1.6 %) and PAH-derived (1.6 ± 0.3 %) pyrolysis products indicate that the peat OM has become more recalcitrant as a result of drainage. This increase in recalcitrance is likely to have implications for C cycling in drained tropical peatlands (see Section 7.4).

7.2 Short term effects of fire on tropical peat organic matter composition

The peat sample pyrolysate data indicate that there are significant chemical changes in peat OM shortly (one month) after a fire; these changes are particularly observed in the upper 5 cm of the 50 cm peat profile. The Py-GC/MS data indicate that peat OM becomes more recalcitrant when burnt. A shift occurs from a highly complex assemblage of compounds in the unburnt peat, likely to have been derived from a range of different organic sources, to a less diverse range of compounds in the recently burnt peat. These results provide clear evidence that fires in the study area are altering the chemical composition of peat OM. This result is in agreement with other published studies including those of González-Pérez *et al*. (2004) and Schellekens *et al*. (2009). Both of these studies report a similar trend for soils and peats, respectively, subject to fire and, in particular, a reduction in the most labile components and accumulation of recalcitrant components. Shellekens *et al*. (2009) also suggest various parameters that may indicate the presence of charcoal in soil and therefore the incidence of fire. These include an overall reduction in lignin and polysaccharide compounds coupled with an increase in PAHs, including naphthalene and benzofurans. The results of this study comply broadly with many of these proposed parameters. There was a polysaccharide reduction (from 22.6 to 0.1 ± 0.1 %); a lignin reduction (from 10.1 to 0.8 ± 1.2 %) and an increase in PAHs (from 1.2 to 5.5 ± 2.6 %) observed in the upper 5 cm of peat one month post fire.

The overall contributions of polysaccharides and lignins are believed to be reduced due to the utilisation of oxygen molecules during the combustion process which results in a loss of methoxy-groups. Polysaccharides and lignins were also observed to be significantly reduced in burnt Andalusian Mediterranean forest soils (González-Pérez *et al*., 2002). A relative reduction in o-alkyl and di-o-alkyl structures, which are typical of compounds derived from lignin type compounds, identified in peat sample pyrolysates one month post fire, was also reported by Certini (2005) and Tinoco *et al*. (2006) in soil OM that had been subject to burning.

Components of the OM such as polysaccharides and lignins are typically regarded as the most thermally-labile and their transformation in the peat OM one month post-fire resulted in an accumulation of aromatic and aliphatic components. This is commonly considered as an effect of fire on soil OM (Almendros *et al.*, 2003; Neff *et al.*, 2005; De la Rosa *et al.*, 2008). These changes result in an overall increase in the chemical recalcitrance of the peat OM which is likely to enhance biological resistance and result in weak colloidal properties (Doerr *et al.*, 2000; Knicker *et al.*, 2005). In Portuguese maritime pine and eucalypt plantations it was found that wild fires caused the most thermal labile structures to be removed along with an increase in the presence of highly condensed aromatic structures (De la Rosa *et al.*, 2012).

Although peat sample pyrolysates indicate that the OM of the upper 5 cm of peat is significantly altered as a result of fire, the peat pyrolysates of samples from lower in the peat column indicate that fire has little effect on the chemical composition of peat OM. Analyses of samples of subsurface peat showed no significant differences between proportions of compound classes between unburnt (drained) and burnt peat. PCA did not statistically separate the pyrolysates of these samples from one another, which implys that they are chemically similar and that fire had no effect on the peat OM composition below 5 cm. The observed fire-driven changes in the chemical composition of the surface peat OM are likely temperature dependent (González-Pérez *et al.*, 2004). Previous studies have suggested that OM is unlikely to be chemically modified when fire temperatures are less than 130-190 °C, but above this temperature range, the most thermally-labile components (i.e. lignins and hemicelluloses) will begin to degrade (Chandler *et al.*, 1983). This suggests that temperatures in the subsurface peat at depths below 5 cm were not sufficiently high to alter the chemical composition of the OM, explaining why no significant chemical differences were observed between subsurface samples of unburnt (drained) and burnt peat.

In smouldering peat fires, pyrolysis reactions take place. These are endothermic processes which absorb heat from the surroundings and release volatile gases and char. Partial combustion of the peat OM (exothermic reaction) also occurs during the smouldering process (Rein, 2008). Such pyrolysis reactions will only take place when temperatures reach between 250 °C and 300 °C (Usup *et al.*, 2004). Char is a product of this smouldering process due to partial burning of the OM (Certini, 2005). Between 250 °C and 300 ^{o}C, lignins and hemicelluloses are degraded and structural changes, including the production of aromatic structures, will occur (Almendros *et al.,* 1990, 1992). In burnt samples collected one month post-fire, charcoal was detected and it is estimated that 64.9 (± 1.5) % of the material in the upper 5 cm of the burnt peat profile consisted of a combination of charcoal and other highly resistant OM (Chapter 6). In addition, the relative contribution of lignins and cellulose derived compounds (e.g. guaiacols and levoglucosan) in sample pyrolysates had been reduced (0.8 ± 1.2 % vs. 10.1 % (lignins) and 0.1 ± 0.1 % vs. 22.6 % (polysaccharides)) and there was a significant increase in aromatics compared to pyrolysates of drained unburnt peat (12.0 ± 5.3 % vs. 4.5 % in the 0-5 cm depth interval) (Chapter 4). These results suggest that labile compounds have been thermally altered into other organic forms, e.g. aliphatic or aromatic compounds, and thus it can be implyed that the OM of the surface peat is more recalcitrant shortly after a fire.

It has been reported that during a peat fire, significant amounts of OM from the peat surface are combusted and converted to gases that are released to the surrounding atmosphere (Rein *et al*., 2009). The amount of peat OM that is lost in this way is variable dependent on the temperature and duration of the fire as well as the moisture content and fuel load of the peat (i.e. depth of dry peat) (Mickler *et al*., 2010). Soils can be completely combusted when exposed to temperatures of 460-490 °C (Giovanni *et al*., 1998), while at a lower soil temperature of 220 °C, 37 % of the OM in the upper 10 cm of soil under *Pinus sylvestris* was lost through combustion (Fernandez *et al*., 1997).

During the most extensive peat fires that occurred across Indonesia in 1997 an estimated average of 0.51 m of the surface peat was consumed in the study area (Block C) (Page *et al*., 2002). Often, when large amounts of OM are lost during peat fires, pan shaped holes in the peat surface may appear, often around the bases of trees, and leading to local peat subsidence (Rollins *et al*., 2003; Rein *et al*., 2009). Ash that was deposited on the peat surface from the combustion of the upper layers of peat or above ground vegetation may have been lost by the time of sampling due to immediate post-fire aeolian transport or surface-flow transport into waterways.

7.2.1 Short term effects of fire: Subsurface peat OM (5 to 50 cm)

Fires in peatlands are often described as ‘smouldering’ as burning often occurs below the peat surface, propagating slowly underground and lasting for many weeks (Aldhous, 2004; Davidson *et al*., 2004); in addition, temperatures may remain low in comparison to flaming combustion (Rein *et al*., 2009). Smouldering combustion involves a combination of pyrolysis and oxidation reactions where oxygen availability is limited. The pyrolysis reaction is endothermic (Hadden *et al*., 2012) during which charring will take place.

It was initially hypothesised that there would be considerable chemical change to peat OM even below the surface because of the effect of sub-surface smouldering fires. However, the pyrolysis data reveal that sub-surface alterations in drained and burnt peat, below a depth of 5 cm, were minimal. The relative contributions of lignin-derived pyrolysis products were not significantly different from peat sample pyrolysates of equivalent depth intervals from the drained unburnt site (Site 2). Across all the analysed depth intervals, relative lignin contributions did not significantly change at one month post-fire (15-30 cm depth interval (7 – 10.2 ± 10.4 %) and 30-50 cm (10.6 – 13.8 ± 3.6 %)). These results support the idea that fire has not had a significant effect on the peat OM composition below a depth of 5 cm from the surface and that thermal alteration has not occurred in subsurface peat.

Temperature changes during a fire are critical in determining the nature of the chemical, physical and biological changes that will occur within the peat (DeBano *et al*., 1998). Chemical changes, in particular, are temperature dependent. My data suggest that in tropical peatland fires the temperature reached in peat beneath 5 cm is low relative to that of the upper 5 cm. This is supported by studies by Hamada *et al*. (2012) and Usup *et al*. (2008) both of whom investigated peat fire temperatures during experimental burns in the same study area used for this research, who recorded a maximum temperature at 10 cm below the peat surface of 350 °C while at 20 cm depth it was between 50 – 100 °C (Hamada, 2012).

The chemical composition of the OM, as indicated by the peat pyrolysates in this study, reflects this distinct difference in temperature between the upper 5 cm and the lower peat substrate. Factors that influence the peak temperatures reached during a smouldering fire include, firstly peat moisture content. The poor ability of peat to conduct heat would inhibit substantial temperature rises in subsurface peat and therefore any significant alteration of the peat OM composition. Mineral soils have also been identified as poor conductors of heat (DeBano *et al.*, 1981; Bradstock, 1992) and peat is no exception (Ekwue *et al.*, 2006). Organic soils such as peat are typically poor heat conductors because of their considerable pore space reflected by low bulk density values (< 0.1 g cm^{-3}) compared to mineral soils. Wet peat is a better conductor of heat (Hayashi *et al.*, 2011) although latent heat of vapourisation prevents peat temperatures exceeding 95 °C until all water content has been vapourised (Campbell *et al.*, 1994). In addition, the depth of the water table is also likely to inhibit the transfer of heat down the peat profile and the degree to which chemical transformation of the OM. At Site 3, Hirano *et al*. (2013) measured an average water table depth of approximately 80 cm and 50 cm below the peat surface during the dry seasons of 2004 and 2005, respectively. Other authors have discussed how during a tropical peat fire 51 ± 4 cm (Page *et al.*, 2002) of peat can be lost through combustion. The peat that has been sampled in this study is in fact the material remaining following a fire, i.e. the 0-5 cm samples are surface samples following the fire not the 0-5 cm of peat directly preceding the fire. The average water table at this site is only slightly greater than the average depth of peat that has been previously reported to be lost during a peat fire. Taking into consideration previous estimates of peat loss following fire, in addition to pyrolysis data of belowground chemical change, during the 2009 fire in the Site 3 sampling area peat loss is believed to be in the region of 50 cm. This is equivalent to the 50 cm cores used in this analysis and the thus, accounting for the lack of any considerable changes to the peat OM below 5 cm (or 55 cm based on pre-fire measurements) from the post-fire peat surface. The fire that occurred during the dry season of 2009 did not penetrate the peat at sufficient depth to allow chemical differences to be observed in the 5-50 cm peat sample pyrolysates hence they are chemically similar to samples from the drained unburnt site (Site 2).

Many of the observed chemical differences detected after burning, particularly below 5 cm, were mirrored in samples subject only to drainage (discussed in section 7.1). This comparison has also been made by other authors (including Almendros *et al.*, 1984b; González-Vila and Almendros, 2003). Humification of peat OM results in many similar chemical changes to those occurring during heating by fire. Although burning has not had a significant impact on the chemical composition of peat OM below 5 cm from the surface, drainage has altered the composition of the peat throughout the upper 50 cm, compared to samples from the inundated peat swamp forest (Site 1).

7.2.2 Short-term effects of fire: Peat water repellence

Over-drying can lead to shrinkage of peat that also can then lead to the peat becoming difficult to re-wet (water repellent) (Andriesse, 1988, Dekker and Ritsema, 1996). This is seen as a particular problem in areas of peatland used for long-term cultivation. If peat in the former MRP becomes dry and therefore not readily wettable then it may contribute to the occurrence of future fires, as peatland fires persist only on areas of dry peat (Hooijer *et al.*, 2010).

In this study, the assessment of 'potential water repellence' involved measurement of air-dried samples; the purpose of doing this was to standardise the moisture content across all samples allowing the potential water repellence to be compared. It is well known that drying often enhances the water repellence of soils (Dekker, 1998; Michel *et al.*, 2001; Poulenard *et al.*, 2004). This is due to the realignment and redistribution of polar molecules, making the organic molecules water repellent (Valat *et al*, 1991).

When allowed to air-dry, all peat samples analysed, regardless of whether they had been burnt or not, exhibited some degree of water repellence. The only exceptions were the samples that were collected from the upper 5 cm of peat one month post-fire (Chapter 6). Air-dried samples of subsurface peat (5-50 cm) from all three study sites were hydrophobic. Peat samples from the drained unburnt site were more hydrophobic than those from the undrained unburnt peatland. MED values of 27 - 30 % ethanol were obtained for drained peat samples and 18 – 21 % ethanol for intact peat samples, equating to 'Very strongly hydrophobic' and 'Strongly hydrophobic', respectively. This result supports the notion that when peat becomes very dry it is difficult to re-wet. Although these samples were tested under controlled conditions in the laboratory, hydrophobicity is likely to persist in situ. Peat is most likely to become difficult to re-wet during the dry season when rainfall is significantly reduced. All pre-existing hydrophobicity is destroyed in the upper 5 cm of peat when it is subject to burning. MED values of 0 % ethanol were obtained for the 0-5 cm peat samples collected one-month post-fire; this equates to the peat being classified as 'very hydrophilic'.

As well as the peat pyrolysate data indicating that the OM had been significantly altered in the upper 5 cm as a result of burning, the water repellency data showed that this layer of peat was also readily wettable. Water can therefore readily infiltrate the dry peat surface up to one month after a fire. At greater depth (5 to 50 cm), however, the water repellence of the peat remained unchanged from pre-fire (i.e. it was very strongly hydrophobic) and thus remained difficult to re-wet. This result supports the findings from the Py-GC/MS analyses which revealed that despite being burnt, the peat samples collected just one month post-fire had an OM that was relatively similar to the pre-fire composition. Thus the fire that occurred in the dry season of 2009 did not have a significant effect on either the peat OM composition or the degree of water repellency of the subsurface peat.

Peak soil temperature obtained during a fire is believed to influence the degree of hydrophobicity observed post-fire (DeBano and Krammes, 1966, DeBano 2000) and above a specific temperature water repellence can be eliminated. In Australia, for example, soil water repellence was abruptly destroyed at temperatures between 260 °C and 340 ^{o}C in eucalypt forest soils (Doerr *et al*., 2004). The temperature at which water repellence was eliminated varied between the forest soil samples, but this was dependent on temperature duration i.e. lowest temperatures eliminated water repellence when soils were exposed to the greatest duration of burning. It is not currently known what is the maximum temperature beyond which water repellence in tropical peats is eliminated, but the fire that burnt at Site 3 during the dry season of 2009, reached and perhaps exceeded this critical temperature threshold. This is supported by the observation that at one month-post fire all potential water repellence had in fact been eliminated. In an experimental burn in the same study area peak temperatures between 350 and 450 °C were recorded in the upper 10 cm of peat

(Hamada *et al*., 2012), indicating that this may be the temperature range at which pre-existing water repellence is destroyed, although this requires confirmation. Below 5 cm in the peat profile the temperature reached during the fire was likely sufficient to enhance but not eliminate the pre-existing potential water repellence of the peat. Below a depth of 10 cm, Hamada *et al*. (2012) showed that the temperature did not exceed 90 °C, suggesting that at this temperature potential water repellence is slightly enhanced, with samples that were 'strongly hydrophobic' pre-fire becoming 'very strongly hydrophobic' one month post-fire. Ascertaining peat or soil temperatures during a fire remains a challenge, especially when estimates are required retrospectively. Often subjective measures such as ash colour (Bentley and Fenner, 1958, Ketterings, 2000) and nature of the post-fire remains (Moreno and Oechel, 1989) have been used; however, measuring the post-fire water repellence may serve as a more objective method of gauging the heat transferred to peat during a fire (Doerr *et al*., 2004).

Enhancement or elimination of hydrophobicity is a commonly observed phenomenon in soils that have been subject to varying levels of heating (DeBano *et al*., 2000; Doerr *et al*., 2000) and this can have implications for post-fire soil erosion (Macdonald and Huffman, 2004). Soil hydrophobicity is strongly correlated with OM content (Dekker *and Ritsema*, 1994) thus explaining why organic soils such as peats are typically hydrophobic when dry. OM composition is also believed to influence the degree of soil water repellence. In particular, an increase in apolar molecules such as hydrocarbons, waxes and amino acids relative to polar molecules (Poulenard *et al*., 2004), is thought to increase the extent to which water droplets will be repelled by the soil surface. Formation of charcoal, as was detected in the one month post-fire surface peat samples, reduces the OM content as well as increasing the proportion of apolar compounds, thereby eliminating existing hydrophobicity and allowing the peat to become readily wettable.

It is plausible that the reduction in vegetation cover as a result of fire coupled with the formation of a readily wettable surface layer of peat, could have led to enhanced rates of surface peat erosion. When burning intensity and soil temperatures are lower, hydrophobicity is often enhanced shortly after fire (DeBano and Letey, 1969, DeBano, 1981), as was observed in the subsurface peat samples in this study. However, despite water repellence being enhanced shortly after fire in the subsurface peat samples, this was a short term phenomena and no enhancement of peat hydrophobicity from pre-fire levels was observed at 18 months post fire. There were also no further changes in hydrophobicity up to 14.5 years post-fire. Based on these results, it is concluded that water repellence in burnt peatlands is a relatively short term phenomenon, likely only persisting for up to, but probably less than 18 months, post-fire.

The critical moisture content, beyond which soils lose any water repellence they may have, is currently unknown for tropical peat soils. Portuguese sandy loam soils have a critical moisture content of 28 % therefore when soil moisture content is less than 28 % these soils display hydrophobic characteristics and above this value hydrophobic characteristics are eliminated (Doerr and Thomas, 2000). In Dutch clayey peat soils water repellence is eliminated when soil moisture reaches and exceeds 34-38 % (Dekker and Ritsema, 1996). Results from other studies of soil water repellence suggest that hydrophobicity, fire-derived or naturally occurring, is a seasonal phenomenon (DeBano, 1981, Chan, 1992, Doerr *et al.*, 2000). Therefore in the context of the study area, where there is marked seasonal variation in rainfall, it is likely that peat water repellence is will also be seasonally variable. During the dry season (June-September) the uppermost layers of peat in drained areas such as the former MRP area will have a reduced peat moisture content (0-30 cm, approx. 0.52 m^3 m^{-3} (2004) and approx. 0.54 m^3 m^{-3} (2005) (Hirano *et al.*, 2013)) compared to during the wet season ((0-30 cm, approx. 0.64 m^3 m^{-3} (2004 and 2005) (Hirano *et al.*, 2013)). If 'in-situ' water repellence exists it is likely to persist only in the dry season when the upper 50 cm of peat may below the critical moisture content. During the wet season the critical soil moisture content is likely to be exceeded due to heavy and persistent rainfall and subsequent rise in water table levels which would likely eliminate such water repellence. Further research to determine the critical soil moisture content and the peat temperature at which water repellence is eliminated would be useful to understand further the hydrological implications of fires for tropical peatland ecosystems.

7.2.3 Short term effects of fire: Evidence of charcoal

A single method for estimating charcoal content in soils has not yet been developed (Hammes *et al.*, 2007) and therefore estimating charcoal content in tropical peat soils remains a challenge. The results within this thesis provide an approximate charcoal concentration for burnt peats as well as allowing peat from different sites and depths to be compared. It is evident that significant amounts of charcoal are present in the upper 5 cm of peat at one month post-fire. Elemental analysis, charcoal isolation by chemical oxidation and Py-GC/MS analysis all provide evidence that charcoal is present in the upper 5 cm but that there are insignificant quantities below this depth.

Alongside other fire-driven changes to the chemical composition of the surface peat OM, a significant quantity of charred material (64.94 (± 1.51) % w/w / 82 % of soil organic C) was detected at one month post-fire (Chapter 6). Charcoal is typically a highly condensed form of C (Skjernstad *et al.*, 1999) and previous studies have published C contents of up to 30-45 % of the total soil organic C (Skjemstad *et al* 1996, Glaser *et al.*, 2000). Samples of peat collected one month post-fire had a very high total C content in the upper 5 cm (79.03 % C) implying that total C stocks become more concentrated as a consequence of burning. Aside from C, other molecules including oxygen are lost during combustion, again indicating the presence of charcoal. Results of other studies reveal that C concentrations increase in response to fire (Johnson and Curtis, 2001; Czcmizik *et al.*, 2003) although no change was observed in burnt soils of an oak forest (Almendros *et al.*, 1990). C contents in the upper 5 cm of peat increased from between 48 – 55 % to 79 % following burning which suggests that considerable quantities of charred material are being produced during peat fires and that this material remains within the upper 5 cm of the peat column for at least one month.

A charcoal concentration of 64.94 (± 1.51) % was estimated using the chemical oxidation method (Chapter 6) and although this is a tentative estimate, comparison with the result obtained for unburned peat (3.05 %), suggests that significant quantities of charcoal are present at one month post-fire. There were no significant charcoal quantities detected in the subsurface peat layers from the burnt site, with concentrations not statistically different from equivalent samples analysed from unburned sites. High estimates of charcoal concentrations coupled with significantly greater C recently burnt peat provide strong evidence that a significant proportion of the upper 5 cm of the burnt peat (~65 %) is composed of charcoal.

Further evidence for the formation and presence of charcoal was provided by detection of condensed aromatic structures in the pyrolysates of recently burnt peat. Concentrations were greater in samples collected one month post-fire than in peat that had not been affected by burning (5.5 ± 2.6 vs. 1.2 % of the total identified pyrolysis products). Compounds such as fluorene, naphthalene and alkylbenzene and other PAHs have previously been identified as precursors for charcoal and thermally-altered refractory OM (Tinoco *et al*., 2006; Knicker *et al*., 2008).

It is evident that burning only forms charcoal in the uppermost layer of peat and the results (from charcoal analysis, elemental analysis and Py-GC/MS) do not reveal any significant concentrations of charcoal in subsurface (5-50 cm) peat, even when sampled almost immediately (at one month) post-fire. The lack of charcoal at depth may be due to inadequate transfer of heat below a depth of 5 cm (see discussion on this Section 7.2.1). Charcoal is typically formed at temperatures between 250 ^{o}C and 500 ^{O}C (Baldock and Smnernik, 2000). Ordinarily temperatures obtained during a peat fire in the subsurface peat are, therefore, not sufficiently high to cause thermal alteration of the OM to form charcoal; (see Section 7.2.2.). Therefore although peat fires may smolder beneath the peat surface the belowground heat transfer is clearly not sufficient to significantly alter the OM and thus to form charcoal below a depth of 5 cm.

As well as insufficient transfer of heat during a fire to the subsurface peat, insignificant quantities of charcoal may also reflect a lack of woody material readily available for conversion to charcoal. Pyrolysates from the drained site (unburned) contained significantly less lignin derived molecules than those analysed from the inundated site (unburned) (10.1 vs. 35.3 (±2.1) at the 30-50 cm depth interval). Lignins are relatively labile in soils therefore bacteria can readily breakdown such OM under aerobic conditions (Kuder and Krudge, 1998). The low availability of woody material within the peat could also explain why no significant amounts of charcoal were detected below 5 cm. Aerobic decomposition is evident in the drained site and so when these drained areas are affected by burning the low lignin content ensures that charcoal formation in minimal.

There are no other published estimates of charcoal content in tropical peats affected by fire, although charcoal addition as a result of the combustion of vegetation (rather than peat) during fires on UK peatlands has been investigated (Clay and Worrall, 2011). The charcoal estimations made in this study are semi quantitative due to the limitations of the methodology; nevertheless, it is clear that burning has led to the formation of charcoal within the upper 5 cm of the peat column. These findings provide an initial estimation of the charcoal content of fire-affected tropical peat which will be of value for peatland C modeling, although further investigation is required to refine the method and the precision of the results.

7.2.4 Short term effects of fire: Summary

The key chemical and physical changes, as identified in this study, that have taken place during burning and observed shortly after a fire in the upper 50 cm of a tropical peat column are summarised below.

i) Distinct compositional alteration of peat OM occurs as a consequence of fire. The peat pyrolysates from the burnt site contained compounds derived predominantly from aromatic and aliphatic compound classes when analysed by Py-GC/MS, e.g. alkenes and alkanes, whereas unburned peat had greater OM diversity, including contributions from a range of polysaccharide, lignin and phenol-derived compounds.

ii) Burning caused preferential removal and/or alteration of labile organic compounds such as those derived from polysaccharides and lignins. This is evident as contributions of molecules such as levoglucosan (primary polysaccharide) and guaiacol (lignin). In addition, the total relative contributions of polysaccharide and lignin-derived pyrolysis products were significantly reduced between 5 and 50 cm below the peat surface. These changes were initially due to the effects of drainage, with subsequent burning resulting in an almost complete absence of both compound classes in the upper 5 cm of peat.

iii) There is a decline in the overall chemical diversity of the peat OM, as indicated by the pyrolysate data, particularly for surface (0-5 cm) peats.

iv) Charcoal is present in the upper 5 cm of peat; however, no significant quantities were present between 5 and 50 cm below the surface.

v) Drained peat has hydrophobic properties; these are destroyed following fire, but only in the upper 5 cm of the peat profile. Below 5 cm, drained peat retains its hydrophobic properties. .

7.3 Influence of different fire regimes

It was initially hypothesised that a Py-GC/MS analysis could be used to monitor the post-fire recovery of peat OM by analysing peat samples along a fire chronosequence.

A significant result from this particular analysis is that although the short term effects of fire cause highly significant alteration of the peat OM these changes did not persist and there were no statistically significant differences in the pyrolysate data between peat that had been burnt 1.5 years prior to sampling and peat that had been drained but not affected by fire (Site 2). PCA analysis revealed that between 1.5 years and 14.5 years post-fire, the peat pyrolysates were chemically similar to those from the drained, unburnt site.

Although these results suggest that fire does not have a long term effect on the peat OM composition, the effects of drainage alone are clearly significant. Drainage of the MRP area commenced approximately 15 years ago and the results from this study indicate that the OM composition of the peat remains significantly less chemically diverse and thus likely to of a reduced 'quality' than peat in intact PSF. Soil or peat 'quality' is a term that has been used by soil scientists to indicate the capacity of OM to be utilized by soil microbes as a source of energy (Rovira and Vallijo, 2002) and is dependent on the ratio of recalcitrant to labile C components. Drained peat consists largely of recalcitrant components thus the ‘quality’ is reduced, reflecting prolonged exposure to aerobic conditions in upper peat column and reduced biomass additions to the peat surface.

Wildfires are variable in their spatial and temporal distribution resulting in a host of different burning regimes in a particular location. Remote sensing-based analysis of the larger study area (i.e. Block C) characterised the fire regime (Hoscilo, 2009) and showed that many areas had been burnt more than once. One third of Block C (~150,000 ha) was burnt during the 1997 fires (Hoscilo, 2009) however large areas also burnt during the dry seasons of subsequent years, particularly 2002, 2006 and 2009. Between 1997 and 2005, 45 % of the burnt area burnt had been subject to multiple fires, many of which were located in close proximity to drainage canals, allowing ease of access for humans whose activities provide ignition sources.

7.3.1. Effect of fire regimes: Fire Chronosequence

Although one month post-fire peat OM was chemically very different to its pre-fire composition these differences were not sustained in the medium or longer term. This result suggests that the peat OM composition had recovered its pre-fire characteristics at 1.5 years post-fire, implying that the effects of fire are relatively short-lived. Vegetation recovery is typically limited following a fire, for example Hoscilo *et al.* (2011) indicates that nine years after the 1997 fires, in the study area, just 10-15 % of the biomass of the intact forest had been restored. Therefore there is insufficient post-fire addition of fresh OM to the burnt peat surface between one month and 1.5 years post-fire to explain the differences in OM composition observed during this same time period. Post-fire erosion of the upper 5 cm of peat is a valid explanation for the apparent recovery of peat OM composition back to its pre-fire state over such a short time scale. Soil erosion following fire has been reported in temperate peat fires (Rein *et al.*, 2008). Erosion of the upper 5 cm of peat between one month and 1.5 years post-fire would expose the subsurface peat which did not undergo any significant thermal alteration. The suggestion that there is significant post-fire erosion immediately following a fire is also supported by the higher than average DOC and POC concentrations measured in drainage canals following the 2009 fires in the same study area (Moore *et al*., 2011).

7.3.2. Effects of fire regimes: Fire Frequency

Comparison of the chemical composition of peat OM from multiple burn sites and sites affected by a single fire revealed that repeated burning had no significant additional effect. The significance of this result is that the peat OM is thermally altered the first time an area is burnt and thus the 'peat quality' is reduced under a single fire regime regardless of whether the same area is repeatedly burnt. When peatlands first experience fires, peat swamp forest vegetation dominates the landscape thus providing a deep rooting system into the peat substrate that allows greater transfer of heat down the peat profile facilitating a belowground smouldering peat fire (Rein *et al*., 2008). After the initial fire the original peat swamp forest is replaced with fern and sedge vegetation which with a lower biomass will favour surface fires of shorter duration. This could explain why there were no observed differences in chemical composition of peat pyrolysates from sites exposed to single or multiple fires. It is therefore proposed that the vegetation type or fuel load has a more significant influence on the degree of thermal alteration to the below-ground peat than the fire frequency.

7.4 Impacts for the C cycle

Globally, soils including peats provide a larger C store than all aboveground vegetation or the atmosphere (Kleber, 2010). Tropical peatlands have a disproportionally large store of terrestrial C, which is primarily located belowground within the peat substrate (Gorham 1991; Immirzi & Maltby 1992, Page *et al*., 2011). Under natural waterlogged conditions tropical peatlands are a store of C but clearance of the aboveground vegetation and drainage cause release of CO_2 through oxidation. Lowering of the natural water table brings about oxic conditions in the peat profile enhancing microbial decomposition and ultimately amplifying C loss to the atmosphere (Charman, 2002). A study by Hooijer *et al*. (2006) estimated C losses of 97 to 238 M t C yr^{-1} from degraded (deforested and drained) peatlands in South East Asia (Page *et al*., 2002). The results of this study have revealed that drainage also leads to alteration of the peat OM composition that could have additional implications for C cycling.

The tropical peatland C store must be closely monitored if accurate predictions of global climatic change are to be made. When peat is burnt, the OM is often lost by partial combustion, contributing to global C emissions. When heated to a sufficient temperature, a proportion of the C pools in the remaining peat are altered, thus modifying their biological stability. Various chemical reactions occur under smouldering and flaming combustion including; pyrolysis, depolymerisation, water elimination, volatilization, fragmentation, oxidation and char formation (Graham *et al*., 2002). .

'Soil OM quality' is a term used to assess the OM composition of soils and the capacity of the OM to be utilized by soil microbes as a source of energy (Rovira and Vallijo, 2002). Results of this study indicate that drainage has significant effects on peat OM composition, reducing the overall 'peat quality'. This result supports the findings of Leifield *et al*. (2012) who,. in a study of peatlands in Switzerland of different drainage status, used ^{13}CNMR analysis, diffuse reflectance infrared spectroscopy (DRIFT) and elemental analysis to determine the chemical composition of the OM in order to investigate the link between peat OM composition and decomposability and ultimately C loss from drained peatlands. The overall findings were that drainage led to C loss from peatlands, however the vulnerability of the C loss was dependent on the peat OM composition, particularly the amount of O-alkyl-C, which included the polysaccharide content. Oxidative decomposition was enhanced when the O-alkyl-C content was high. The results of this study imply that peat quality may be an important factor in explaining the missing relationship between water table level and heterotrophic respiration in some peatland studies.

Other studies have also highlighted that a reduction in the quality or an increase in the recalcitrance of peat OM leads to a reduction in peat heterotrophic respiration (Hardie *et al*., 2011). For example, a recent study carried out in the same study area in Central

Kalimantan found a reduced rate of heterotrophic respiration in drained and burnt peatlands (Hirano *et al.*, 2013). The results presented in this thesis compliment these published findings (Hardie *et al.*, 2011, Leifield *et al.*, 2012, Hirano *et al.*, 2013) by demonstrating that when peat is drained and then burnt there is a significant reduction in the labile C component of the peat OM, potentially reducing the substrate available for microbial decomposition and thereby oxidative CO_2 emissions. A reduction in labile C as a consequence of fire, a result that has also been found in other studies of fire-affected OM (Harden *et al.*, 2000; Neff *et al.*, 2005), and the observed accumulation of recalcitrant OM forms such as aromatics and aliphatics, both indicate that a larger portion of the peat C is resistant to decomposition and has entered a more a slowly cycling soil reservoir (Kuhlbusch and Crutzen, 1995; Knicker *et al.*, 2005). The degree to which organic compounds are decomposed or degraded is thought to be controlled by different activation energies associated with the different chemical bonds in the peat OM (Conant *et al.*, 2011, Kögel-Knaber, 2009). Aliphatics and aromatic compounds are regarded as recalcitrant molecules (Buurman and Roscoe, 2011). The reduction in peat quality in the study area due to artificial lowering of the water table is likely to be a key factor in explaining the retarded CO_2 efflux observed in the study of Hirano et al. (2013) of burnt peatland. As fire has no significant effect on the chemical composition of peat OM below 5 cm from the post-fire surface, it is implyed that drainage is the overriding factor influencing the chemical composition of the peat OM and thus post-fire CO_2 emissions.

It was originally hypothesised that the presence of charcoal in burnt peat may further reduce the rate of post-fire peat decomposition. Charcoal or pyrogenic OM (PyOM) has long been thought to reduce the average turnover rate in soils, making the OM more stable and reducing overall CO_2 emissions from decomposition. PyOM additions in soils in Sierra Norte (Southern Spain) caused a deceleration of soil turnover by a factor of two or three comparable to an increase in the mean residence time of between 12-17 years to up to 40 years (Knicker *et al.*, 2012). In this study, however, charcoal was detected shortly after fire (one-month) in only the upper 5 cm of peat and by 1.5 years post-fire charcoal was not detected in any significant quantity. It is therefore concluded that charcoal is unlikely to reduce the rate of decomposition because it is not retained for any length of time in the peat.

It has been estimated that globally 30 % of the land surface is subjected to a significant frequency of fires (Chuvieco *et al.*, 2008). There is a limited but growing number of studies on the effects of fire on a range of soil properties (Bento- Gonclaves *et al.*, 2011; Certini *et al.*, 2005; González-Pérez *et al.*, 2004; Shakesby and Doerr, 2006; Ballard, 200). In the future, fire regimes are predicted to change in response to climatic change, with tropical peatlands no exception to this shift. By understanding how fires affect the OM composition of tropical peat soils, deductions can now be made regarding the degree to which peat decomposition, and hence land-atmosphere C transfer, is likely to be affected under different fire regimes.

7.5 Recommendations for future research

Suggestions for future research that would expand upon the results of this study are given below:

- Continue to monitor the effects of fire on peat OM composition by establishing regular sampling following any future fire events. By analysing a wider range of peat samples collected immediately post-fire and following different types of fire events (e.g. fires in different land covers) the results could be compared across different fire severity levels, thereby gaining an improved understanding of the landscape variation in peat fire effects.

- A controlled burning experiment could yield insightful results e.g. analysis of post-fire samples from fires of known temperatures and duration. By obtaining ‘in-situ’ temperature data the OM compositional changes that occur at specific temperatures could be obtained. Predictions could then be made about the effects of fire on OM thermal alteration and peat water repellence under different fire regimes.

- To understand more about the chemical composition of the peat a quantitative analysis could be performed using the Py-GC/MS data rather than the semi-quantitative analysis used in this study. Development and use of an appropriate chemical standard would allow each pyrolysis product to be quantified, resulting in enhanced between sample comparisons.

- Experimental work should be continued to develop a method more appropriate to quantify the charcoal content of peat. The use of a technique such as Thermo-Gravimetric (TG) analysis could also be used to measure the fuel quality before and after fire under different fire regimes. A more accurate quantification of the peat charcoal content would lead to improved soil, and specifically, peat C models.

References

Abbott, G.D., Swain, E.Y., Muhammed, A.B., Allton, K., Belya, L.R., Laing, C.G., Cowie G.L. (2013) Effect of water-table fluctuations on the degradation of Sphagnum phenols in surficial peats. *Geochimica et Cosmochimica Acta*. 106,177-191.

Agee, J.K. (1993) Fire Ecology of Pacific Northwest Forests. Island Press, Washington, DC.

Aldhous, P. (2004) Land remediation: Borneo is burning. *Nature.* 432, 144-146.

Alexis, M.A., Rasse, D.P., Rumpel, C, Bardoux, G., Pechot, N., Schmalzer, P., Drake, B., and Mariotti, A. (2007) Fire impact on C and N losses and charcoal production in a scrub oak ecosystem. *Biogeochemistry.* 82, 201-216.

Alexis, M. A., Rumpel, C., Knicker, H., Leifeld, J., Rasse, D.P., Pechot, N., Bardoux, G., and Mariotti, A. (2010) Thermal alteration of organic matter after a shrubland fire: A field study. *Organic Geochemistry.* 41, 690-697.

Alexis, M.A., Rasse, D.P., Knicker, H., Anquetil, C., and Rumpel, C. (2012) Evolution of soil organic matter after prescribed fire: A 20-year chronosequence. *Geoderma.* 189, 98-107.

Almendros, G., Dorado, J., González-Vila, F.J., and Martin, F. (1997) Pyrolysis of carbohydrate-derived macromolecules: its potential in monitoring the carbohydrate signature of geopolymers. *Journal of Analytical and Applied Pyrolysis.* 40–41, 599–610.

Almendros, G., González-Vila, F.J., and Martin, F. (1990) Fire-induced transformation of soil organic matter from an oak forest – an experimental approach to the effects of fire on humic substances. *Soil Science.* 149, 158-168.

Almendros, G., González-Vila, F.J., Martin, F., Fründ, R., and Lüdemann, H.D. (1992) Solid state NMR studies of fire-induced changes to the the structure of humic substances. *Science of the Total Environment.* 117-118*,* 63-74.

Almendros, G., Knicker, H., and González-Vila, F.J. (2003) Rearrangement of carbon and nitrogen forms in peat after progressive isothermal heating as determined by solid-state 13C- and 15 N-NMR spectroscopies. *Organic Geochemistry.* 34, 1559–68.

Almendros, G., Martin, F., and González-Vila, F.J. (1988). Effects of fire on humic and lipid fractions in a Dystric Xerochrept in Spain. *Geoderma.* 42, 115–127.

Almendros, G., Polo, A., Lobo, M.C., and Ibanez, J.J. (1984b) Contribution to the study of fire-induced soil organic matter characteristics .2. humus transformations by heating in laboratory controlled conditions. *Revue d'Ecologie et de Biologie du Sol.* 21, 145-160.

Andreae, M.O*.,* and Merlet, P. *(*2001*).* Emission of trace gases and aerosols from biomass burning. Global Biogeochemistry Cycles. 15*,* 955–966.

Anderson, J.A.R. (1961) The ecology and forest types of the peat swamp forests of Sarawak and Brunei in relation to their silviculture. Ph.D. Thesis, University of Edinburgh, UK

Anderson, J.A.R. (1963) The flora of peat swamp forest of Sarawak and Brunei including a catalogue of all recorded species of flowering plants, ferns, and fern allies. *Garden Bulletin (Singapore).* 29, 131-228.

Anderson, J.A.R. (1964) The structure and development of the peat swamps of Sarawak and Brunei. *Journal of Tropical Geography.* 18, 7-16.

Anderson, J.A.R. (1976) Observations on the ecology of five peat swamp forests in Sarawak and Kalimantan. *Soil Research Institute Bogor, Indonesia. Bulletin.* 3, 44-45.

Anderson, I.P., and Bowen, M.R. (2000) Fire zones and the threat to the wetlands of Sumatra, Indonesia. *Forest fire prevention and control project. European Union Ministry of Forestry.*

Andriesse, J.P. (1988) Nature and Management of Tropical peat soils. *FAO Bulletin 59. Food and Agricultural Organisation of the United Nations, Rome.*

Antal, M.J., and Gronli, M. (2003) The art, science, and technology of charcoal production. *Journal America Chemical Society.* 42, 1619-1640.

Atanassova, I. and Doerr, S.H. (2011) Changes in soil organic compound composition associated with heat-induced increases in soil water repellency. *European Journal of Soil Science.* 62, 516–532.

Badia, D., and Marti, C. (2003) Plant ash and heat intensity effects on Chemical and Physical properties of two contrasting soils. *Arid Land Research and Management.* 17 (1), 23-41.

Baker, P.J., Bunyavejchewin, S., Oliver, C.D. and Ashton, P.S. (2005) Disturbance history and historical stand dynamics of a seasonal tropical forest in Western Thailand. *Ecological Monographs.* 75, 317–343.

Baldock, J.A., and Smernik, R.J. (2002) Chemical composition and bioavailability of thermally altered *Pinus Resinosa* (Red Pine) wood. *Organic Geochemistry*. 33, 1093-1109.
Ballard, T.M. (2000) Impacts of forest management on northern forest soils. *Forest Ecology and Management*. 133, 37-42.

Ballhorn, U., Siegert, F., Mason, M., and Limin, S. (2009) Derivation of burn scar depths and estimation of carbon emissions with LIDAR in Indonesian peatlands. *Proceedings of the National Academy of Sciences of the United States of America.* 50, 21213-21218.

Baum, A., Rixen, T., and Samiaji, J. (2007) Relevance of peat draining rivers in central Sumatra for the riverine input of dissolved organic carbon into the ocean. *Estuarine, Coastal and Shelf Science*, 73, 563–570.

Béguin, P., and Aubert' J. (1994) The biological degradation of cellulose. *FEMS Microbiology reviews.* 13, 25-58.

Bell, M.J., and Worrall, F. (2011) Charcoal addition to soils in NE England: A carbon sink with environmental co-benefits? *Science of the Total Environment.* 409, 1704-1714.

Benito, E., Santiago, J.L., de Blas, E., and Varela, M.E. (2003) Deforestation of water-repellent soils in Galicia (NW Spain): effects on surface runoff and erosion under simulated rainfall. *Earth Surface Processes and Landforms.* 28, 145–155.

Bentley, J.R., and Fenner, R.L. (1958) Soil temperatures during burning related to postfire seedbeds on woodland range. *Journal of Forestry.* 56, 737-740.

Bento-Gonçalves, A., Vieira, A., Úbeda, X., and Martin, D. (2012) Fire and soils: key concepts and recent advances. *Geoderma.* 191, 3-13.

Bird, M.I.*,* Moyo*, C., V*eenendaal*,* E.M., Lloyd*,* J., and Frost, P. *(*1999) Stability of elemental carbon in a savanna soil. *Global Biogeochemical Cycles.* 13*,* 923–932.

Bormann, B.T., Homann, P.S., Darbyshire, R.L., and Morrissette, B.A. (2008) Intense forest wildfire sharply reduces mineral soil C and N: the first direct evidence. *Canadian Journal of Forest Research.* 38, 2771-2783.

Boehm, V., Siegert, F., Rieley. J., Page, S., Jauhiainen, J., Vasander, H., and Jaya, A. (2001) *Fire impacts and carbon release on tropical peatlands in Central Kalimantan, Indonesia*. Paper presented of 22nd Asian conference of Remote Sensing, 5-9 November 2001.

Boom, A., Damsté, J.S., and de Leeuw, J.W. (2005) Cutan, a common aliphatic biopolymer in cuticles of drought-adapted plants. *Organic Geochemistry.* 36, 595–601

Bowman, D.M.J.S., Balch, J.K., Artaxo, P., Bond, W.J., Carlson, J.M., Cochrane, M.A., D'Antonio, C.M., DeFries, R.S., Doyle, J.C., Harrison, S.P., Johnston, F., Keeley, J.E., Krawchuk, M.A., Kull, M.A., Marston, J.B., Moritz, M.A., Prentice, I.C., Roos, C.L., Scott, A.C., Swetnam, T.W., van der Werf, G.R., and Pyne, S.J. (2009) Fire in the Earth System. *Science*. 324, 481-484.

Bracewell, J.M., Haider, K., Larter, S.R., and Schulten, H.-R. (1989) Thermal degradation relevant to structural studies of humic substances. *Humic Substances ii.* Edited by Hayes, M.H.B., MacCarthy, P., and Swift, R.S. (181-222. Wiley, New York.

Bradstock, R.A., Auld, T.D., Ellis, M.E., and Cohn. J.S. (1992) Soil temperatures during bushfires in semi-arid, mallee shrublands. *Australian Journal of Ecology.* 17, 433-440.

Brady, M.A. (1997) Organic matter dynamics of coastal peat deposit in Sumatra, Indonesia. Ph.D. Thesis. The University of British Columbia, Canada.

Bruchet, A., Rousseau, C., and Mallevialle, J., (1990) Pyrolysis-GC-MS for investigating high-molecular-weight THM precursors and other refractory organics. *Journal AWWA.*82, 66– 74.

Buurman, P., Nierop, K.G., and Pontevedra-Pombal, X. (2006) Molecular chemistry by pyrolysis-GC/MS of selected samples of the Penido Vello deposit Galacia, NW Spain. *Developments in Earth Surface Processes.* 9, 217-240. In: Peatlands: evolution and records of environmental and climate changes. Edited by: Martini, I.P., Cortizas, A.M., and Chesworth, W.

Buurman, P., Peterse, F., and Almendros, M. (2007) Soil Organic Matter chemistry in allophonic soils: a pyrolysis-GC/MS study of a Costa Rican Andsol catena. *European Journal of Soil Science.* 58, 1330-1347.

Buurman, P., and Roscoe, R. (2011) Different chemical composition of free light, occluded light and extractable SOM fractions in soils of Cerrado and tilled and untilled fields, Minas Gerais, Brazil: a Py-GC/MS study. European Journal of Soil Science. 62, 253-266.

Camill, P., McKone, M.J., Sturges, S.T., Severud, W.J., Ellis, E., Limmer, J., Martin, C.B., Navratil, R.T., Purdie, A.J., Sandel, B.S., Talukder, S., and Trout, A. (2004) Community and ecosystem-level changes in a species-rich tallgrass prairie restoration. *Ecological Applications.* 14,1680–1694

Campbell, G. S.; Jungbauer, J. D. JR.; Bidlake, W. R.; and Hungerford, R. D. (1994) Predicting the Effect of Temperature on Soil Thermal Conductivity. *Soil Science*. 158, 114-126.

Campo, J., Nierop, K.G.J., Cammeraat, E., Andreu, V., and Rubio, J.L. (2011) Application of pyrolysis-gas chromatography/mass spectrometry to study changes in organic matter of the macro and micro aggregates of a Mediterranean soil upon heating. *Journal of Chromatography A.* 1218, 4817-4827.

Campo, J., Solis, E., and Gallardo, J.F. (2012) Effects of fertilisation on soil nutrient characteristics and the growth of tree stand in secondary seasonally dry tropical forests in Mexico. *Journal of Tropical Forest Science.* 22, 408-415.

Capriel, P. (1997) Hydrophobicity of organic matter in arable soils: influence of management. *European Journal of Soil Science*. 48, 457–462.

Capogna, F., Persiani, A.M., Maggi, O., Dowgiallo, G., Puppi, G., and Manes, F (2009) Effects of different fire intensities on chemical and biological soil components and related feedbacks on a Mediterranean shrub *(*Phillyrea angustifolia *L.) Plant Ecology*. 204, 155-171.

Caria, G., Arrouays, D., Dubromel, E., Jolivet, C., Ratié, C., Bernoux, M., Barthès, B.G., Brunet, D., and Grinand, C. (2011) Black carbon estimation in French calcareous soils using chemo-thermal oxidation method. *Soil Use and Management*. 27, 333–339.

Carr, A.S., Boom, A., Chase, B.M., Roberts, D.L., and Roberts, Z.E. (2010) Molecular Fingerprinting of wetland organic matter using Py-GC/MS: an example from the southern cape coastline of South Africa. *Journal of Palaeolimnology*. 44, 947-961.

Cerdà, A., and Lasanta, T. (2005) Long-term erosional responses after fire in the Central Spanish Pyrenees: 1. Water and sediment yield. *CATENA*. 60, 59–80.

Certini, G. (2005) Effects of fire on properties of forest soils: a review. *Acta Oecologica.* 143, 1-10.

Chandler, C., Cheney, P., Thomas, P., Trabaud, L., and Williams, D. (1983) Fire in Forestry. *Forest Fire Behavior and Effects.* Wiley, New York.

Charman, D.J. (2002) Peatlands and Environmental Change. Wiley. 93-96.

Chafer, C., Noonan, M., and Mcnaught, E. (2004) The post-fire measurement of fire severity and intensity in the Christmas 2001 Sydney wildfires. International Journal of Wildfire. 13, 227-240.

Cheng, C., Lehmann, J., and Engelhard, M.H. (2008) Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochimica et Cosmochimica Acta*, 72, 1598–1610.

Christensen, J.P., Murray, J.W., Devol, A.H., and Codispoti, L.A. (1987). Denitrification in continental shelf sediments has major impact on the oceanic nitrogen budget. *Global Biogeochemical Cycles.* 1, 97–116.

Christensen, N.B., Lindemann, W.C., Salazar-Sosa, E., and Gill, L.R. (1994) Carbon and Nitrogen dynamics in a No-Till and stubble mulch tillage systems. *American Society of Agronomy.* 86, 298-303.

Choromanska, U., and DeLuca, T.H. (2002) Microbial activity and nitrogen mineralization in forest mineral soils following heating: evaluation of post-fire effects *Soil Biology and Biochemistry.* 34, 263–271.

Chuvieco, E., Giglio, L., and Justice, C. (2008) Global characterization of fire activity: toward defining fire regimes from Earth observation data. *Global Change Biology*. 14, 1488-1502.

Clay, G.D., and Worrall, F. (2011) Charcoal production in a UK moorland wildfire – How important is it? *Journal of Environmental Management*. 92, 676–682.

Collins, M., An, S., Cai, W., Ganachaud, A., Guilyardi, E., Jin, F., Jochum, M., Lengaigne, M., Power, S., Timmermann, A., Vecchi, G., and Wittenberg, A. (2010) The impact of global warming on the tropical Pacific Ocean and El Niño. *Nature Geoscience*. 3, 391–397.

Cochrane, M.A. (2001) Synergistic Interactions between Habitat Fragmentation and Fire in Evergreen Tropical Forests. *Conservation Biology*, 15, 1515–1521.

Cochrane, M. (2003) Fire science for rainforests. *Nature.* 421, 913-919.

Cochrane, M., and Ryan, C. (2009) Fire and fire ecology: Concepts and Principles. In: Tropical Fire Ecology. 25-62. Springer Praxis Books.

Cofer III, W.R., Winstead, E.L., Stocks, B.J., Goldammer, J.G., and Cahon, D.R. (1998) Crown fire emissions of CO2, CO, H2, CH4 and TNMHC from a dense jack pine boreal forest fire. *Geophysical Research Letters*. 25, 3919–3922.

Conant, R.T., Ryan, M.G., Ågren, G.I., Birge, H.E., Davidson, E.A., Eliasson, P.E., and Bradford, M. A. (2011) Temperature and soil organic matter decomposition rates–synthesis of current knowledge and a way forward. *Global Change Biology*. 17, 3392-3404.

Conard, S., Sukhinin, A., Stocks, B.J., Cahoon, D.J., Davidenko, E., and Ivanova, G. (2002) Determining effects of area burned and fire severity on carbon cycling and emissions in Siberia. *Climate Change*. 55, 197–211.

Cook, G.D. (1994) The fate of nutrients during fires in a tropical savanna. *Australian Journal of Ecology.* 19, 359–365.

Covington, W.W., DeBano, L.F., and Huntsberger, T.G. (1991) Soil nitrogen changes associated with slash pile burning in pinyon-juniper woodlands. *Forest Science.* 37, 347–355.

Curran, L.M., Trigg, S.N., McDonald, A.K., Astiani, D., Hardiono, Y.M., Siregar, P., Caniago, I., and Kasischke, E. (2004) Lowland forest loss in protected areas of Indonesian Borneo. *Science*. 303, 1000–1003.

Czimczik, C.L., Preston, C., Schmidt, M., and Ernst-Delft S. (2003) How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: Stocks, molecular structure, and conversion to black carbon (charcoal). *Global Biogeochemical Cycles*. 17, 1020-1028.

Czimczik, C.L., Schmidt, M.W.I., and Schulze, E.D. (2005) Effects of increasing fire frequency on black carbon and organic matter in Podzols of Siberian Scots pine forests. *European Journal of Soil Science*. 56, 417-428.

Dai, X., Boutton, T.W., Glaser, B., Ansley, R.J., Zech, W. (2005) Black Carbon in a temperate mixed grassland savanna. *Soil Biology & Biogeochemistry.* 37, 1879-1881.

DeBano, L.F., and Krammes, J.S., (1966) Water repellent soils and their relation to wildfire temperatures. *International Association of Scientific Hydrology Bulletin.* 11, 14–19.

DeBano, L., and Letey, J. (1969) Proceedings of a Symposium on water repellent soils. Riverside C.A. University of California.

DeBano, L.F., and Conrad, C.E. (1978) Effect of fire on nutrients in a chaparral ecosystem. *Ecology.* 59, 489-497.

Debano, L.F., and Schmidt, L.J. (1990) Potential for enhancing riparian habitats in the southwestern United States with watershed practices. *Forest Ecology and Management*. 33–34, 385–403.

DeBano, L.F. (1991). The effects of fire on soil properties. *United States Department of Agriculture, Forest Service, General Technical Report.* 280, 151-156.

DeBano, L.F., Neary, D.G., and Folliot, P.F. (1998) Fire Effects on Ecosystems. John Wiley & Sons. NY.

DeBano, L.F. (2000a) The role of fire and soil heating on water repellency in wildland environments: a review. *Journal of Hydrology*. 231-231, 195-206.

DeBano, L. F. (2000b). Water repellency in soils: a historical overview. *Journal of Hydrology*, 231, 4-32.

Dekker, L.W., and Ritsema, C.J. (1994) How water moves in a water-repellent sandy soil .1. Potential and actual water repellency. *Water Resources Research*. 30, 2507-2517.

Dekker, L.W., and Ritesma, C.J. (1996) Variation in water content and wetting patterns in Dutch water repellent peaty clay and clayey peat soils. *Catena.* 28, 89-105.

Dekker, L.W., Ritsema, C.J., Oostindie, K., and Boersma, O.H. (1998) Effect of drying temperature on the severity of soil water repellency. *Soil Science.* 163, 780-796.

Dekker, L.W., and Ritsema, C.J. (2000) Wetting patterns and moisture variability in water repellent Dutch soils. *Journal of Hydrology.* 231–232, 148–164.

De la Rosa, J.M., Francisco A., González-Vila, J., López-Capel, E., Manning, D.A.C., Knicker, H., and González-Pérez, J.A. (2009) Structural properties of non-combustion-derived refractory organic matter which interfere with BC quantification. *Journal of Analytical and Applied Pyrolysis*. 85, 399–407.

DeLuca, T.H,. Nilsson, M.C., Zackrisson, O. (2002) Nitrogen mineralization and phenol accumulation along a fire chronosequence in northern Sweden. *Oecologia.* 133, 206-214.

DeLuca, T.H., MacKenzie, M.D., Gundale, M.J., and Holben, W.E. (2006) Wildfire-produced charcoal directly influences nitrogen cycling in Ponderosa pine forests. *Soil Science Society of America Journal.* 70, 448–453.

DeLuca, T., and Aplet G. (2008). Charcoal and carbon storage in forest soils of the Rocky Mountain West. *Frontiers in Ecology and the Environment.* 6, 18–24

De La Rosa, J.M., González-Peréz, J.A,, González-Vázquez, R., Knicker, H., Lopez-Capel, E., Manning, D.A.C, and González-Vila, F.J. (2008) Use of pyrolysis-GC/MS combined with thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest. *Catena.* 74, 296-303.

De la Rosa , J.M., Faria, S.R., Varela, M., Knicker, K., González-Vila, F., González-Pérez, Antonio, J., and Keizer J. (2012). Characterization of wildfire effects on soil organic matter using analytical pyrolysis. *Geoderma*. 191, 24-30.

Derenne, and S., Largeau, C. (2001) A review of some important families of refractory macromolecules: Composition, origin, and fate in soils and sediments. *Soil Science*. 166, 214-226

Dikici, H., and Yilmaz, C.H. (2006) Peat fire effects on some properties of an artificially drained peatland. *Journal of Environmental Quality*. 35, 866-870.

Doerr, S.H., Shakesby, R.A., and Walsh, R.P.D. (1998) Spatial variability of soil hydrophobicity in fire-prone eucalyptus and pine forests, Portugal. *Soil Science.* 163, 313–324.

Doerr, S.H., Shakesby, R.A., and Walsh, R.P.D. (2000) Soil water repellency: its causes characteristics and hydrogeomorphological significance. *Earth Science Reviews.* 51 (1-4), 33-65.

Doerr, S.H., and Thomas, A.D., (2000) The role of soil moisture in controlling water repellency: new evidence from forest soils in Portugal. *Journal of Hydrology*. 231–232, 134–147.

Doerr, S.H., Blake, W.H., Shakesby, R.A., Stagnitti, F. Vuurens, S.H., Humphreys, G.S., and Wallbrink, P. (2004) Heating effects on water repellency in Australian eucalypt forest soils and their value in estimating wildfire soil temperatures. *International Journal of Wildland Fire.* 13, 157–163.

Doerr, S.H., Llewellyn, C.T., Douglas, P., Morley, C.P, Mainwaring, K.A., Haskins, C., Johnsey, L., Ritsema, C.J., Stagnitti. F., Allinson, G., Ferreira, A.J.D., Keizer, J.J., Ziogas, A.K., and Diamantis,

J. (2005) Extraction of compounds associated with water repellency in sandy soils of different origin. *Soil Research.* 43, 225–237.

Dommain, R., Couwenburg, J., and Joosten, H. (2010) Development and carbon sequestration of tropical peat domes in south-east Asia: links to post-glacial sea-level changes and Holocene climate variability. *Quaternary Science Reviews.* 30, 999-1010.

Drysdale, D. (1998) A*n introduction to fire dynamics.* Second Edition. Wiley and Sons.

Duguy, B., and Rovira, P. (2010) Differential thermogravimetry and differential scanning calorimetry of soil organic matter in mineral horizons: Effect of wildfires and land use. *Organic Geochemistry.* 41, 742–752.

Eden, M.J., Bray, W., Herrera, L., and McEwan, C. (1984) Terra Preta Soils and Their Archaeological Context in the Caqueta Basin of Southeast Colombia. *American Antiquity*. 49, 125-140.

Elias, V., Simoneit, B., Corderio, R., and Turcq, B. (2001) Evaluating Levoglucosan as an indicator of biomass burning in Carajas, Amazonia: A comparison to the charcoal record. *Geochimica et Cosmochimica Acta.* 65, 267-272.

Ekwue, E.I., Stone, R.J., and Bhagwat, R. (2006) Thermal conductivity of some Trinidadian soils as affected by peat content. *Biosystems Engineering*. 94, 461-469.

Emrich, W., (1985) Handbook of charcoal making. The traditional and industrial methods.

Fabbri, D., Mongardi, M., Montanri, L., Ghalletti, G.C., Chiavari, G., and Scotti, R. (1998) Comparison between CP/MAS 13C-NMR and pyrolysis-GC/MS in the structural characterization of humins and humic acids of soil and sediments. *Fresenius' Journal of Analytical Chemistry*. 362, 299-306.

Fearnside, P.M., Leal, N., and Fernandes, F.M. (1993) Rainforest burning and the global carbon budget – biomass, combustion efficiency and charcoal formation in the Brazilian Amazon. *Journal of Geophysical Research Atmospheres. 98*, 16733-16743.

Fearnside, P.M. (1997) Transmigration in Indonesia: Lessons from its social and environmental impacts. *Environmental Management.* 21, 553-570.

Fearnside, P.M, Graca, P.M.L.D., and Rodrigues, F.J.A. (2001) Burning of Amazonian rainforests: burning efficiency and charcoal formation in forest cleared for cattle pasture near Minaus, Brazil. *Forest Ecology and Management.* 146, 115-128.

Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.E., and Stottlemyer, R. (1998) Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecological Applications.* 8, 706-733.

Fenn, M.E., and Bytnerowicz, A., (1993) Dry deposition of nitrogen and sulfur too Ponderosa and Jeffrey Pine in the San-Bernardino National Forest, southern California. *Environmental Pollution.* 81, 277-285.

Fernández, I., Cabaneiro, A., and Carballas, T. (1999) Carbon mineralization dynamics in soils after wildfires in two Galician forests. *Soil Biology and Biochemistry*. 31, 1853–1865.

Flannigan, M., Campbell, I., Wotton, M., Carcaillet, C., Richard, P., and Bergeron, Y. (2001) Future fire in Canada’s boreal forest: paleoecology results and general circulation model – regional climate model simulations. *Canadian Journal of Forest Research.* 31, 854-864.

Flanner, M.G.*,* Zender*,* C.S., Randerson*, J.T.,* and Rasch, P.J. *(*2007*)* Present-day climate forcing and response from black carbon in snow*. Journal of Geophysical Research. 112*, D11202.

Forbes, M.S., Raison, R.J., and Skjemstad, J.O. (2006) Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Science of The Total Environment.* 370, 190–206.

Fuller, D.O., Hardiono, M., and Meijaard, E. (2011) Deforestion projections for carbon rich peat swamp forests of Central Kalimantan. *Environmental Management*. 48, 436-447.

Freitas, J.C.C., Bonagamba, T.J., and Emmerich F.G. (1999) 13C High-Resolution Solid-State NMR Study of Peat Carbonization. *Energy Fuels*. 13, 53–59.

Fuhrmann, A.*,* Fischer*, T.,* Lücke*,* A., Brauer*, A.,* Zolitschka*,* B., Horsfield*, B.,* Negendank*, J.F.W.,* Schleser*, G.H.,* and Wilkes, *H. (*2004*)* Late Quaternary environmental and climatic changes in central Europe as inferred from the composition of organic matter in annually laminated maar lake sediments*. Geochemistry Geophysical Geosystems*. 5*, 110-115.*

Garcia, E., and Carignan, R. (1999) Impact of wildfire and clear-cutting in the boreal forest on methyl mercury in zooplankton. *Canadian Journal of Fisheries and Aquatic Sciences.* 56, 339-345.

Gardini , A., Nesto, C., and Silvestre, A. (2006) Suberin: A promising renewable resource for novel macromolecular materials. *Progress in Polymer Science*. 31,878-892.

Giesen, W. (2004) Causes of peatswamp forest degradation in Berbak National Park and recommendations for restoration, Water for food & ecosystems programme project on: ‘Promoting the river basin and ecosystem approach for sustainable management of SE Asian lowland peatswamp forests’ *(Arnhem, The Netherlands: ARCADIS Euroconsult).*

Gill, A.M., and Stephens, S.L. (2009) Scientific and social challenges for the management of fire-prone wildland–urban interfaces. *Environmental Research Letters*. 4, 14-35.

Gimeno-García, E., Andreu, V., and Rubio, J.L. (2000). Changes in organic matter, nitrogen, phosphorus and cations in soil as a result of fire and water erosion in a Mediterranean landscape. *European Journal of Soil Science*. 51, 201–210.

Giovannini, G., Luchessi, S., and Giachetti, M. (1988) Effects of heating on some physical and chemical parameters related to soil aggregation and erodibility. *Soil Science.* 146, 255– 262.

Giovannini, G. (1994) The effect of fire on soil quality. In: Sala M, Rubio JL, editors. *Soil erosion as a consequence of forest fires*. Logron Geoforma Ediciones. 15 –27.

Giovannini, G., and Lucchesi, S., (1997) Modifications induced in soil physico-chemical parameters by experimental fires at different intensities. *Soil Science*. 162, 479-486.

Glaser, B., Haumeier, G., Guggenberger, and Zech, W. (1998) Black Carbon in soils: the use of benzencarboxylic acids as specific markers. *Organic Geochemistry*. 29. 811-819.

Glaser, B., Balashov, L., Haumeier, G., Guggenberger, G., and Zech, W. (2000) Black Carbon in density fraction of anthropogenic soils of the Brazilian Amazon region. *Organic Geochemistry*. 31, 669-678.

Glaser, B., Haumeier, G., Guggenberger, G., and Zech, W. (2001). The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften.* 88, 37–41.

Glaser, B., & Birk, J. J. (2012). State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (*terra preta de Índio*). *Geochimica et Cosmochimica Acta*. 82, 39-51.

Glover, D. (2006). *Indonesia's fires and haze: the cost of catastrophe*. IDRC.

Goldammer, J.G., (1993a) Historical biogeography of fire–tropical and subtropical. In: Crutzen PJ, Goldammer JG (eds) *Fire in the environment: the ecological, atmospheric, and climatic importance of vegetation fires.* Dahlem Workshop Reports. Environmental Sciences Research Report 13. John Wiley & Sons, Chichester, 297–314.

Goldammer, J.G. (2007) History of equatorial vegetation fires and fire research in Southeast Asia before the 1997–98 episode: A reconstruction of creeping environmental changes. *Mitigation and Adaptation Strategies for Global Change.* 12, 13-32.

Goldammer, J.G., and Hoffmann, A.A. (2002) Fire situation in Indonesia. *International Forest Fire News.* 26, 37–45.

Goldammer, J.G., and Seibert, B. (1990) The impact of droughts and forest fires on tropical lowland rainforest of East Kalimantan. In J.G. Goldammer (Ed.) *Fire in the tropical Biota.* Springer-Verlag, Berlin.

Goldammer, J.G., Seibert, B., and Schindele, W. (1996) Fire in dipterocarp forests. In Schulte A, Sch¨one D (eds) *Dipterocarp forest ecosystems: Towards sustainable management.* World Scientific Publ., Singapore, New Jersey, London and Hong Kong, 155–185.

Goldberg, E.D. (1985) Black Carbon in the Environment. Wiley.

González-Pérez, J.A., González-Vila, F.J., Polvillo, O., Almendros, G., Knicker, H., Salas, F., and Costa, J.C., (2002) Wildfire and black carbon in Andalusian Mediterranean forest. 1–7. *In* D.X. Viegas (ed.) *Forest fire research and wildland fire safety*. Millpress, Rotterdam, The Netherlands.

González-Pérez, J.A., González-Vila, F.J., Almendros, G., and Knicker, H. (2004) The effect of fire on soil organic matter – a review. *Environment International.* 30, 855-70.

González-Vila, F.J., Tinoco, P., Almendros, G., and Martin, F. (2001) Py-CG-MS analysis of the formation and degradation stages of charred residues from lignocellulosic biomass. *Journal of Agriculture and Food Chemistry.* 49, 1128– 31.

Gorham, E. (1991) Northern Peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecological Applications*. 1, 182-195.

Graham, B., Mayol-Bracero, O.L., Guyon, P., Roberts, G.C., Decesari, S., Facchini, M.C., and Andreae, M.O. (2002) Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS. *Journal of Geophysical Research.* 107, 1-14.

Grandy, A. S., & Neff, J. C. (2008). Molecular C dynamics downstream: the biochemical decomposition sequence and its impact on soil organic matter structure and function. *Science of the Total Environment* 404, 297-307.

Gross, J., (2011) Mass Spectrometry. A textbook. 2nd Edition. Springer.

Gupta, N.S., Michels, R., Briggs, D.E.G., Collinson, M.E., Evershed, R.P., and Pancost, R.D. (2007) Experimental evidence for the formation of geomacromolecules from plant leaf lipids. *Organic Geochemistry*. 38, 28-36.

Hadden, R.M., Rein, G., and Belcher, C.M. (2013) Study of the competing chemical reactions in the initiation and spread of smouldering combustion in peat. *Proceedings of the Combustion Institute.* 34, 2547–2553.

Hamada, J.-I., Yamanaka, M.D., Matsumoto, J., Fukao, S., Winarso, P.A., and Sribimawati, T. (2002) Spatial and temporal variations of the rainy season over Indonesia and their link to ENSO. *Journal Meteorological Society Japan*. 80, 285–310.

Hamada, Y., Darung, U., Limin, S., and Hatano, R. (2012) A small scale field experiment of peat burning in a tropical peatland located in Central Kalimantan, Indonesia. *In proceedings of the 14th International Peat Congress*, Stockholm Sweden. Extended Abstract No. 82.

Hamman, S.T., Burke, I.C., and Stromberger, M.E. (2007) Relationships between microbial community structure and soil environmental conditions in a recently burned system. *Soil Biology and Biochemistry.* 39, 1703–1711.

Hammes, K., Smernik, R.J., Skjemstad, J.O., Herzog, A., Vogt, U.F., and Schmidt, M.W. (2006a) Synthesis and characterisation of laboratory-charred grass straw and chestnut wood as reference materials for black carbon quantification. *Organic Geochemistry.* 37, 1629-1633.

Hammes, K*., et al. (2007)* Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere*. Global Biogeochemical Cycles.* 21*,* GB3016.

Harden, J. Trumbore, S., Stocks, B., Hirsch, A., Gower, S., O'Neill, K., and Kasischke, E., (2000) The role of fire in the boreal carbon budget. *Global Change Biology.* 6, 174-184.

Hardie, S.M.L., Garnett, M.H., Fallick, A.E., Rowland, A.P., Ostle, N.J., and Flowers, T.H. (2011) Abiotic drivers and their interactive effect on the flux and carbon isotope (14C and δ 13 C) composition of peat-respired CO2. *Soil Biology and Biochemistry*. 43, 2432-2440.

Haslam, S.F.I., Chudek, J.A., Goldspink, C.R. and Hopkins, D.W. (1998) Organic matter accumulation following fires in a moorland soil chronosequence. *Global Change Biology*. 4, 305–313.

Hatten, J.A., and Zabowski, D., (2010) Fire severity effects on soil organic matter from a ponderosa pine forest: a laboratory study. *International Journal of Wildland Fire.* 19, 613–623.

Hayashi, M., McClymont, A.F., Christensen, B.S., Bentley, L.R., Quinton, W. (2011) Thawing of permafrost peatlands: Effects of water-energy feedback on landscape evolution. Geohydro conference proceedings, Quebec, Canada 2011

Hedges, J.I., (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic Geochemistry.* 31, 945– 958

Heil, A., and Goldammer, J. (2001) Smoke-haze pollution- a review of the 1997 fire episode in Southeast Asia. *Regional Environmental Change*. 2, 24-37.

Hilscher, A., Heister, K., Siewert, C., and Knicker, H. (2009) Mineralisation and structural changes during the initial phase of microbial degradation of pyrogenic plant residues in soil. *Organic Geochemistry*. 40, 332–342.

Hirano, T., Segah, H., Harada, T., Limin, S., June, T., Hirata, R., and Osaki, M. (2007) Carbon dioxide balance of a tropical peat swamp forest in Kalimantan, Indonesia. *Global Change Biology.* 13, 412-425.

Hirano, T., Segah, H., Kusin, K., Limin, S., Takahashi, H., and Osaki, M. (2012) Effects of disturbances on the carbon balance of tropical peat swamp forests. *Global Change Biology.* 18, 3410–22.

Hirano, T., Kusin, K., Limin, S., and Osaki, M. (2013) Carbon dioxide emissions through oxidative peat decomposition on a burnt tropical peatland. *Global Change Biology.* [e-pub ahead of print]

Hogg, E. H., Lieffers, V. J., & Wein, R. W. (1992). Potential carbon losses from peat profiles: effects of temperature, drought cycles, and fire. *Ecological Applications*, 2, 298-306.

Hogg, E.H. (1992) Potential losses from peat profiles- effects of temperature, drought cycles and fire. *Ecological Applications*. 2, 298-306.

Hooijer, A., Silvius, M., Wosten, H.D., and Page, S.E. (2006) PEAT-CO2 Assessment of CO2 emissions from drained peatlands in SE Asia. *Delft Hydraulics report*.

Hooijer, A., Page, S., Canadell, J., Silvius, M., Kwadijik, J., Wösten, H., and Jauhiainen, J. (2010) Current of future CO_2 emissions from drained peatlands in Southeast Asia. *Biogeosciences*. 7, 1505-1514.

Hooijer, A., Page, S., Jauhiainen, J., Lee, W.A., Lu, X., Idris, A., and Anshari, G. (2012) Peatland subsidence and carbon loss in pulp tree and oil palm plantations in Sumatra, SE Asia: reducing uncertainty and implications for emission reduction options. *Biogeosciences.*

Hoscilo, A. (2009) The role of fire in the land use dynamics and restoration of tropical peatlands: developing techniques to assess post-fire vegetation recovery, fire risk and the emission of greenhouse gases. *PhD Thesis submitted to University of Leicester.*

Hoscilo, A., Page, S.E., Tansey, K., and Rieley, J.O. (2011) Effect of repeated fire on land-cover change in on peatland in southern Central Kalimantan, Indonesia from1973 to 2005. *International Journal of Wildland Fire*. 20, 578- 588.

Hoscilo, A., Tansey, K., and Page, S. (2013) Post-fire vegetation response as a proxy to quantify the magnitude of burn severity in tropical peatlands. International Journal of Remote Sensing. 34, 412-433.

Houghton, R.A. (2005). Tropical deforestation as a source of greenhouse gas emissions.

Humphreys, F.R., and Craig, F.G. (1981) Effects of fire on soil chemical, structural and hydrological properties. *Fire and the Australian biota*. 177-200.

Immirzi, C.P. and Maltby, E. (1992) The global status of peatlands and their role in carbon cycling: a report for Friends of the Earth by the Wetlands Ecosystem Research Group. Report 11, Department of Geography, University of Exeter, UK. Friends of the Earth, London.

IPCC (1996) Climate change 1995 impacts, adaptations and mitigation of climate change: scientific-technical analyses. Cambridge: Cambridge University Press. 878.

IPCC (2001) Climate Change 2001: The Scientific Basis. Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.

Ishiwatari, M., Ishiwatari, R., Sakashita, T., Tatsumi, T., and Tominaga., H. (1991) Pyrolysis of chlorophyll a after preliminary heating at a moderate temperature: implications for the origin of prist-1-ene on kerogen pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 31, 249-260.

Jauhiainen, J., Takahashi, H., Heikkenen, J., Martikainen, P., and Vasander, H. (2005) Carbon fluxes from a tropical peat swamp forest floor. *Global Change Biology*. 11, 1788-1797.

Jauhiainen, J., Limin, S., Silvennoinen, H., and Vasander, H. (2008) Carbon dioxide and methane fluxes in drainage affected tropical peat before and after hydrological restoration. *Ecology.* 89, 3503-3514.

Jauhiainen, J., Hooijer, A., and Page, S.E. (2012) Carbon Dioxide Emissions from an Acacia plantation on peatland in Sumatra, Indonesia. *Biogeosciences.* 9, 617-630.

Jauhiainen, J., Silvennoinen, H., Hamalainen, R., Kusin,K., Limin, S., Raison, R.J., and Vasander, H. (2012b) Nitrous Oxide fluxes from tropical peat with different disturbance history and management. *Biogeosciences.* 9, 1337-1350.

Jaya, A., Siregar, U. J., and Massijaya, M. Y. (2009). Biomass content and biodiversity of peat swamp forest under various land cover conditions. In *Proceedings of the International Symposium on Tropical Peatland Management: Wise Use of Tropical Peatland: 14-15 July 2009, Bogor*.

Jaya, A., Takashi, I., Limin, S., Darung, U., and Banuwa, I. (2010) Microclimate of developed peatland of the mega-rice project in Central Kalimantan. *Journal of Tropical Soils.* 15, 63-71.

Johansen, M.P., Hakonson, T.E., and Breshears, D.D. (2001) Post-fire runoff and erosion from rainfall simulation: contrasting forests with shrublands and grasslands. *Hydrolological Processes*. 15, 2953–2965.

Johnson, D.W., and Curtis, P.S. (2001) Effects of forest management on soil C and N storage: meta analysis. *Forest Ecology and Management*. 140, 227–238.

Johnson, M.S., Lehmann, J., Steenhuis, T.S., Vargem-de-Oliveira, L, and Fernandes, E.C.M. (2005) Spatial and temporal variability of soil water repellency of Amazonian pastures. *Soil Research.* 43, 319–326.

Joosten, H., and Clarke, D. (2002) Wise Use of Mires and Peatlands. Background and Principles – Including a framework for decision making. International Mire Conservation Society and International Peat Society.

Kaal, J., Baldock, J.A., Buurman, P., Nierop, K.G.J., Pontevedra-Pombal, X., and Martinez-Cortizas, A.M. (2007) Evaluating pyrolysis-GC/MS and 13404 C CPMAS NMR in conjunction with a molecular mixing model of the Penido Vello peat deposit, NW Spain. *Organic Geochemistry*. 38, 1097–1113.

Kaal, J., Martinez-Cortizas, A., Buurmann, P., and Boado, F. (2008) 8000 yr of black carbon accumulation in a colluvial soil from NW Spain. *Quaternary Research*. 69, 56-61.

Kaal, J., Martinez-Cortizas, A., Buurmann, P., and Neirop, K. (2008) A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW Spain. *Applied Geochemistry.* 23, 2395-2405.

Kaal, J., and Rumpel, C. (2009) Can pyrolysis-gc/ms be used to estimate the degree of thermal alteration of black carbon? *Organic Geochemistry.* 40, 1179-1187.

Kang, B.T., and Sajjapongse, A. (1980) Effect of heating on properties of some soils from Southern Nigeria and growth of rice. *Plant and Soil Science*. 55, 85-95.

Kauffman, J.B., Sanford-Jr, R.L., Cummings, D.L., and Salcedo, I.H. (1993) Biomass and nutrient dynamics associated with slash fires in neotropical dry forests. *Ecology.*140-151.

Kauffman, J.B., Holben, N., Tanré, D., and Ward, D. (1994) Remote sensing of biomass burning in the Amazon. *Remote Sensing Review.* 10, 51-90.

Kauffman, J., Cummings, D.L., Ward, D.E., and Babbitt, R. (1995) Fire in the Brazilian Amazon: 1. Biomass, nutrient pools, and losses in slashed primary forests. *Oecologia.* 104, 397-408.

Kasischke, E.S., Christensen, N.L., and Stocks, B. (1995) Fire, global warming and the carbon balance of boreal forests. *Ecological Applications.* 5, 437-451.

Kasischke, E.S., and Turetsky, M.R. (2006) Recent changes in the fire regime across the North American boreal region — spatial and temporal patterns of burning across Canada and Alaska. *Geophysical Research Letters.* 33, L09703.

Kavdır, Y., Ekinci, H., Yüksel, O., and Mermut, A.R. (2005) Soil aggregate stability and ^{13}C CP/MAS-NMR assessment of organic matter in soils influenced by forest wildfires in Çanakkale, Turkey. *Geoderma.* 129, 219–229.

Keeley, J.E. (2009) Fire intensity, fire severity and burn severity: a brief review and suggested usage. *International Journal of Wildland Fire.* 18, 116–126.

Keeley, J. E., Morton, B. A., Pedrosa, A. and Trotter, P. (1985) Role of allelopathy, heat and charred wood in the germination of chaparral herbs and suffrutescents. *Journal of Ecology* 73, 445-458.

Kershaw, A.P., and Bohte, A. (1997) The impact of prehistoric fires on tropical peatland forests. In: Rieley, J.O. and Page, S.E. (eds), *Biodiversity and Sustainability of Tropical Peatlands.* 73-80. Samara Press, Tresaith, Cardigan.

Ketterings, Q.M., and Bingham, J.M. (2000) Soil colour as an indicator of slash-and-burn fire severity and soil fertility in Sumatra, Indonesia. *Soil Science Society of America Journal*. 64, 1826-1833.

Kiladis, G.N., and Diaz, H. (1989) Global Climate Anomalies associated with extremes in the Southern Oscillation. *Journal of Climate*. 2, 1069-1090.

Kiem, R., and Kögel–Knaber, I. (2003) Contribution of lignin and polysaccharides to the refractory carbon pool in C-depleted arable soils. *Soil Biology and Biochemistry*. 35, 101- 118.

Kim, E., Oh, J., and Chang, Y. (2003) Effects of forest fire on the level and distribution on PCDDF's and PAH in forest soils. *The Science of the Total Environment*. 311, 177-189.

Kleber, M. (2010) What is recalcitrant soil organic matter? *Environmental Chemistry*. 7, 320-332.

Klopatek, J.M., Klopatek, C.C., and DeBano, L.F. (1990) Potential variation of nitrogen transformations in pinyon±juniper ecosystems resulting from burning, *Biology and Fertility of Soils.* 10, 35-44.

Knicker, H., González-Vila, F.J., Polvillo, O., González, J., and Almendros, G. (2005a) Fire induced transformations of C and N forms in different organic soil fractions from a Dystric Cambisol under a Mediterranean pine forest (*Pinus Pinaster*). *Soil Biology and Biogeochemistry.* 37, 701-718.

Knicker, H., Totsche, K.U., Almendros, G., and González-Vila, H.J. (2005b) Condensation degree of burnt peat and plant residues and the reliability of solid-state VACP MAS 13C NMR spectra obtained from pyrogenic humic material. *Organic Geochemistry.* 36, 1359–1377.

Knicker, H., Almendros, G., González-Vila, F.J., González-Pérez, J., and Polvillo, O. (2006) Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Meditteranean ecosystems: a 13419 C NMR study. *European Journal of Soil Science*. 57, 558-569.

Knicker, H. (2007) How does fire affect the nature and stability of soil organic nitrogen and carbon? A review. *Biogeochemistry*. 85, 91-118.

Knicker, H., Müller, P., and Hilscher, A. (2007) How useful is chemical oxidation with dichromate for the determination of "Black Carbon" in fire-affected soils? *Geoderma.* 142, 178−196.

Knicker, H., Weismeier, M., and Dick, D.P. (2008) A simplified method for the quantification of pyrogenic organic matter in grassland soils via chemical oxidation. *Geoderma.* 147, 69-74.

Knicker, H., González Vila, F.J., and González Vázquez, R. (2013) Biodegradability of organic matter in fire-affected mineral soils of Southern Spain. *Soil Biology and Biochemistry.* 56, 31-39.

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K., and Leinweber, P. (2008) Organo-mineral associations in temperate soils: integrating biology, mineralogy and organic matter chemistry. *Journal of Plant Nutrition and Soil Science.* 171, 61–82.

Kögel-Knabner, I., de Leeuw, J.W., and Hatcher, P.G. (1992) Nature and distribution of alkyl carbon in forest soil profiles: implications for the origin and humification of aliphatic biomacromolecules. *Science of The Total Environment*. 117–118, 175–185.

Koh, L., Miettinen, J., Liew, S.C., and Ghazoul, J. (2011) Remotely sensed evidence of tropical peatland conversion to oil palm. *PNAS.* 108, 5127-5132.

Kuder, T., and Kruge, M.A. (1998) Preservation of biomolecules in sub-fossil plants from raised peat bogs — a potential paleoenvironmental proxy. *Organic Geochemistry*. 29, 1355–1368.

Kuhlbusch, T.A.J., and Crutzen, P.J. (1995) Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO2 and a source of O2. *Global Biogeochemical Cycles*. 9, 491-501.

Kuhlbusch, T.A.J. (1998) Black carbon and the carbon cycle. *Science.* 280, 1903–1904.

Kuhry, P., 1994. The role of fire in the development of Sphagnumdominated peatlands in western boreal Canada. *Journal of Ecology.* 82, 899–910.

Kurth, V.J., Mackenzie, M.D., and DeLuca, T.H. (2006) Estimating charcoal content in forest mineral soils. *Geoderma.* 137, 135-139.

Kutiel, P., and Shaviv, A. (1993) Effects of soil type, plant composition and leaching on soil nutrients following a stimulated forest fire. *Forest Ecology and Management*. 53, 329-343.

Kuzyakov, Y., Subbotina, I., Chen, H., Bogomolova, I., and Xu, X. (2009) Black carbon decomposition and incorporation into soil microbial biomass estimated by ^{14}C labelling. *Soil Biology and Biochemistry.* 41, 210–219.

Lafleur, P.M., Moore, T.R., Roulet, N.T., and Frolking, S., (2005) Ecosystem respiration in a cool temperate bog depends on peat temperature but not water table. *Ecosystems.* 8, 619-629.

Langner, A., Meittinen, J., and Siegert, F. (2007) Landcover change 2002-2005 in Borneo and the role of fire-derived from MODIS imagery. *Global Change Biology*. 13, 2329- 2340.

Langner, A., and Siegert, F., (2009) Spatiotemporal fire occurrence in Borneo of a period of 10 years. *Global Change Biology*. 15, 48-62.

Larsen, I., MacDonald, L., Brown, E., Rough, D., Walsh, M., Pietrazek, J., Libohova, Z., Binavides- Solorio, J., and Shcaffrath, K. (2009) Causes of post-fire run-off and erosion: Water repellency, cover or soil sealing? *Soil Science Society of America Journal*. 73, 1393-1407.

Lavoie, C., and Pellerin, S. (2007). Fires in temperate peatlands (southern Quebec): past and recent trends. *Botany*. 85, 263-272.

Lehmann, J., da Silva Jr., J.P., Steiner, C, Nehls, T., Zech, W., and Glaser, B. (2003a) Nutrient availabilty and leaching in a archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant and Soil.* 249, 343-357.

Lehmann, J., Skjemstad, J., and Sohi, S. (2008) Australian climate-carbon feedback reduced by soil black carbon. *Nature Geoscience.* 1, 832-835.

Leifield, J., Steffens, M., and Galego-Sala, A. (2012) Sensitivity of peatland carbon loss to organic matter quality. *Geophysical Research Letters*. 39, L14704.

Leinweber, P., and Schulten, H. (1999) Advances in analytical pyrolysis of soil organic matter. *Journal of Analytical and Applied Pyrolysis*. 49, 459-468.

Lentile, L.B., Holden, Z.A., Smith, A.M.S., Falkowski, M.J., Hudak, A.T., Morgan, P., Lewis, S.A., Gessler, P.E., and Benson, N.C. (2006) Remote sensing techniques to assess active fire characteristics and post-fire effects. *International Journal of Wildland Fire.* 15, 319–345.

Letey, J., Carrillo, M.L.K., and Pang, X.P. (2000) Approaches to characterize the degree of water repellency. *Journal of Hydrology*. 231–232, 61–65.

Lewis, S.A., Wu, J.Q., and Robichaud, P.R. (2006) Assessing burn severity and comparing soil water repellency, Hayman Fire, Colorado. *Hydrological Processes.* 20, 1–16.

Li, W., Dickinson, R., Fu, R., Niu, G., Liang, Z., and Canadell, J. (2007) Future precipitation changes and their implications for tropical peatlands. *Geophysical Research Letters*. 34.

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., and Neves, E.G. (2006) Black Carbon Increases Cation Exchange Capacity in Soils. *Soil Science.* 70, 1719–1730.

Liang, C., and Balser, T.C. (2008) Preferential sequestration of microbial carbon in subsoils of a glacial-landscape toposequence, Dane County, WI, USA. *Geoderma.* 148, 113–119.

Lorenz, K., Lal, R., Preston, C. M., and Nierop, K. G. (2007). Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio (macro) molecules. *Geoderma*, 142, 1-10.

Lorenz, K., Lal, R., and Jimenez, J.J. (2010) Characterization of soil organic matter and black carbon in dry tropical forests of Costa Rica. *Geoderma.* 158, 315-321.

Ludang, Y., Jaya, A., and Inoue, T. (2007) Geohyrdrological conditions of the developed peatland in Central Kalimantan. *World Applied Sciences Journal.* 2, 198-203.

MacDonald, L.H., and Huffman, E.L. (2004) Post-fire soil water repellency. *Soil Science Society of America Journal*. 68, 1729-1734.
Mackenzie, M.D., McIntire, E., Quideau, S., and Graham, R. (2008) Charcoal distribution affects nitrogen contents in forest soils of California. *Soil Science Society of America Journal*. 72, 1774-1785.

Major, J., Lehmann, J., Rondon, M., and Goodale, C. (2010) Fate of soil-applied black carbon : downward migration, leaching and soil respiration. *Global Change Biology*. 16, 1366-1379.

Martin, A., Mariotti, A., Balesdent, J., Lavelle, P., and Vuattoux, V. (1990) Estimate of organic matter turnover rate in savanna soil by 13C natural abundance measurements. *Soil Biology and Biochemistry.* 22, 517–523.

Masiello, C.A. (2004) New directions in black carbon organic geochemistry. *Marine Chemistry.* 92, 201−213.

Meijaard, E., Sheil, D., Nasi, D.R., Augeri, D., Rosenbaum, B., Iskandar, D., Setyawati, T., Lammertink, M., Rachmatika, I., Wong, A., Soehartono, T., Stanley, S., and O'Brien, T.G., (2005) Life After Logging: Reconciling Wildlife Conservation and Production Forestry in Indonesian Borneo. *Center for International Forestry Research, Jakarta, Indonesia.*

Melling, L., Hatano, R., and Goh, K.J. (2005) Methane fluxes from three ecosystems in tropical peatland of Sarawak, Malaysia. *Soil Biology and Biochemistry.* 37, 1445–1453.

Michel, J., Riviere, L., and Bellon-Fontaine, M. (2001) Measurement of wettability of organic materials in relation to water content by the capillary rise method. *Journal of Colloid Interface Science.* 189, 299- 304.

Mickler, R, Geron, C., Rorig, M. (2010) Predicting prescribed and wildland fire behavior in deep organic soils In 'Proceedings of 3rd fire behavior and fuels conference,' CD ROM. *International Association of Wildland Fire.*

Miettinen, J., Shi, C., & Liew, S. C. (2011). Two decades of destruction in Southeast Asia's peat swamp forests. *Frontiers in Ecology and the Environment*. 10, 124-128.

Miettinen, J., Shi, C., Tan, W. J., & Liew, S. C. (2012). 2010 land cover map of insular Southeast Asia in 250-m spatial resolution. *Remote Sensing Letters*. 3, 11-20.

Mikutta, R., Kleber, M., Kaiser, K., and Jahn, R. (2005) Review: organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. *Soil Science Society America.* 69, 120–135.

Mills, A.J., and Fey, M.V. (2004) Frequent fires intensify soil crusting: physicochemical feedback in the pedoderm of long-term burn experiments in South Africa. *Geoderma.* 121, 45–64.

Moldoveanu, S. (1998) Analytical pyrolysis of natural polymers. Elsevier Science. 20-25.

Mooney, S.D., and Tinner, W. (2011) The analysis of charcoal in peat and organic sediments. *Mires and Peat*. 7, 1–18.

Moore, S., Gauci, V., Evans., C.D., and Page, S.E. (2011) Fluvial organic carbon losses from a Bornean blackwater river. *Biogeosciences.* 8, 901–909.

Moore, S., Evans, C.D., Page, S.E., Garnett, M.H., Jones, T.G., Freeman, C., Hooijer, A., Wiltshire, A.J., Limin, S.H., Gauci, V. (2013) Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes. *Nature*. 493, 660-663.

Moreno, J.M., and Oechel, W.C. (1991) Fire intensity effects on germination of shrubs and herbs in southern California chaparral. *Ecology.* 1993-2004.

Morgan. P., Hardy, C.C., Swetnam, T.W., Rollins, M.G., and Long, D.G. (2001) Mapping fire regimes across time and space: Understanding coarse and fine-scale fire patterns. *International Journal of Wildland Fire*. 10, 329–342.

Murdiyarso, D., Hergoualc'h, K., and Verchot, L.V. (2010) Opportunities for reducing greenhouse gas emissions in tropical peatlands. *Proceedings of the National Academy of Sciences.* 107, 19655-19660.

Morrogh-Bernard, H., Husson, S., Page, S. E., & Rieley, J. O. (2003). Population status of the Bornean orang-utan (*Pongo pygmaeus*) in the Sebangau peat swamp forest, Central Kalimantan, Indonesia. *Biological Conservation*, 110, 141-152.

Neary, D.G., Klopatek, C.C., DeBano, L.F., and Folliott, P.F. (1999) Fire Effects on Belowground Sustainability: a review and synthesis. *Forest Ecology and Management.* 122, 51-71.

Neff, J.C., Harden, J.W., and Glexiner, G. (2005) Fire effects on soil organic matter content, composition andnutrients in boreal Alaska. *Canadian Journal of Forestry Research*. 35, 2178-2187.

Nierop, K. G., van Lagen, B., & Buurman, P. (2001). Composition of plant tissues and soil organic matter in the first stages of a vegetation succession. *Geoderma*. *100*, 1-24.

Nierop, K., and Jansen, B. (2009) Extensive transformation of organic matter and excellent lipid preservation at the upper superhumid Guandera paramo. *Geoderma*. 151, 357-369.

Notohadiprawiro, T. (1998) Conflict between problem-solving and optimising approach to land resources development policies: the case of Central Kalimantan wetlands. *The Spirit of Peatlands: 30 Years of the International Peat Society*. 14-24.

Novakov, T. (1984) The role of soot and primary oxidants in atmospheric chemistry. *Science of The Total Environment.* 36, 1-10

Ohlson, M., Dahlberg, B., Økland, T., Brown, K.J., and Halvorsen, R. (2009) The charcoal carbon pool in boreal forest soils. *Nature Geoscience.* 2, 692 – 695.

Otto, A., Gondokusumo, R., and Simpson, M.J. (2006) Characterization and quantification of biomarkers from biomass burning at a recent wildfire site in Northern Alberta. *Canada Applied Geochemistry*. 21, 166–183.

Odion, D.C., and Hanson, C.T., (2008) Fire Severity in the Sierra Nevada Revisited: Conclusions Robust to Further Analysis. *Ecosystems*. 11, 15-16.

Page, S.E., Doody, K., Hodgson, S., Husson, S., Jenkins, P. and Morrogh-Bernard, H. (1997) Biodiversity of tropical peat swamp forest: A case study of animal diversity in the Sungai Sebangau catchment of Central Kalimantan. In: Rieley, J.O. and Page, S.E. (eds) (1997) *Biodiversity and Sustainability of Tropical Peatlands.* Samara, Cardigan, pp. 231-242.
Page, S.E. & Rieley, J.O. (1998) Tropical peat swamp forests: Management at the catchment scale. In: Harper, D.M. & Brown, A. (eds) *Sustainable Management of Tropical Catchments.* Wiley. pp. 165-186.

Page, S.E., Rieley, J.O., Shotyk, W., and Weiss, D., (1999) Interdependence of peat and vegetation in a tropical swamp forest. *Philosophical Transactions of the Royal Society*. 354, 1885-1897.

Page, S.E., Siegert, F., Rieley, J.O., Boehm, H-D.V., Jaya, A., and Limin, S. (2002) The amount of carbon released from peat and forest fires in Indonesia in 1997. *Nature*. 420, 61-65.

Page, S.E., Wüst, R.A.J., Weiss, D., Rieley, J.O., Shotyk, W., and Limin, S.H. (2004) A record of Late Pleistocene and Holocene carbon accumulation and climate change from an equatorial peat bog (Kalimantan, Indonesia): implications for past, present and future carbon dynamics. *Journal of Quaternary Science.* 19, 625-635.

Page, S.E**.**, Rieley, J.O. & Wüst, R. (2006) Lowland tropical peatlands of Southeast Asia. In: Martini, P., Martinez-Cortizas, A. & Chesworth, W. (eds) *Peatlands: basin evolution and depository of records on global environmental and climatic changes*. Elsevier, Amsterdam (Developments in Earth Surface Processes series), pp. 145-172.

Page, S.E., Hoscilo, A., Langner, A., Tansey, K., Siegert, F., Limin, S., and Rieley, J. (2009) Tropical Peatland fires in Southeast Asia. In: Cochrane (2009) *Tropical Fire Ecology*. Praxis Publishing Ltd, Chicester, UK.

Page, S.E**.,** Wüst, R. & Banks, C. (2010) Past and present carbon accumulation and loss in Southeast Asian peatlands. *PAGES News.* 18, 25-26.

Page, S.E., Rieley, J.O., and Banks, C.J. (2011) Global and regional importance of the tropical peatland carbon pool. *Global Change Biology.* 17, 798–818.

Page-Dumroese, D. S., Jurgensen, M. F., Tiarks, A. E., Ponder, Jr, F., Sanchez, F. G., Fleming, R. L., and Scott, D. A. (2006). Soil physical property changes at the North American Long-Term Soil Productivity study sites: 1 and 5 years after compaction. *Canadian Journal of Forest Research*. 36, 551-564.

Palmer, K.N. (1957) Smouldering combustion in dusts and fibrous materials. *Combustion and Flame*. 1, 129–154.

Paris, O., Zollfrank, C.,and Zickler, G.A. (2005) Decomposition and carbonisation of wood biopolymers. *Carbon*. 43, 53–53

Parson, A. (2003) Burned area emergency rehabilitation (BAER) soil burn severity definitions and mapping guidelines. *USDA forest service. Rocky Mountain research*.

Pastova, I., Botto, R.E., Arisz, P.W., and Boon, J.J. (1994) Cellulose char structure: A combined analytical Py-GC-MS, FTIR, and NMR study. *Carbohydrate Research.* 262, 27–47.

Pearce, F. (2007). Indonesias' carbon catastophe. *New Scientist*. 196, 50-53.

Pessenda, L.C.R., Gouveia, S.E.M., and Aravena, R. (2001) Radiocarbon dating of total soil organic matter and humin fraction and its comparison with 14C ages of fossil charcoal. *Radiocarbon.* 43, 595–601.

Plante, A.F., Pernes, M., and Chenu, C. (2005) Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. *Geoderma.* 129, 186–199.

Poirier, N., Derenne, S., Rouzaud, J.-N., Largeau, C., Mariotti, A., Balesdent, J., and Maquet, J. (2000) Chemical structure and sources of themacromolecular, resistant, organic fraction isolated from a forest soil (Lacadée, south-west France). *Organic Geochemistry.* 31, 813–827.

Pontevedra-Pombal, X., Martínez-Cortizas, A., García-Rodeja, E., Buurman, P., and Van Lagen, B. (2001) Composicíon y transformacíon de la material orgánica en un histosol de la Serra do Xistral (norte de Galicia) mediante CPMAS-13C-NMR. *Edafología.* 8, 67–79.

Poulenard, J., Michel, J.C., Bartoli, F., Portal, J.M., and Podwojewski, P. (2004) Water repellency of volcanic ash soils from Ecuadorian páramo: effect of water content and characteristics of hydrophobic organic matter. *European Journal of Soil Science*. 55, 487–496.

Preston, C.M., and Schmidt, M.W. (2006) Black (pyrogenic) carbon : a synthesis of current knowloege and uncertainties with special consideration of boreal regions. *Biogeosciences*. 3, 397-420.

Prentice, I.C., Farquhar, G.D., Fasham, M.J.R., Goulden, M.L., Heimann, M., Jaramillo, V.J., Kheshgi, H.S., LeQuéré, C., Scholes, R.J. and Wallace, W.R. (2001) *The Carbon Cycle and Atmospheric Carbon Dioxide* In: Climate Change 2001: the Scientific Basis. Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. , ed. by Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K. and Johnson, C.A. Cambridge University Press, Cambridge, UK, 185-237.

Qualls, R. G., & Haines, B. L. (1990). The influence of humic substances on the aerobic decomposition of submerged leaf litter. *Hydrobiologia*. 206, 133-138.

Rasion, R.J. (1979) Modification of the soil environment by vegetation fires with particular reference to nitrogen transformations: a review. *Plant and Soil*. 53, 71-108.

Raison, R.J., Khanna, P.K., and Woods, P.V. (1985b) Mechanisms of element transfer to the atmosphere during vegetation fires. *Canadian Journal of Forestry Research*. 15, 132-140.

Ramanathan, V., and Carmichael, G. (2008) Global and regional climate changes due to black carbon. *Nature Geoscience.* 1, 221 – 227.

Ranzi, E., Dente, M., Faravelli, T., Bozzano, G., Fabini, S., Nava, R., Cozzani, V., and Tognotti, L. (1997) Kinetic Modeling of Polyethylene and Polypropylene Thermal Degradation. *Journal of Analytical and Applied Pyrolysis.* 40-41, 305-319.

Ravi, S., D'Odorico, P, Zobeck, T. M. Over, T.M., and Collins, S.L. (2007) Feedbacks between fires and wind erosion in heterogeneous arid lands. *Journal of Geophysical Research*. 112, G04007.

Reiche, M., Gleixner, G., and Küsel, K. (2010) Effect of peat quality on microbial greenhouse gas formation in an acidic fen. *Biogeosciences*. 7, 187-198.

Rein, G., Cleaver, N., Ashton, C., Pironi, P., and Torero, J.L. (2008) The severity of smouldering peat fires and damage to the forest soil. *Catena*. 74, 304–309.

Rein, G., Cohen, S., and Simeoni, A. (2009) Carbon emissions from smouldering peat in shallow and strong fronts. *Proceedings of the Combustion Institute*. 32, 2489–2496.

Rieley, J. O., and Page, S. E. (2005). Wise use of tropical peatlands: focus on Southeast Asia. *ALTERRA—Wageningen University and Research Centre and the EU INCO—STRAPEAT and RESTORPEAT Partnership, Wageningen, The Netherlands*.

Rieley, J.O. & Page, S.E. (editors) (1997) *Biodiversity and Sustainability of Tropical Peatlands.* Samara, Cardigan. 370 p. ISBN 1-873692-10-2.

Robichaud, P.R., and Hungerford, R.D. (2000) Water repellency by laboratory burning of four northern Rocky Mountain forest soils. *Journal of Hydrology*. 231–232, 207–219.

Robinson, S.D., and Moore, T.R. (2000)The Influence of Permafrost and Fire upon Carbon Accumulation in High Boreal Peatlands, Northwest Territories, Canada. *Arctic, Antarctic and Alpine Research.* 32, 155-166.

Rollins, M.S., Cohen, A.D., and During, J.R., (2003) Effects of fires on the chemical and petrographic composition of peat in the Snuggedy Swamp, South Carolina. *International Journal of Coal Geology.* 22, 101-117.

Romanya, J., Khanna, P.K., and Raison, R.J. (1994) Effects of slash burning on soil phosphorus fractions and sorption and desorption of phosphorus. *Forest Ecology and Management*. 65, 89-103.

Romanya, J., Casals, P., & Vallejo, V. R. (2001). Short-term effects of fire on soil nitrogen availability in Mediterranean grasslands and shrublands growing in old fields. *Forest Ecology and Management*. 147, 39-53.

Rovira, P., Duguy, B., and Vallejo, R.V. (2009) Black carbon in wildfire-affected shrubland Mediterranean soils.. *Z. Pflanzenernähr. Bodenk*., 172, 43–52.

Rovira, P., and Vallejo, V.R. (2002) Labile and recalcitrant pools of carbon and nitrogen in organic matter decomposing at different depths in soil: an acid hydrolysis approach. *Geoderma.* 107, 109-141.

Roy, J.L., and McGill, W.B. (2000) Flexible conformation in organic coatings: a hypothesis about water repellency. *Canadian Journal of Soil Science.* 80, 143-152.

Ryan, K.C. (2002) Dynamic interactions between forest structure and fire behavior in boreal ecosystems. *Silva Fennica.* 36, 13–39.

Ryan, K., and Noste, N. (1985) Evaluating prescribed fires, pp. 230-238 in: JE Lotan et al.(tech. coor) *Proceedings - Symposium and Workshop on Wilderness Fire.* USDA Forest Service Intermountain Forest and Range Experiment Station, General Technical Report INT-182.

Saiz-Jimenez, C. (1994) Analytical Pyrolysis of Humic Substances: Pitfalls, Limitations, and Possible Solutions. *Environment Science and Technology. 28,* 1773–1780.

Sajarwan, A., Notohadiprawiro, T., Radjagukguk, B., and Hastuti, S. (2002) Diversity of tropical peat characteristics in intact peatland forest, under the influence of forest type, peat thickness, and position of peat deposit. In: *Peatlands for People: Natural Page 37 of 56 Global Change Biology Resource Functions and Sustainable Management* (eds Rieley, 1 JO, Page, SE, Setiadi, B), pp. 119-124. Proceedings of the International Symposium on Tropical Peatland, Jakarta, Indonesia. BPPT (Badan Pengkajian dan Penerapan Teknologi) and Indonesian Peat Association, Jakarta.

Santín, C., Knicker, H., Fernández, S., Menéndez-Duarte, R., and Álvarez, M.A. (2008) Wildfires influence on soil organic matter in an Atlantic mountainous region (NW of Spain). *Catena.* 74, 286–295.

Savage, S.M. (1974) Mechanism of Fire-Induced Water Repellency in Soil. *Soil Science. Society of America Journal*. 38, 652–657.

Scanlon, D., and Moore, T. (2000) Carbon dioxide production from peatland soil profiles: the influence of temperature, oxic/anoxic conditions and substrate. *Soil Science*. 165, 153-160.

Schimel, D.S., House, J.I., Hibbard, K.A., Bousquet, P., Ciais, P., Peylin, P., Braswell, B.H., Apps., M.J., Baker., D., Bondeau., A., Canadell., J., Churkina., G., Cramer., W., Denning., S., Field., C.B., Friedlingstein., P., Goodale., C., Heimann., M., Houghton., R.A., Melillo., J.M., Moore., B., Murdiyarso., D., Noble., I., Pacala., S.W., Prentice., I.C., Raupach., M.R., Rayner., P.J., Scholes., R.J., Steffen., W.L., and Wirth., C. (2001) Recent Patterns and mechanisms of carbon exchange by terrestrial systems*. Nature*. 291, 481-484.

Schellekens, J., Buurmann, P., and Pontevedra-Pombal X. (2009) Selecting parameters for the environmental interpretation of peat molecular chemistry- a Py-GC/MS study. *Organic Geochemistry.* 40, 678-691.

Schmidt, M., Skjemstad, J.O., Czimczik, C., Glaser, B., Prentice, K.M., Gelinas, Y., and Kuhlbusch, T., (2000) Comparative analysis of black carbon in soils. *Global Biogeochemical Cycles.* 15, 777-794.

Schmidt, M. W., & Noack, A. G. (2000). Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. *Global Biogeochemical Cycles*. 14, 777-793.

Schmidt, M. W., Skjemstad, J. O., Czimczik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., & Kuhlbusch, T. A. (2001). Comparative analysis of black carbon in soils. *Global Biogeochemical Cycles*. 15, 163-167.

Schmidt, M. W., Skjemstad, J. O., & Jäger, C. (2002). Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning. *Global Biogeochemical Cycles*. 16, 1123.

Schnitzer, M. (1991) Soil organic matter- the next 75 years. *Soil Science*. 151, 39-46.

Shneour, E.A. (1966) Oxidation of Graphitic Carbon in Certain Soils. *Science.* 25, 991-992.

Schulten, H.R., and Schnitzer, M., (1998) The chemistry of soil organic nitrogen: a review. *Biology and Fertility of Soils.* 26, 1-15.

Schulze, E., Wirth, C., and Heimann, M. (2000) Perspectives climate change: Managing Forests After Kyoto (2000). *Science.* 289, 2058 – 2059.

Schweithelm, J. (1998). The fires this time: An overview of Indonesia's forest fires in 1997/98. Jakarta, World Wide Fund for Nature Indonesia Programme.

Schweithelm, J., and Glover, D. (1999). Causes and impacts of the fires. *Indonesia's fires and haze: The cost of catastrophe*, 1-13.

Siegert, F., and Hoffmann, A. A. (2000). The 1998 forest fires in East Kalimantan (Indonesia): a quantitative evaluation using high resolution, multitemporal ERS-2 SAR images and NOAA-AVHRR hotspot data. *Remote Sensing of Environment*. 72, 64-77.

Siegert, F., Ruecker, G., Hinrichs, A., and Hoffmann, A. A. (2001). Increased damage from fires in logged forests during droughts caused by El Nino. *Nature*. 414, 437-440.

Siegert, F., Zhukov, B., Oertel, D., Limin, S., Page, S. E., and Rieley, J. O. (2004). Peat fires detected by the BIRD satellite. *International Journal of Remote Sensing*. 25, 3221-3230.

Shackleton, C.M., and Scholes, R.J. (2000) Impact of fire frequency of woody community structure in the Kruger National Park. *Koedoe – African Protected Area Conservation and Science.* 43, 75-81.

Shakesby, R.A., and Doerr, S.H. (2006) Wildfire as a hydrological and geomorphological agent. *Earth-Science Reviews.* 74, 269-307.

Shotyk, W. (1989) An overview of the geochemistry of methane dynamics in mires. *International Peat Journal*. 3, 25-44.

Shimada, S., Takahashi, H., Haraguchi, A., and Kaneko, M. (2001) The carbon content characteristics of tropical peats in Central Kalimantan, Indonesia: Estimating their spatial variability in density. *Biogeochemistry.* 53, 249-267.

Simpson, M.J., and Hatcher, P.G. (2004) Determination of black carbon in natural organic matter by chemical oxidation and solid-state ^{13}C nuclear magnetic resonance spectroscopy. *Organic Geochemistry*. 35, 923–935.

Skjemstad, J.O., Taylor, J.A., and Smernik, R.J. (1999) Estimation of charcoal (char) in soils. *Commnication in Soil Science Plant Analysis.* 30, 2283-2298.

Smith, N. J. H. (1980). Anthrosols and human carrying capacity in Amazonia. *Annals of the Association of American Geographers*. 70, 553–566.

Smith, S.M., Newman, S., Garrett, P.B., and Leeds, J.A. (2001) Differential effects of surface and peat fire on soil constituents in a degraded wetland of the northern Florida everglades. *Journal of Environmental Quality.* 30, 1998-2005.

Sobieh, K.L., Baron, M., and Gonzalez-Rodriguez, J. (2008) Recent Trends and developments in pyrolysis-gas chromatography. *Journal of Chromatography A*. 1186, 51-66.

Sodhi, N., Koh, L.P., Brook, B., and Ng, P. (2004) Southeast Asian Biodiversity: An impending disaster. *Trends in Ecology and Evolution*. 19, 654-660.

Sorenson, K. (1993) Indonesian peat swamp forests and their role as a carbon sink. *Chemosphere*. 27, 1065-1082.

Stegemoller, K.A., and Chappell, H.N. (1990) Growth response of unthinned and thinned Douglas-fir stands to single and multiple applications of nitrogen. *Canadian Journal of Forest Research.* 20, 343–349.

Stauffer, E. (2003) Concept of pyrolysis for fire debris analysts. *Science & Justice.* 43, 29-40.

Stuczynski, T. I., McCarty, G. W., Reeves, J. B., and Wright, R. J. (1997). Use of pyrolysis GC/MS for assessing changes in soil organic matter quality. *Soil Science*, 162, 97-105.

Sulistiyanto, Y., Rieley, J., and Limin, S. (2004) Nutrient dynamics in different sub-types of ombrotrophic peat swamp forest in Central Kalimantan, Indonesia. In *Proceedings of the 12th International Peat Congress, Tampere Finland*. 6, 2004.

Suyanto, S., Applegate, G., Permana, R. P., Khususiyah, N., and Kurniawan, I. (2004). The role of fire in changing land use and livelihoods in Riau-Sumatra. *Ecology and Society*, 9, 15.

Swain, E Y., and Abbott, G.D. (2013) The effect of redox conditions on spagnum acid thermochemolysis product distributions in northen peatland. *Journal of Analytical and Applied Pyrolysis*. 103, 2-7.

Tacconi, L. (2003) Fires in Indonesia: Causes, costs and policy implications. *Centre for International Forestry Research. (CIFOR).*

Tacconi, L., Moore, P. F., and Kaimowitz, D. (2007). Fires in tropical forests–what is really the problem? Lessons from Indonesia. *Mitigation and adaptation strategies for global change*, 12, 55-66.

Takahashi H, Yonetani Y (1997) Studies on microclimate and hydrology of peat swamp forest in Central Kalimantan, Indonesia. In: Tropical Peatlands (eds Rieley JO, Page SE), pp. 179–187. Samara Publishing Limited, Cardigan

Takahashi H, Usup A, Hayasaka H et al. (2003) Estimation of ground water level in a peat swamp forest as an index of peat/forest fire. In: Proceedings of the International Symposium on Land Management and Biodiversity in Southeast Asia, Bali, Indonesia, 17–20 September 2002 (eds Osaki M, Iwakuma T, Kohyama et al.), pp. 311–314. Hokkaido University & Indonesian Institute of Sciences, Sapporo, Japan and Bogor, Indonesia.

Tan, K.T., Lee, K.T., Mohamed, A.R., and Bhatia, S. (2009) Palm oil: Addressing issues and towards sustainable development. *Renewable and Sustainable Energy Reviews*. 13, 420–427.

Täumer, K., Stoffregen, H., and Wessolek, G. (2005) Determination of repellency distribution using soil organic matter and water content. *Geoderma*. 25, 107–115.

Tegelaar, E.W., Hollman, G., Van Der Vegt, P., De Leeuw, J.W., and Holloway, P.J. (1995) Chemical characterization of the periderm tissue of some angiosperm species: recognition of an insoluble, non-hydrolyzable, aliphatic biomacromolecule (Suberan). *Organic Geochemistry*. 23, 239–251.

Thomas, A.D., Walsh, R.P.D., and Shakesby, R.A. (1999) Nutrient losses in eroded sediment after fire in eucalyptus and pine forests in the wet Mediterranean environment of northern Portugal. *Catena.* 36, 283–302.

Tinker, D., and Knight, D. (2000) Coarse Woody Debris following Fire and Logging in Wyoming Lodgepole Pine Forests. *Ecosystems.* 3, 472-483.

Tinoco, P., Almendros, G., Sanz, J., González-Vázquez, R., and González-Vila, F.J. (2006) Molecular descriptors of the effect of fire on soils under pine forest in two continental Mediterranean soils. *Organic Geochemistry*. 37, 1995–2018.

Tomkins, I.B., Kellas, J.B., and Tolhurst, K.D. (1991) Effects of fire intensity on soil chemistry in a eucalypt forest. *Australian Journal of Soil Research*. 29, 25-47.

Turetsky, M., Weider, K., Halsey, L., and Vitt, D., (2002) Current disturbance and the diminishing peatland carbon sink. *Geophysical Research Letters 29, No. 11*.

Turetsky, M. R., Kane, E. S., Harden, J. W., Ottmar, R. D., Manies, K. L., Hoy, E., andKasischke, E. S. (2010). Recent acceleration of biomass burning and carbon losses in Alaskan forests and peatlands. *Nature Geoscience*. 4, 27-31.

Turner, D. P., Ollinger, S. V., and Kimball, J. S. (2004). Integrating remote sensing and ecosystem process models for landscape-to regional-scale analysis of the carbon cycle. *BioScience*. 54, 573-584.

Uden, P. (1993) Nomenclature and terminology for analytical pyrolysis. (IUPAC Recommendations 1993). *International Union of Pure and Applied Chemistry.* 65, 2405-2409.

Usup, A., Hashimoto, H., Takahasi, H., and Hayasaka, A. (2004) Combustion and thermal characteristics of peat fire in tropical peatland in Central Kalimantan. *Tropics.* 14, 1-9.

Valat, B., Jouany, C., and Riviere, L. (1991) Characterisation of the wetting properties of air-dried peats and composts. *Soil Science.* 152, 100-107.

Van de Vijver, C.A.D.M., Root, P., and Prins, H.H.T. (1999) Causes of increased nutrient concentrations in post-fire regrowth in an East African savanna. *Plant and Soil.* 214, 173-185.

Vancampenhout, K., Wouters, K., De Vos, B., Buurman, P., Swennen, R., and Deckers, J. (2009) Differences in chemical composition of soil organic matter in natural ecosystems from different climatic regions A pyrolysis GC/MS study. *Soil Biology & Biochemistry.* 41, 568-573.

Vancampenhout, K., De Vos, B., Wouters, K., Swennen, R., Buurman, P., and Deckers, J. (2012) Organic matter of subsoil horizons under broadleaved forest: Highly processed or labile and plant-derived? *Soil Biology and Biochemistry*. 50, 40-46.

Van der Werf, G.R., Dempewolf, J., Trigg, S.N., Randerson, J.T., Kasibhatia, P.S., Giglio, L., Murdiyarso, D., Peters, W., Morton, D.C., Collatz, G.J., Dolman, A.J., and DeFries, R.S. (2008) Climate regulation of fire emissions and deforestation in equatorial Asia. *Proceedings of the National Academy of Sciences*. 105, 20350-20355.

Vitt, D.H., Li, Y., and Belland, R.J. (1990) Patterns of bryophyte diversity in peatlands of Western Canada. *Bryologist*. 98, 218-227.

Waddington, J.M., Rotenberg, P.A., and Warren, F.J. (2001) Peat CO2 production in a natural and cutover peatland: Implications for restoration. *Biogeochemistry.* 54, 115-130.

Wallis, M.G., and Horne, D.J. (1992) Soil water repellency. *Advances in Soil Science.* 20, 91–140.

Wampler, T. P. (1995). *Analytical pyrolysis: an overview* (pp. 1-29). Marcel Dekker, New York.

Wampler, T. P., Bishea, G. A., and Simonsick, W. J. (1997) Recent changes in automotive paint formulation using pyrolysis-gas chromatography/mass spectrometry for identification. *Journal of Analytical and Applied Pyrolysis*, 40, 79-89.

Wampler, T.P. (1999) Introduction to pyrolysis–capillary gas chromatography. *Journal of Chromatography A.* 842, 207–220.

Wampler, T. P. (Ed.) (2006). *Applied pyrolysis handbook*. CRC Press.

Wan, S.Q., Hui, D., and Luo Y. (2001) Fire effects on nitrogen pools and dynamics in terrestrial ecosystems: a meta-analysis. Ecological Applications 11, 1349–1365.

Wardle, D.A., Zackrisson, O., and Nilsson, M.C. (1998) The charcoal effect in Boreal forests: Mechanisms and ecological consequences. *Oecologia*. 115, 419–426.

Weast, R.C. (1988) Handbook of Chemistry and Physics. CRC Press, Boca Raton, FL.

Weiss, D., Shotyk, W., Rieley, J., Page, S., Gloor, M., Reese, S., and Martinez-Cortias, A. (2002) The geochemistry of major and selected trace elements in a forested peat bog, Kalimantan, SE Asia, and its implications for past atmospheric dust deposition. *Geochimica et Cosmochima Acta*. 66, 2307-2323.

Whelan, R.J. (1995) The Ecology of Fire. Cambridge University Press.

Williams, R.J., Cook, G.D., Gill, A.M., and Moore, P.H.R. (1999) Fire regime, fire intensity and tree survival in a tropical savanna in northern Australia. *Australian Journal of Ecology.* 24, 50–59.

Wondzell, S.M., and King, J.G. (2003) Postfire erosional processes in the Pacific Northwest and Rocky Mountain regions. *Forest Ecology and Management*. 178, 75–87.

Worden, J., Wecht, K., Frankenberg, C., Alvarado, M., Bowman, K., Kort, E., Kulawik, S., Lee, M., Payne, V., and Worden, H. (2013) CH4 and CO distributions over tropical fires during October 2006 as observed by the Aura TES satellite instrument and modeled by GEOS-Chem. *Atmospheric Chemistry and Physics*. 13, 3679–3692.

Worral, F., Burt, T., and Adamson, J. (2003) Can climate change explain increases in DOC flux from upland peat catchments? *Science of the Total Environment.* 326, 95-112.

Wösten, J.H.W., Van den Berg, J., Van Eijk, P., Gevers, G.J.M., Giesen, W.B.J.T., Hooijer, A., Idris, A., Leenman, P.H., Satriadi, D.S., Siderius, C., Silvius, M.J., Suryadiputra, N., and Wibisono, I.W. (2006) Interrelationships between Hydrology and Ecology in Fire Degraded Tropical Peat Swamp Forests. *International Journal of Water Resources*. 22, 157–174.

Wösten, J.H.W., Clymans, E., Page, S.E., Rieley, J.O., and Limin, S.H. (2008) Peat-water interrelationships in a tropical peatlands ecosystem in Southeast Asia. *Catena*. 73, 212-224.

Yu, Z.C., Loisel, J., Brosseau, D.P., Beilman, D.W., and Hunt, S.J. (2010) Global peatland dynamics since the Last Glacial Maximum. *Geophysical Research Letters.* 37*, L13402.*

Yule, C., and Gomez, L. (2008) Leaf litter decomposition in a tropical peat swamp forest in Peninsular Malaysia. *Wetlands Ecology and Management.* 17, 231-241.

Yunos, D. (2010) Masters Thesis. Geography Department. University of Leicester.

Zavala, L.M., Arturo, J.P., Granged, A.J., and Bárcenas-Moreno, G. (2010) Effect of burning temperature on water repellency and aggregate stability in forest soils under laboratory conditions. *Geoderma.* 158, 366–374.

Zaccone, C., Said-Pullicino, D., Gigliotti, G., and Miano, T.M. (2008) Diagenetic trends in the phenolic constituents of Sphagnum-dominated peat and its corresponding humic acid fraction. *Organic Geochemistry*. 39, 830–838.

Zimmermann, M., Leifeld, J., and Fuhrer, J. (2007) Quantifying soil organic carbon fractions by infrared-spectroscopy. *Soil Biology & Biochemistry.* 39, 224−231.

Zimmerman, M., and Bird, M. (2012) Temperature sensitivity of tropical forest soil respiration increase along an altitudinal gradient with ongoing decomposition. *Geoderma*. 187, 1-15.

Appendix 1: Full list of identified pyrolysis products in peat sample pyrolysates. Table includes; 1- Compound Class, 2 – Code used in PCA, 3- Rentention Time, 4- Molecular Weight.

Compound Class[1]	**Code**[2]	**R.T**[3]	**Compound**	**Molecular Formula**	**m.w**[4]	***m/z***	***Kovats R.I***
Polysaccharide	Ps1	5.69	Furfural	$C_5H_4O_2$	96	95+96	745.9
Polysaccharide	Ps2	9.84	3-Methyl-2-cyclopentenone	C_9H_8O	132	53+67	829.1
Polysaccharide	Ps3	27.8	Levoglucosan	$C_6H_{10}O_5$	162	60+73	*1446.9*
Polysaccharide	Ps4	2.8	3-Methylfuran	C_5H_6O	86	53+82	734.9
Polysaccharide	Ps5	3.46	2,5-Dimethylfuran	C_6H_8O	96	95+96	700.4
Polysaccharide	Ps6	4.98	2-(5*H*)-Furanone	$C_4H_4O_2$	84	55+84	762.6
Polysaccharide	Ps7	5.09	(2H)-Furan-3-one	$C_6H_6O_2$	84	54+84	767.1
Polysaccharide	Ps8	8.28	2-Acetylfuran	$C_6H_6O_2$	110	95+110	882.1
Polysaccharide	Ps9	8.95	Dihydro-5-methylfuran-2-one	$C_5H_8O_2$	110	55+98	904.2
Polysaccharide	Ps10	10.01	5-Methyl-2-furaldehyde	$C_6H_6O_2$	110	109+110	935.8
Polysaccharide	Ps11	15.62	Maltol	$C_6H_6O_3$	126	71+126	1087.8
Polysaccharide	Ps12	2.67	Acetic Acid	CH_3COOH	59	60	703.3
Aromatic	Ar1	2.84	Benzene	C_6H_6	78	78	649.7
Aromatic	Ar2	4.61	Toluene	C_7H_8	92	91+92	747.4
Aromatic	Ar3	7.2	Ethylbenzene	C_8H_{10}	106	91+106	845.0
Aromatic	Ar4	7.36	Styrene	C_8H_8	104	78+104	850.5
Aromatic	Ar5	7.9	Xylene	C_8H_{10}	106	91+106	869.1
Aromatic	Ar6	9.78	Benzaldehyde	C_7H_6O	106	77+106	927.4
Aromatic	Ar7	10.29	Propylbenzene	C_9H_{12}	120	91+120	941.6
Aromatic	Ar8	13.38	Indene	C_9H_8	116	115+116	1027.1
Aromatic	Ar9	13.75	Acetophenone	C_8H_8O	120	77+105	1037.1
Aromatic	Ar10	17.2	*o*-methyl Indene	$C_{10}H_{10}$	130	130+115	1131.4
Aromatic	Ar11	17.36	*m*-methyl Indene	$C_{10}H_{10}$	130	130+115	1135.8
Lignin	Lg1	14.84	Guaiacol	$C_7H_8O_2$	124	109+124	1066.7
Lignin	Lg2	18.49	Methyl Guaiacol	$C_8H_{10}O_2$	138	123+138	1167.2
Lignin	Lg3	19.96	Vinyl Phenol	$C_8H_{10}O_2$	138	91+120	1209.6
Lignin	Lg4	22.68	*m*-Vinyl Guaiacol	$C_9H_{10}O_2$	150	135+150	1299.7
Lignin	Lg5	23.63	Syringol	$C_8H_{10}O_3$	154	139+154	1324.5
Lignin	Lg6	24.17	Vinylveratole	$C_{10}H_{12}O_2$	164	149+164	1338.6
Lignin	Lg7	25.59	z-isoeugenol	$C_{10}H_{12}O_2$	164	149+164	1375.7
Lignin	Lg8	26.89	e-isoeugenol	$C_{10}H_{12}O_2$	164	149+164	1410.9

Compound Class[1]	Code[2]	R.T[3]	Compound	Molecular	m.w[4]	*m/z*	*Kovats R.I*
Lignin	Lg9	27.95	Acetyl Guaiacol	$C_9H_{10}O_3$	166	151+166	1442.1
Lignin	Lg10	30.2	Vinyl Syringol	$C_{10}H_{12}O_3$	180	165+180	1512.6
Lignin	Lg11	25.12	Vanillin (4-formylguaiacol)	$C_8H_8O_3$	152	151+152	1363.0
Lignin	Lg12	27.01	Trimethoxbenzene	$C_9H_{12}O_3$	168	153+168	1414.4
Lignin	Lg13	29.02	Guaiacylacetone	$C_{10}H_{12}O_3$	180	137+180	1473.5
Lignin	Lg14	34.83	4-Acetyl Syringol	$C_{10}H_{13}O_6$	229	181+196	1701.1
Lignin	Lg15	33.80	Syringic Acid	$C_9H_{10}O_5$	198	183+198	1610.1
Lignin	Lg16	21.45	4-Ethyl Guaiacol	$C_9H_{12}O_2$	152	137+152	1258.9
Nitrogen	N1	3.87	1-Methyl-1*H*-pyrrole	C_5H_7N	81	80+81	717.0
Nitrogen	N2	6.29	2-Methyl-1*H*-pyrrole	C_5H_7N	81	80+81	813.7
Nitrogen	N3	6.66	3-Methyl-1*H*-pyrrole	C_5H_7N	81	80+81	826.5
Nitrogen	N4	10.43	Benzonitrile	C_7H_5N	103	76+103	945.5
Nitrogen	N5	15.97	Benzeneacetonitrile	C_8H_2N	117	116+117	1097.3
Nitrogen	N6	22.87	Benzamide	C_7H_7NO	121	77+121	1304.7
Nitrogen	N7	34.09	Tetradecanenitrile	$C_{14}H_{27}N$	209	97+209	1673.3
Nitrogen	N8	36.71	Pentadecanenitrile	$C_{15}H_{29}N$	223	97+223	1772.1
Nitrogen	N9	39.42	Hexadecanenitrile	$C_{16}H_{31}N$	237	97+237	1880.4
Nitrogen	N10	44.04	Octadecanenitrile	$C_{18}H_{35}N$	265	97+265	2080.0
Nitrogen	N11	3.99	Pyridine	C_5H_5N	79	52+79	722.0
Nitrogen	N12	7.01	Methyl Pyridine	C_6H_7N	93	66+93	838.5
Nitrogen	N13	21.84	Indole	C_8H_7N	117	90+117	1271.9
Nitrogen	N14	33.99	Diketodipyrrole	$C_{10}H_6N_2O_2$	186	93+186	1669.5
Polyaromatic	PAH1	18.31	Naphthalene	$C_{10}H_8$	128	128	1162.2
Polyaromatic	PAH2	22.17	Methyl Naphthalene	$C_{11}H_{10}$	142	141+142	1282.8
Polyaromatic	PAH3	24.98	Biphenyl	$C_{12}H_{10}$	154	153+154	1359.8
Polyaromatic	PAH4	26.32	1,6-Dimethylnapthalene	$C_{12}H_{12}$	156	141+156	1394.8
Polyaromatic	PAH5	31.09	1,3,5-Trimethylnapthalene	$C_{13}H_{14}$	170	155+170	1552.7
Polyaromatic	PAH6	32.34	Naphthalene compound	n/a		128+142	1597.3
Phenol	Ph1	11.84	Phenol	C_6H_6O	94	66+98	984.9
Phenol	Ph2	18.49	2- methyl phenol	C_7H_8O	108	107+108	1167.2
Phenol	Ph3	19.96	3-methyl phenol	C_7H_8O	108	107+108	1209.6
Phenol	Ph4	22.68	4-methyl phenol	$C_8H_{10}O$	122	107+108	1299.7
Phenol	Ph5	23.63	2-ethyl phenol	C_7H_8O	108	107+122	1324.5

Compound Class[1]	Code[2]	R.T[3]	Compound	Molecular	m.w[4]	*m/z*	***Kovats R.I***
Phenol	Ph6	24.17	3- ethyl phenol	C_7H_8O	122	107+122	1338.6
Phenol	Ph7	25.59	4-ethyl phenol	C_7H_8O	122	107+122	1375.7
Phenol	Ph8	30.95	3-Methoxy-1,2-Benzenediol	$C_7H_8O_3$	140	125+180	1646.4
Aliphatic	Al1	3.31	*n*c7:1	C_7H_{14}	98	55+69	688.1
Aliphatic	Al2	5.36	*n*c8:1	C_8H_{16}	112	55+69	778.2
Aliphatic	Al3	5.89	*n*c8	C_8H_{18}	114	57+71	800
Aliphatic	Al4	8.40	*n*c9:1	C_9H_{18}	126	55+69	886.3
Aliphatic	Al5	8.80	*n*c9	C_9H_{20}	128	57+71	900
Aliphatic	Al6	11.97	*n*c10:1	$C_{10}H_{20}$	140	55+69	988.5
Aliphatic	Al7	12.38	*n*c10	$C_{10}H_{22}$	142	57+71	1000
Aliphatic	Al8	15.67	*n*c11:1	$C_{11}H_{22}$	154	55+69	1089.2
Aliphatic	Al9	16.07	*n*c11	$C_{11}H_{24}$	156	57+71	1100
Aliphatic	Al10	19.25	*n*c12:1	$C_{12}H_{24}$	168	55+69	1188.3
Aliphatic	Al11	19.67	*n*c12	$C_{12}H_{26}$	170	57+71	1200
Aliphatic	Al12	22.03	*n*c13:1	$C_{13}H_{26}$	182	55+69	1278.1
Aliphatic	Al13	22.69	*n*c13	$C_{13}H_{28}$	184	57+71	1300
Aliphatic	Al14	25.91	*n*c14 :1	$C_{14}H_{28}$	196	55+69	1384.1
Aliphatic	Al15	26.52	*n*c14	$C_{14}H_{30}$	198	57+71	1400
Aliphatic	Al16	28.97	*n*c15:1	$C_{15}H_{30}$	210	55+69	1472.1
Aliphatic	Al17	29.26	*n*c15	$C_{15}H_{32}$	212	57+71	1500
Aliphatic	Al18	31.86	*n*c16:1	$C_{16}H_{32}$	224	55+69	1587.4
Aliphatic	Al19	32.14	*n*c16	$C_{16}H_{34}$	226	57+71	1600
Aliphatic	Al20	34.60	*n*c17:1	$C_{17}H_{34}$	238	55+69	1692.5
Aliphatic	Al21	34.80	*n*c17	$C_{17}H_{36}$	240	57+71	1700
Aliphatic	Al22	35.50	Prist-1-ene	$C_{19}H_{38}$	266	56+57	1726.4
Aliphatic	Al23	35.80	Prist-2-ene	$C_{19}H_{38}$	266	56+57	1737.7
Aliphatic	Al24	37.21	*n*c18:1	$C_{18}H_{36}$	252	55+69	1790.9
Aliphatic	Al25	37.45	*n*c18	$C_{18}H_{38}$	254	57+71	1800
Aliphatic	Al26	39.68	*n*c19:1	$C_{19}H_{38}$	266	55+69	1891.0
Aliphatic	Al27	39.90	*n*c19	$C_{19}H_{40}$	268	57+71	1900
Aliphatic	Al28	42.05	*n*c20:1	$C_{20}H_{40}$	280	55+69	1991.5
Aliphatic	Al29	42.24	*n*c20	$C_{20}H_{42}$	282	57+71	2000
Aliphatic	Al30	44.30	*n*c21:1	$C_{21}H_{42}$	294	55+69	2091.6
Aliphatic	Al31	44.49	*n*c21	$C_{21}H_{44}$	296	57+71	2100
Aliphatic	Al32	46.45	*n*c22:1	$C_{22}H_{44}$	308	55+69	2201.6
Aliphatic	Al33	46.62	*n*c22	$C_{22}H_{46}$	310	57+71	2200
Aliphatic	Al34	48.51	*n*c23:1	$C_{23}H_{46}$	322	55+69	2292.5

Compound Class[1]	**Code[2]**	**R.T[3]**	**Compound**	**Molecular**	**m.w[4]**	***m/z***	***Kovats R.I***
Aliphatic	Al35	48.68	*n*c23	$C_{23}H_{48}$	324	57+71	2300
Aliphatic	Al36	50.50	*n*c24:1	$C_{24}H_{48}$	336	55+69	2392.4
Aliphatic	Al37	50.65	*n*c24	$C_{24}H_{50}$	338	57+71	2400
Aliphatic	Al38	52.40	*n*c25:1	$C_{25}H_{50}$	350	55+69	2492.6
Aliphatic	Al39	52.54	*n*c25	$C_{25}H_{52}$	352	57+71	2500
Aliphatic	Al40	54.23	*n*c26:1	$C_{26}H_{52}$	364	55+69	2593.4
Aliphatic	Al41	54.35	*n*c26	$C_{26}H_{54}$	366	57+71	2600
Aliphatic	Al42	56.00	*n*c27:1	$C_{27}H_{54}$	378	55+69	2693.2
Aliphatic	Al43	56.12	*n*c27	$C_{27}H_{56}$	380	57+71	2700
Aliphatic	Al44	57.70	*n*c28:1	$C_{28}H_{56}$	392	55+69	2793.5
Aliphatic	Al45	57.81	*n*c28	$C_{28}H_{58}$	394	57+71	2800
Aliphatic	Al46	59.23	*n*c29:1	$C_{29}H_{58}$	406	55+69	2887.1
Aliphatic	Al47	59.44	*n*c29	$C_{29}H_{60}$	408	57+71	2900
Aliphatic	Al48	60.61	*n*c30:1	$C_{30}H_{60}$	420	55+69	2974.1
Aliphatic	Al49	61.02	*n*c30	$C_{30}H_{62}$	422	57+71	3000
Aliphatic	Al50	62.45	*n*c31:1	$C_{31}H_{62}$	434	55+69	3094.7
Aliphatic	Al51	62.53	*n*c31	$C_{31}H_{64}$	436	57+71	3100
Aliphatic	Al52	63.79	*n*c32:1	$C_{32}H_{64}$	448	55+69	3191.3
Aliphatic	Al53	63.91	*n*c32	$C_{32}H_{66}$	450	57+71	3200
Aliphatic	Al54	64.39	*n*c33:1	$C_{33}H_{66}$	462	55+69	3252.2
Aliphatic	Al55	64.83	*n*c33	$C_{33}H_{68}$	464	57+71	3300