Effects of ecosystem disturbance on fluvial carbon losses from tropical peat swamp forests

Thesis

The Open University

Effects of ecosystem disturbance on fluvial carbon losses from tropical peat swamp forests

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Abstract

Investigations into the effects of anthropogenic disturbance on greenhouse gas emissions from tropical peatlands are relatively well documented. However, the effects of such disturbance on fluvial carbon (C) losses has, thus far, been overlooked and remains unaccounted for in these ecosystem C budgets. Here, three land-cover classes in Central Kalimantan, Indonesia, were investigated in order to determine the effect of tropical peatland disturbance on fluvial organic C budgets.

Intact peat swamp forest (IPSF), moderately disturbed and severely disturbed peat swamp forest (DPSF1 and 2) catchments were monitored for one year. Results demonstrate a trend of increasing annual total organic carbon (TOC) yields with increasing drainage severity, from 63 in IPSF to 105 and 131 g C m^{-2} yr^{-1} in DPSF1 and 2, respectively. Including this routinely-ignored fluvial C loss component in the disturbed peatland ecosystem C budget increases the estimated total C loss by 30%. Radiocarbon analysis of dissolved organic carbon (DOC) reveals that whilst DOC leaching from IPSF was derived from recent primary production, DOC leaching from the two disturbed sites was comprised of much older C, originating from deep within the peat column.

The TOC flux from the Sebangau River basin was estimated to be 0.46 teragrams yr^{-1}, which upon regional extrapolation indicates that Indonesian rivers account for 10% of the global annual riverine DOC export to the ocean. There were no significant differences between sites in the quality of the organic C lost, but DOC lost from disturbed sites was generally less aromatic than from the intact site. It is recognized that a large portion of this labile C will be emitted to the atmosphere via biotic decomposition. Since 1990, peatland disturbance has resulted in a 53% increase in fluvial organic C export from Southeast Asia, an increase that alone approximates the entire annual fluvial organic C flux from European peatlands.

Acknowledgements

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"Waktu jaman huran, pambelum kalonen tagantung bara himba akan kakare uras ah.
Andau toh, keadaan himba jituh tagantung dengan kalonen."

"In the past, we depended on the forest for everything.
Today, the very existence of the same forest depends on us."
(Dayak elder, Sebangau, 2009)

Dayak are the indigenous people of Borneo, within which, Sebangau is one of the largest remaining areas of peat swamp forest.

Chapter One

Introduction

1.1 General overview

To date, the best estimate of the total area of tropical peatlands in the world is 440,000 km^2 (with a range of 387,201 - 657,430 km^2), of which Indonesia alone accounts for just under half (206,950 km^2, 47%), making it the largest contributor to the world's reserves (Page *et al.*, 2011). Within Indonesia, the islands of Sumatra and Kalimantan, collectively, are estimated to have a peatland area of 130,000 km^2 (Wahyunto *et al.*, 2003; 2004), storing a vast reservoir of about 30,000 Tg (1 Tg = 1 g × 10^{12}) of carbon (Jaenicke, *et al.*, 2008). This is equivalent to almost four times the amount of carbon that was released globally by the burning of fossil fuels in 2006 (8,000 Tg; IPCC, 2007). Peatlands in Southeast Asia, and in particular within Indonesia are subject to the most rapid rates of degradation and land use change in the world as a result of strong economic and social pressures for timber, land for agriculture and plantations of oil palm and pulp trees (Koh *et al.*, 2009). As a consequence, in the last two decades this region's peatlands have undergone rapid deforestation (Langner *et al.*, 2007; Langner & Siegert, 2009), widespread drainage (Hooijer *et al.*, 2006; 2010) and frequent and intensive fires (Page *et*

al., 2002; 2009a; Langner *et al.*, 2007; Langner & Siegert, 2009). These have caused high levels of carbon gas emissions to the atmosphere through loss of biomass, peat oxidation and combustion (Page *et al.*, 2002; van der Werf *et al.*, 2004; 2008; Hooijer *et al.*, 2006; 2010). It was recently calculated that globally, deforestation is the second largest anthropogenic source of carbon dioxide (CO_2) to the atmosphere, after fossil fuel combustion (van der Werf *et al.*, 2009).

With so much attention given to the emission of gaseous carbon to the atmosphere, alternative pathways of carbon loss have been overlooked and, to date, there has been no investigation into what effect disturbance of tropical peatlands has on the export of fluvial carbon. Globally, the transport and loss of fluvial carbon from terrestrial ecosystems such as peatlands into rivers and oceans accounts for approximately 1000 Tg carbon each year (Ludwig *et al.*, 1996) and it is an important pathway as it links the terrestrial and marine carbon cycles (Meybeck, 1993). Whilst in transport, fluvial carbon also has the potential to feed straight back into the atmosphere as CO_2 and/or methane (CH_4) through biotic decomposition, or it can remain climatically neutral through benthic deposition and storage as riverine and estuarine sediments. The fate of fluvial carbon draining tropical peatlands remains largely unknown, but a substantial proportion derived from cool northern peats is thought to be emitted to the atmosphere (Cole *et al.*, 2007; Battin *et al.*, 2009; Tranvik *et al.*, 2009). The aim of this thesis is to help answer some of these remaining knowledge gaps surrounding tropical peatland disturbance and its effect on 'the forgotten' fluvial carbon budget.

1.2 Tropical peatlands

Characteristics of boreal and temperate peatlands including rates of carbon sequestration and the amount of carbon stored, are well documented (e.g. Turunen, 2003 and refs therein). Tropical peatlands on the other hand are less well documented and have only recently received increased interest as more information on the size and global

importance of these tropical deposits is gathered (Jauhiainen *et al.*, 2005). By area, boreal and temperate peatlands have the greatest global extent (Immirzi *et al.*, 1992), but due to their large aboveground biomass in the form of peat swamp forest (PSF) and thick underlying peat deposits, tropical peatlands contribute significantly to the global peatland resource and terrestrial carbon store (Rieley *et al.*, 1996; Page *et al.*, 1999; 2011).

1.2.1 Global distribution

Tropical peatlands are located in Asia, Africa, the Caribbean and Central and South America. Within these regions, most are located at low altitude, but some occur in the mountains of Africa, South America and Papua New Guinea. The current best estimate of the total area of tropical peatlands is 441,025 km^2 (range of 387,201 - 657,430 km^2; Page *et al.*, 2011). Over half of this is found within Southeast Asia (Brunei, Indonesia, Malaysia, Myanmar, Papua New Guinea, Philippines, Thailand, Vietnam; 247,778 km^2, which equates to 56% of the best estimate). The next largest share is found in South America (107,486 km^2, 24%), followed by Africa (55,860 km^2, 13%), Central America and the Caribbean (23,374 km^2, 5%), Asia (Bangladesh, China, India, Sri Lanka; 6,337 km^2, 1%) and the Pacific region (190 km^2, less than 1%; table 1.1).

Table 1.1: Area of tropical peatland on a regional basis, expressed as minimum, best estimate and maximum values (table adapted from Page *et al.*, 2011).

Region	Area (km^2)		
	Minimum	Best estimate	Maximum
Africa	29464	55860	135043
Asia (Southeast)	236647	247778	336115
Asia (other)	4804	6337	10936
Central America & Caribbean	20761	23374	31210
Pacific	190	190	190
South America	95335	107486	143936
Total	387201	441025	657430

Of the total global peatland extent (3,997,435 km^2), tropical peatlands account for 10% (minimum estimate) to 16% (maximum estimate). These tropical peatlands are estimated to have a peat volume of 1,758 Giga cubic meters (Gm^3; 1 Gm^3 = 1 m^3 × 10^9) which accounts for up to 25% of the global peat volume (7,093 Gm^3), making a much larger contribution to global volume than their area would infer (Page *et al.*, 2011). The most recent estimate of the global peatland carbon store is 480 petagrams (Pg; 1 Pg = 1 g × 10^{15}) and the total tropical peatland carbon store is 89 Pg (Page *et al.*, 2011). This is based on an average peat thickness of 1.5 m and a peat carbon density value of 1100 tonnes carbon per hectare (t carbon ha^{-1}; Immirzi *et al.*, 1992). Using a greater mean peat thickness of 2.3 m for boreal and sub-arctic peat (Gorham, 1991) and thus a higher carbon density value of 1466 t carbon ha^{-1} results in a larger estimate of the global peat carbon store of between 598 and 618 Pg. The tropical peat carbon pool therefore accounts for between 14% and 19% of the global peat carbon pool.

1.2.2 Peatlands in Southeast Asia, Indonesia and Kalimantan

Of the 247,778 km^2 of tropical peatlands found in Southeast Asia, the vast majority are found within Indonesia (206,950 km^2, 84%). The country with the next largest share is Malaysia (25,889 km^2, 10%), followed by Papua New Guinea (10,986 km^2, 4%), which, when combined account for less than 20% of Indonesia's total. Collectively, the remaining countries in this region (Brunei, Myanmar, the Philippines, Thailand and Vietnam) account for about 1% (figure 1.1).

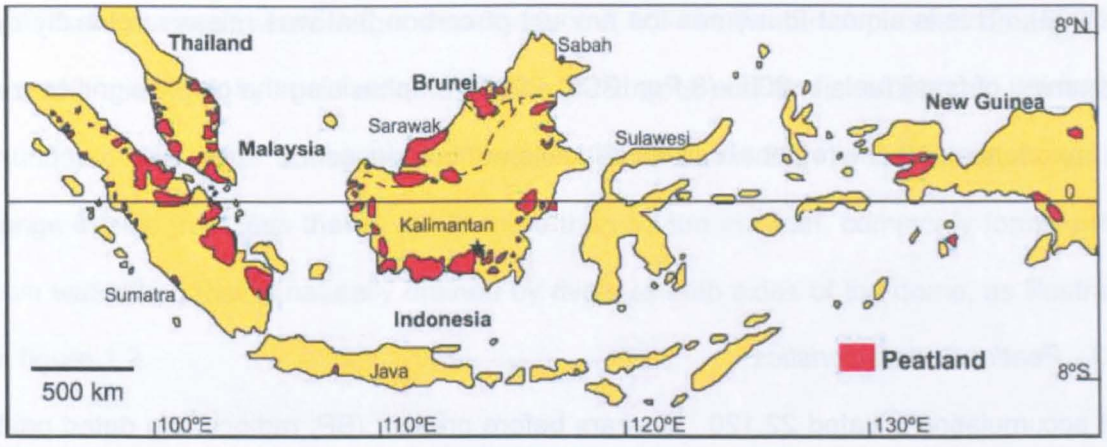


Figure 1.1: The distribution of peatlands in Southeast Asia (Source: Page *et al.*, 2004)

Of the total tropical peatland volume, Southeast Asia has the largest share (1359 Gm^3, 77%), and within this region, Indonesia accounts for the vast majority of it (1138 Gm^3, 84%). As with peatland area, Malaysia has the next largest peatland volume (181 Gm^3, 13%) followed by Papua New Guinea (28 Gm^3, 2%). The remaining countries in this region, when combined, contribute less than 1% to the total Southeast Asian peat volume. The Southeast Asia peatland carbon store is estimated to be 69 Pg (77% of the total tropical peatland carbon pool). Again, Indonesia accounts for the largest share of the tropical peatland carbon pool both within Southeast Asia/the world (57 Pg, 83%/65%), followed by Malaysia (9 Pg, 13%/10%), with Papua New Guinea, Brunei, Myanmar, the Philippines, Thailand and Vietnam collectively contributing a smaller portion of the total (4%/2%).

Peat thickness in Sumatra and Kalimantan (Indonesia) ranges from 0.5 to 20 m (Page *et al.*, 2002), making these peatlands one of the largest near-surface reserves of terrestrial organic carbon in the world. Covering around 15% and 11% of the total land area, Sumatra and Kalimantan, respectively, are the two most peat-dominated regions in Indonesia. The province of Central Kalimantan contains about 30,000 km^2 of peatland, making this region one of the largest continuous areas of tropical peatland in the world (Vries, 2003). The peatlands within Sumatra and Kalimantan alone are estimated to cover 130,000 km^2 (Wahyunto *et al.*, 2003; 2004) and hold about 30 Pg of carbon (Jaenicke, *et*

al., 2008). This is almost four times the amount of carbon that was released globally by the burning of fossil fuels in 2006 (8 Pg; IPCC, 2007), emphasising the global significance and importance of these regional carbon deposits within Indonesia.

1.2.3 Peatland characteristics

Peat accumulation initiated 22,120 ^{14}C years before present (BP; radiocarbon dated peat from the peat-sediment interface at 8.4 m depth) in the Sebangau catchment (Central Kalimantan), making this peat deposit the oldest reported in any Southeast Asian peatland (Weiss *et al.*, 2002). However, Page *et al.* (1996) report that depth of peat accumulations may reach 13 m at the summit of the peat dome in Sebangau, which implies even older deposits of peat may exist. The peat in the Sebangau catchment consists primarily of trunks (at different stages of decomposition), branches and roots of trees within a matrix of almost structureless organic material that originates from PSF flora, mainly trees (Rieley *et al.*, 1996). The decomposition status of the peat is as follows; fibric (least humified) on the surface, hemic (moderately humified) throughout most of its depth and sapric (most humified) near to the bottom (Wösten *et al.*, 2008). From a peat core sampled in the Sebangau catchment under low pole forest, the following soil characteristics were determined; dry bulk density and ash content are low compared to mineral soils, ranging from 0.02 to 0.21 g cm^{-3} and from 0.33% to 1%, respectively. Mean pH of peat samples for the entire length of the core was 3.2 (Page *et al.*, 1999; Weiss *et al.*, 2002).

1.2.4 Peat dome structure

Most tropical peatlands in Southeast Asia form characteristically elliptical domes, with a convex surface. Most are ombrogenous, meaning that their water and nutrient supply is entirely supplied from rainfall as opposed to lateral transfer from adjacent catchments (Page *et al.*, 2004). The uneven peat dome surface consists of a mixture of hummocks

(drier/raised areas) where larger trees grow and hollows (wetter/depressed areas) which are characterised by a dense mat of fine tree roots and pneumatophores, commonly inundated with water during the wet season (Page *et al.*, 2004). Each peat dome can range in size from less than 1 km to more than 50 km in width, commonly forming their own watershed that is naturally drained by rivers at both sides of the dome, as illustrated in figure 1.2.

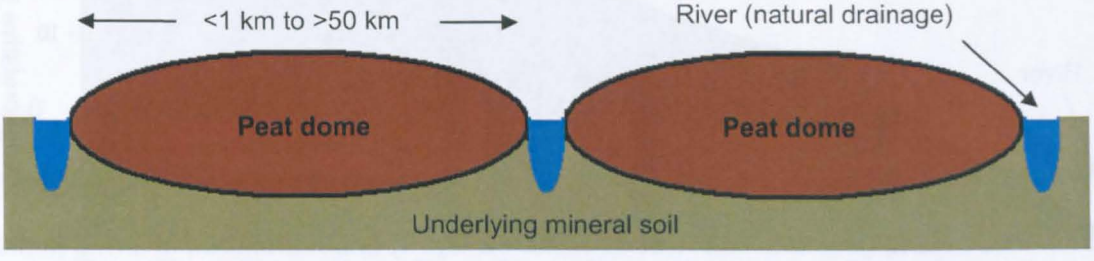


Figure 1.2: Typical Southeast Asian peat dome structure and natural drainage system.

The surface level of the peat dome slowly increases with distance from the river, but at a very low gradient. Over the entire Sebangau peat dome there is a vertical increase of 0.8 m for every 1 km away from the river (figure 1.3). This gradient varies and is even lower between 5.5 km to 12.5 km from the river (surface elevation of 0.6 m km^{-1}), but reaches greater elevation gradients between 14 km to 17 km from the river (surface elevation of 1.8 m km^{-1}). These areas of different elevation gradients often coincide with changes in tree species composition, known as phasic community transition zones (see Chapter 1.2.6; Page *et al.*, 1999). Generally, peat depth increases with distance from river. For the first 12 km from the river, peat thickness increases gradually to a depth of 10 m and reaches its maximum depth of 11 m at the top of the peat dome, 25 km from the river (figure 1.3). Peat depth also seems to coincide with phasic community transition. For example, mixed swamp forest is located on shallow peat (less than 2 m), while low pole, tall interior and very low canopy forest are all found on thick peat (up to 11 m). While the peat depth and elevation gradient does not directly affect the overlying phasic community

type, it affects other peatland characteristics such as hydrology and organic matter dynamics which in turn affect the phasic communities that can be supported.

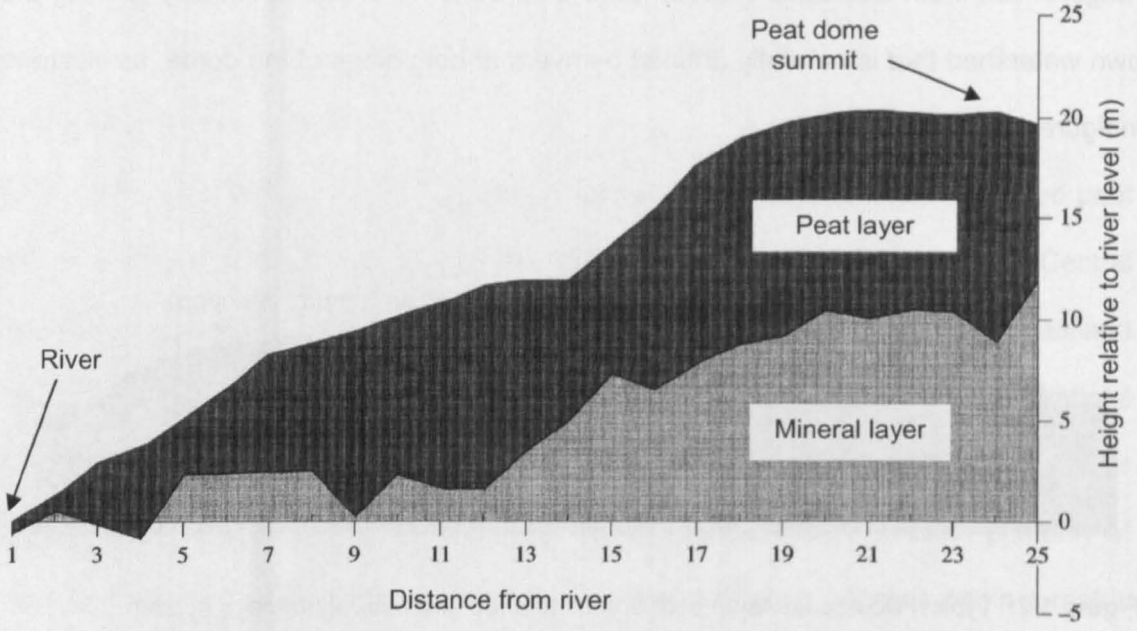


Figure 1.3: Composite profile through a peat dome in Southeast Asia (Sebangau, Kalimantan) from the river to the watershed (summit of peat dome). The profile shows the surface level, bottom topography (mineral soil) and the intervening peat thickness (vertical scale exaggerated; Page *et al.*, 1999).

1.2.5 Peatland hydrology

In general, water tables in the Sebangau catchment are lower than in other Indo-Malaysian peatlands (Moore *et al.*, 1996). During maximum water table drawdown at the end of the dry season in 1994, the water table was 150 cm below the peat surface in the tall interior forest. At the same time, the water table was 24 to 40 cm below the peat surface in low pole and mixed swamp forest respectively, suggesting that water tables remain higher closer to the river. During the rainy season, the water table is at or above the peat surface in all forest types except for tall interior forest where it can be as low as 20 to 30 cm below the peat surface but never above it (Page *et al.*, 1999). According to Takahashi *et al.* (2002), evapotranspiration rates in the PSF of the Sebangau catchment vary between 3.2 and 3.6 mm day^{-1}.

Hydraulic conductivity varies with peat depth as well as land use. In the Sebangau catchment it ranges from 0.48 to 12.48 m day^{-1}, with values in the top layer of peat generally exceeding 10 m day^{-1} (Sajarwan *et al.*, 2002). Hydraulic conductivity under agricultural land is much lower than under forest and can be as low as 0.00195 m day^{-1} (Takahashi & Yonetani, 1997). The surface water itself is acidic (average pH 3.6), very low in electrical conductivity (average 50 μS cm^{-1}) and also low in ion concentration (K, Ca, Mg, NO_3-N, PO_4-P; Page *et al.*, 1999).

1.2.6 Peatland community

Intact tropical PSF makes an important contribution to regional and global biodiversity both in terms of flora and fauna (Page & Rieley, 1998). The changing phasic communities across peat domes provide habitats for a number of rare and threatened species, many specialists included, perhaps most notably, the orang-utan. Page *et al.* (1999) surveyed the peat dome west of the River Sebangau and described the five typical intact phasic communities of PSF that form the peat dome from the river's edge to the peat dome summit.

1) Located close to the river at the peat dome edge is the *marginal riverine forest*. It sits on shallow organic soils where peat reaches depths of up to 1.5 m and is flooded by river water during the rainy season. The average canopy height is 25 to 30 m and the principal canopy tree species is *Shorea balangeran* which is the only species that exceeds a height of 35 m. The principle ground vegetation species is *Thorachostachyum bancanum*, which makes up low-growing, species-poor sedge swamp and is present in some of the upper River Sebangau basin where riverine forest has been destroyed due to logging and burning.

2) *Mixed swamp forest* reaches 4 km from the peat dome edge (beyond the limit of river flooding) and sits on peat 1.5 to 6 m in thickness. The upper canopy reaches heights of

35 m with a closed layer between 15 and 25 m and another more open canopy of smaller trees about 7 to 12 m in height. The peat surface is very uneven with trees tending to grow on the hummocks and water filling the hollows, particularly in the wet season. Stilt/buttress roots and pneumatophores are common. There is a wide range of tree species, including *Combretocarpus rotundatus*, *Dactylodadus stenostachys* and *Shorea balangeran.* The forest floor supports a dense covering of seedlings and saplings, the sedge, *Thorachostachyum bancanum* as well as climbers, epiphytes, insectivorous pitcher plants and orchids.

3) *Low pole forest* occurs between 6 and 11 km from the river on peat that is 7 to 10 m thick. The upper canopy reaches a maximum height of about 20 m with a lower, closed canopy at about 12 to 15 m. The principal species in this type of forest are *Combretocarpus rotundatus* and *Calophyllum fragrans,* with less *Dactylodadus stenostachys.* Pandans form a dense, continuous ground cover on peat that is permanently waterlogged due to high water table levels.

4) *Tall interior forest* occupies most of the upper regions of the peat dome, 12 km from the river, on peat up to 13 m thick. The water table is below the peat surface throughout the year and can be as low as 1.5 m below the peat surface during an extremely dry season. The upper canopy reaches heights of 45 m and is dominated by, amongst others, *Agathis dammara, Dyera cotulata and Shorea teysmanniana.* Underneath the upper canopy, there are two more layers reaching 15 to 25 m and 8 to 15 m. Due to this thick canopy and the resultant low light levels, ground flora is poorly developed except for under gaps in the canopy where pandans and a greater abundance of climbers and epiphytes are found.

5) Very low canopy forest occupies a discrete area of about 13 km by 6 km, which is encompassed by tall interior forest between the two river systems (Sebangau and Katingan) on the summit of the peat dome. Few of the trees exceed 1.5 m in height and

the common species include *Calophyllum* spp., *Combretocarpus rotundatus,* and *Cratoxylum* spp. As a result of the open canopy, greater levels of light support a high diversity in ground-covering vegetation, where the sedge *Thorachostachyum bancanum* is dominant over pandans.

1.3 Tropical peatland disturbance

Since the 1980s an increasing amount of logging activities, drainage, fires, conversion to plantations and expansion of small holder agricultural landscape has occurred in tropical peatlands around the world, but perhaps none more so than in Southeast Asia (Silvius & Diemont, 2007). The global rate of tropical forest loss is 0.52% yr^{-1} and is highest in Southeast Asia (0.91% yr^{-1}; Achard *et al.*, 2002). The primary drivers of peatland disturbance and forest loss in Southeast Asia are strong economic and social pressures for timber, land for agriculture and plantations of oil palm and pulp-wood (Koh *et al.*, 2009). Consequently, in the last two decades, Southeast Asian peatlands have been subject to rapid and widespread deforestation (Langer *et al.*, 2007; Langer & Siegert, 2009), severe drainage (Hooijer *et al.*, 2006; 2010) and frequent and intensive fires that often follow such forms of land use change (Page *et al.*, 2002; 2009b; Langer *et al.*, 2007; Langer & Siegert, 2009).

1.3.1 Carbon balance (sources vs. sinks)

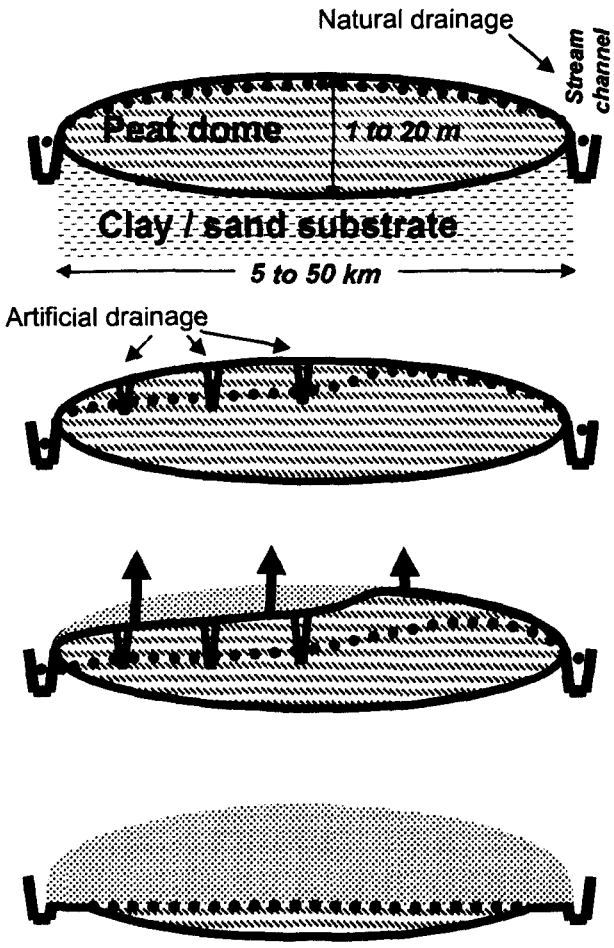
Under natural conditions with no anthropogenic disturbance, tropical peatlands are a long-term carbon store. However, increasing levels of disturbance (in all forms mentioned above), are impacting on the net carbon balance of peatlands. This balance is dominated by five flux components: (i) Net Ecosystem Productivity (NEP), which is the balance between Gross Primary Production (GPP) and Respiration (R_{plant}), as described in equation 1.1; (ii) Carbon dioxide (CO_2) emissions from peat decomposition (as a result of

drainage); (iii) CO_2 emissions from fire; (iv) smaller quantities of methane (CH_4) emissions; and (v) fluvial exports of carbon.

$$NEP = GPP - R_{plant} \qquad \textit{(Equation 1.1)}$$

1.3.2 Disturbance effects on the carbon balance

Peatland drainage artificially lowers the water table which leads to aerobic conditions that favour microbial activity in the peat profile above the water table. This results in enhanced CO_2 loss by peat decomposition (Ueda *et al.*, 2000; Jali, 2004; figure 1.4).



Intact peatland (no artificial drainage):
- Water table close to surface
- Peat accumulates from overlying vegetation over thousands of years

Artificial drainage channels dug:
- Water table lowered
- Peat surface begins to subside and CO_2 emission starts

Continued drainage:
- Dry peat decomposes: further CO_2 emissions
- High fire risk in dry peat: further potential for CO_2 emissions
- Peat surface continues to subside due to decomposition and compaction

End stage (drained/degraded peatland):
- Most carbon stored in peat above drainage limit released to atmosphere

Figure 1.4: Schematic illustration of how artificial drainage of tropical peatland results in increased CO_2 emissions and peat dome subsidence over time. The dotted black line represents the water table and the grey arrows represent CO_2 emissions (adapted from Hooijer *et al.*, 2010).

By 2006, almost half (48%) of all tropical peatlands in Southeast Asia were deforested and artificially drained due to land development pressures (Hooijer *et al.*, 2010). In 2006, it was estimated that between 355 and 855 Tg CO_2 yr^{-1} (97 to 233 Tg of carbon) was emitted to the atmosphere from decomposing peatlands in Southeast Asia, with a best estimate of 632 Tg CO_2 yr^{-1} (172 Tg of carbon; Hooijer *et al.*, 2010). Indonesia was responsible for 82% of these emissions. These carbon dioxide emissions are equivalent to 1.3% to 2.9% of the 8,000 Tg of carbon from global fossil fuel emissions during the same year (Canadell *et al.*, 2007).

Under natural conditions PSF is at very low risk of fire. The water table is close to or above the ground surface for most of the year and a moist, humid environment is maintained by a dense overlying forest canopy. However, once the canopy is removed by logging (and other land clearance activities) and drainage channels are dug, the peat profile rapidly dries out. This makes the land far more susceptible to the risk of fire when compared to undisturbed, intact PSF (Siegert *et al.*, 2001). Whilst artificial drainage results in a continuous source of CO_2 through peatland decomposition, annual fire emissions can be of a similar magnitude and far greater during drier El Niño-years. Hooijer *et al.* (2006) estimated average annual fire emissions to be 1,400 Pg CO_2 yr^{-1} (382 Tg of carbon) for the years 1997 to 2006. Page *et al.* (2002) estimated that 2,970 to 9,423 Tg CO_2 (810 to 2,570 Tg of carbon) were released to the atmosphere in 1997 (El Niño-year) as a result of burning peat and vegetation in Indonesia. At the time, this was equivalent to 13-40% of the mean annual global carbon emissions from fossil fuels.

CH_4 emissions from tropical peatlands are generally low (Couwenberg *et al.*, 2010), but due to the stronger global warming potential of CH_4 when compared with CO_2, it is an important greenhouse gas and needs to be accounted for in the net carbon peatland balance. CH_4 emissions show a clear relationship with water table depth in tropical

peatlands; for water levels below -20 cm, emissions are generally low and sometimes negative (net CH_4 uptake from the atmosphere) and at higher water tables, negative values are rarer and values tend to be higher, reaching up to 5.9 g CH_4 m^{-2} yr^{-1} (equivalent to 4.4 g C m^{-2} yr^{-1}; Couwenberg *et al.*, 2010). Given the relationship between CH_4 emissions and water table depth, artificial drainage and a lowering of the water table may actually reduce the CH_4 emissions. It is important however to note that any reduction in CH_4 emissions is significantly offset by an increase in CO_2 emissions.

The remaining flux component to consider is fluvial export of carbon. This flux is important as it provides a link between the terrestrial and marine carbon cycles (Meybeck, 1993). The fate of this fluvial carbon lost from tropical peatlands is also poorly understood, but is of high importance as it has the potential to feed back into the atmosphere as CO_2 and/or CH_4 through biotic decomposition (Hope *et al.*, 1994). Fluvial carbon loss has been studied extensively in the soils of boreal and temperate forests (Mulholland & Kuenzler, 1979; McDowell & Likens, 1988; Michalzik *et al.*, 2001), but has yet to be quantified for tropical PSF and in particular, PSF subject to various forms of anthropogenic disturbance.

1.4 Fluvial carbon overview

The main components of fluvial carbon are dissolved organic carbon (DOC), particulate organic carbon (POC) and dissolved carbonates (inorganic carbon). These components are classed as either allochthonous (derived from organic matter) or autochthonous (derived from in-situ biological production). A further classification includes anthropogenic (derived from agricultural, domestic and industrial activities; Degens, 1982). Figure 1.5 illustrates the common molecules across a continuous spectrum of sizes that make up the organic carbon components in river waters.

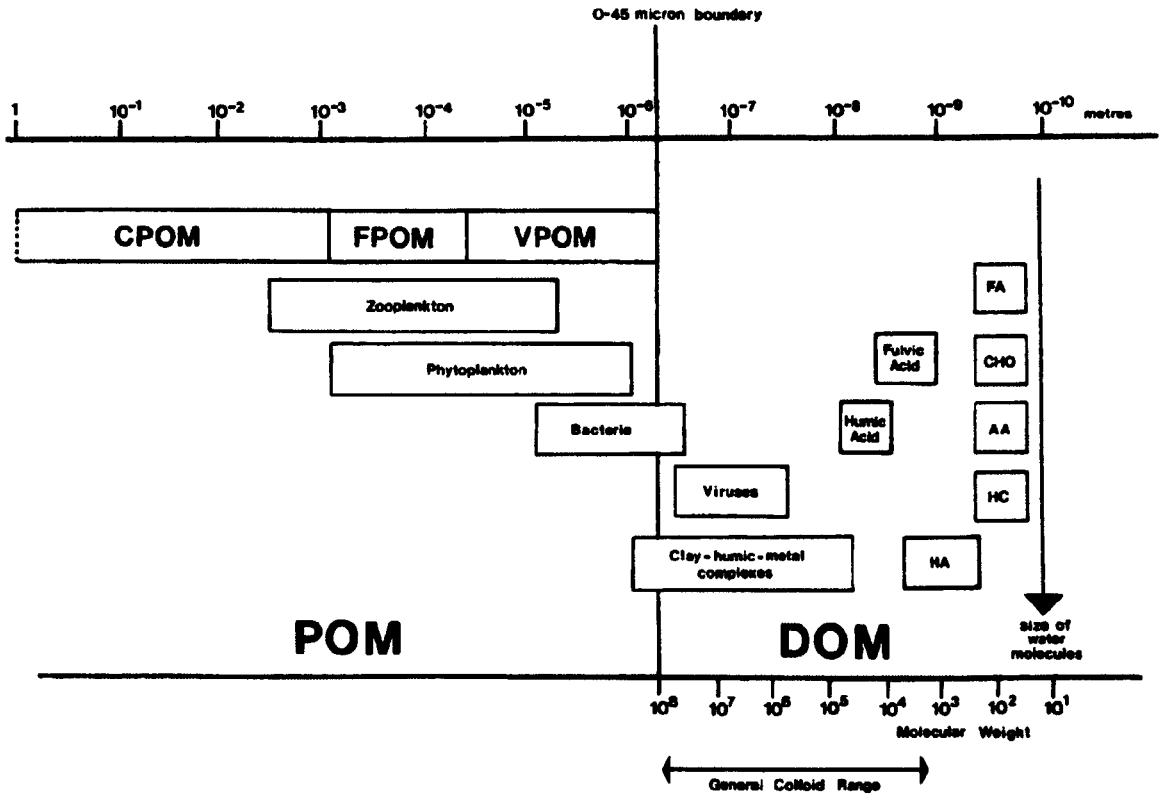


Figure 1.5: Size range of particulate organic matter (POM), dissolved organic matter (DOM) and carbon compounds in natural waters; CPOM = coarse particulate organic matter, FPOM = fine particulate organic matter, VPOM = very fine particulate organic matter, FA = fatty acids, CHO = carbohydrates, AA = amino acids, HC = hydrocarbons, HA = hydrophilic acids (Thurman, 1985).

1.4.1 Riverine carbon components

Organic carbon: The distinction between DOC and POC is generally made on the basis of whether or not it passes through a 0.45 µm filter; DOC will pass through as filtrate and POC will be retained by a filter of this pore size (Thurman, 1985). The vast majority (50-75%) of DOC is comprised of fulvic and humic acids and the remaining fraction is made up of colloidal organic matter, comprising approximately 20%. It is the humic compounds that are responsible for the dark coloured water in organic rich rivers (Hope *et al.*, 1994). POC consists of plant litter, algal debris, invertebrates, coarse eroded soil organic matter and soil detritus. POC can also be subdivided according to size; coarse (greater than 1 mm), fine (1 mm-53 µm), and very fine (53 µm-0.45 µm; Naiman *et al.*, 1987; figure 1.5).

Inorganic carbon: Inorganic carbon in river water is invariably in a dissolved form and therefore termed dissolved inorganic carbon (DIC). It occurs in ionic form or as dissolved, free CO_2. These various carbonate species make up what is called the carbonate system, which is one of the main controls on the pH of river water (Stumm & Morgan, 1981).

Total carbon: Total carbon is the sum of the organic (dissolved and particulate) and inorganic carbon fractions. However, as the amount of inorganic carbon in peatland catchments is negligible (see Chapter 2.3.2; Hope *et al.*, 1994), this fraction has been omitted, so that during the course of this study, total carbon refers to total organic carbon (TOC).

1.4.2 Riverine carbon fluxes to the ocean

The annual global (as opposed to solely tropical) riverine carbon flux from rivers to the ocean is estimated to be 1,000 Tg (Ludwig *et al.*, 1996). Of this carbon, approximately 60% is comprised of inorganic carbon and 40% comprised of organic carbon (Meybeck, 1993; Probst *et al.*, 1994). Therefore, for most rivers a greater proportion of carbon is lost to the ocean in inorganic forms (Meybeck, 1982). However, based on knowledge from northern peatlands, it is believed that in tropical PSF catchments, fluvial carbon fluxes to the oceans are dominated by organic forms (Hope *et al.*, 1994). Two commonly accepted estimates put the annual value of TOC discharged to oceans as somewhere between 330 and 370 Tg yr^{-1} (Degens *et al.*, 1991; Meybeck, 1993). However, revised carbon fluxes of the major world rivers increase this figure to 430 Tg yr^{-1} (250 Tg DOC and 180 Tg POC; Cauwet, 2002).

1.4.3 Riverine carbon as a source of CO_2

With vast quantities of terrigenous organic carbon being transported through fluvial networks to the world's oceans, understanding the fate of this carbon is key to interpreting the global carbon cycle (Hedges *et al.*, 1997). During its time in fluvial transit, organic carbon undergoes a number of biogeochemical reactions that influence both its concentration and composition. Through microbial respiration, microorganisms and invertebrates can convert large quantities of this fluvial organic carbon from the water directly back into the atmosphere as CO_2 (Hope *et al.*, 1994). Previous studies from temperate rivers have shown that variable amounts of organic matter can be removed in this manner, from less than 5% (Amon & Meon, 2004) to more than 20% (Naiman *et al.*, 1987). The portion of carbon that is processed in this way will depend, to some extent, on how much is being transported as DOC and how much as POC. These two carbon fractions travel through fluvial systems in fundamentally different ways and microbial respiration favours the DOC fraction over the POC fraction. Whereas DOC molecules pass straight through the microbial cell membrane and are subsequently subject to metabolism, POC must first be hydrolysed by extracellular enzymes before the resulting DOC molecules can be subject to microbial metabolism (Battin *et al.*, 2008). Although there is still large uncertainty over the fate of fluvial organic carbon, in one of the most comprehensive studies to date, Cole *et al.*, (2007) estimate that of the 1,900 Tg of carbon that inland waters receive annually, 200 Tg is buried in aquatic sediments, 800 Tg (possibly much more) is returned to the atmosphere as gas exchange, while the remaining 900 Tg is delivered to the ocean. This implies that roughly twice as much carbon enters inland waters from land as is exported by rivers to the ocean.

1.5 Thesis aims and layout

It is estimated that approximately 1,000 Tg of fluvial carbon enters the oceans from rivers around the world each year (Ludwig *et al.*, 1996). Expansive areas of peatlands which are known to be an important source of riverine DOC (Hope *et al.*, 1997; Aitkenhead &

McDowell, 2000) combined with high precipitation rates make Indonesia likely to be a significant source of fluvial carbon to the ocean. To date, only a small number of studies have quantified the fluvial carbon loss from Indonesian rivers. Furthermore, no study has investigated the effect of tropical peatland disturbance on the amount of fluvial carbon lost from such ecosystems. The principal aim of this investigation, therefore, was to remedy this deficiency in our understanding by quantifying the amount of fluvial organic carbon lost from three different land-cover classes that vary in their degree of anthropogenic disturbance. This work then goes onto examine whether these findings from catchment scale studies are consistent with findings from a river basin scale study and therefore more applicable to regional scales. Finally, this study aims to go some way in addressing the much debated issue over the fate of this fluvial organic carbon; how much of it is converted into CO_2 and fed into the atmospheric carbon cycle and how much remains in the oceanic carbon cycle as marine sediments.

This thesis contains six chapters. This chapter has presented the background understanding of the key aspects to the research carried out in this thesis, highlighting the remaining knowledge gaps and outlining how the key research aims will help to fill these gaps. Chapter Two gives descriptions of the field sites used during the investigation and describes the general methods employed. Where necessary, more specific methods and field site descriptions are detailed within individual chapters. Chapter Three tackles the principle aim of this thesis which is to quantify annual fluvial organic carbon loss from peatland catchments subject to varying degrees of anthropogenic disturbance. Chapter Four increases the spatial scale of the investigation by looking at fluvial organic carbon losses from the Sebangau River basin, which encompasses all catchments subject to investigation in Chapter Three. Chapter Five considers the qualitative aspects of the fluvial organic carbon such as the age, source and chemical composition, which all give insight into the most likely fate of the carbon. Finally, Chapter Six discusses the three previous data chapters simultaneously, placing the findings in a global context and

summarises the main conclusions of the investigation, with recommendations for further work.

Chapter Two

Materials and Methods

2.1 Introduction

In this chapter, an overview of the climatic region in which the field work was carried out, is followed by a more detailed description of the field sites that were monitored continuously for one year in order to investigate what impact anthropogenic disturbance of tropical peatland has on losses of fluvial organic carbon (Chapter Three). The Sebangau River basin which was subject to a larger spatial scale investigation (Chapter Four) is also characterised. This chapter details the generic methods that were used throughout the investigation and which are referred back to in several chapters such as sample collection, sample preservation and flux/yield calculations. The more specific methods that were tailored to answer particular research objectives are discussed within each of the individual chapters in which they were used. Details of how samples were analysed in the field and in the laboratory in Indonesia and in the UK, such as DOC and POC analysis are also discussed and finally, the statistical analyses employed throughout the investigation are explained and justified.

2.2 Study sites

The study sites are located on the island of Borneo (an island which encompasses parts of Indonesia, Malaysia and Brunei), in Southeast Asia. All the study sites are found within the Indonesian province of Central Kalimantan, which is one of four Indonesian provinces within Kalimantan. All study sites are located within a small range of coordinates (2°15'10.00"S to 2°23'15.00"S and 113°52'30.00"E to 114°08'24.80"E; figure 2.1).

Figure 2.1: Map of Indonesia (right) with enlarged outline of Borneo (left) showing the location of the study sites within Central Kalimantan (shaded grey box).

Central Kalimantan lies within the Inter Tropical Convergence Zone (ITCZ) and experiences a tropical monsoonal climate. The mean annual temperature varies between 25 and 27°C and rainfall averages 2700 mm yr^{-1} (Page *et al.*, 2004). Twenty two years of rainfall records from Central Kalimantan indicate that, annually, there is approximately nine months of wet season (October - June) and three months of dry season (July - September), whereby dry months are defined as periods of moisture deficit, indicated by evapotranspiration exceeding rainfall (Hooijer *et al.*, 2008; figure 2.2).

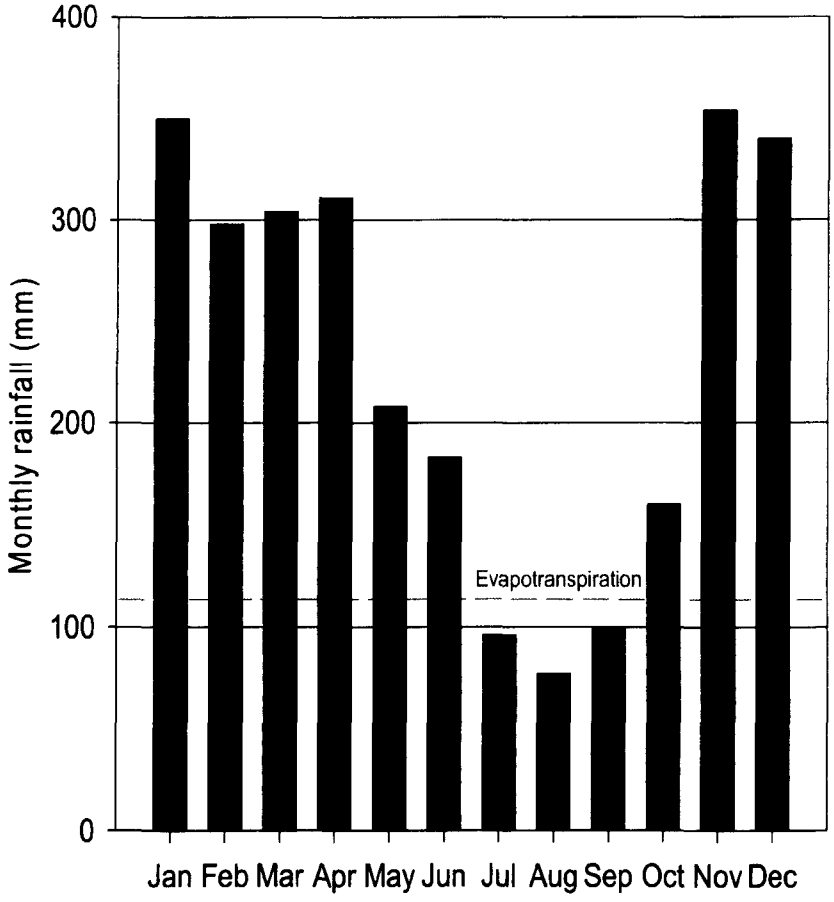


Figure 2.2: Average monthly rainfall over 22 year record (1984-2006) in Central Kalimantan. Dashed grey line represents the average evapotranspiration over the same time period. Where evapotranspiration is greater than rainfall, month is defined as dry season. All data collected from Palangka Raya Meteorological Office (Hooijer *et al.*, 2008).

In Central Kalimantan, all study sites are located within or close to the Sebangau River basin. The river basin is bordered by the City of Palangka Raya, the provincial capital of Central Kalimantan to the north, the River Kahayan to the east, the Java Sea to the south and the River Katingan to the west (figure 2.3). The Sebangau River basin is approximately 5,200 km^2, most of which is covered in peat which forms extensive domes between the River Kahayan and the River Katingan. The maximum recorded thickness of the peat to the west of the River Sebangau is 13 m (at the summit of the peat dome) and to the east of the River Sebangau is about 8 m (Page *et al.*, 1999; 2002). This peat overlies a heavily-weathered, quartz podzol that is often more than 5 m thick. Underneath this layer is an impervious hard pan of up to 2 m (Sieffermann, 1990).

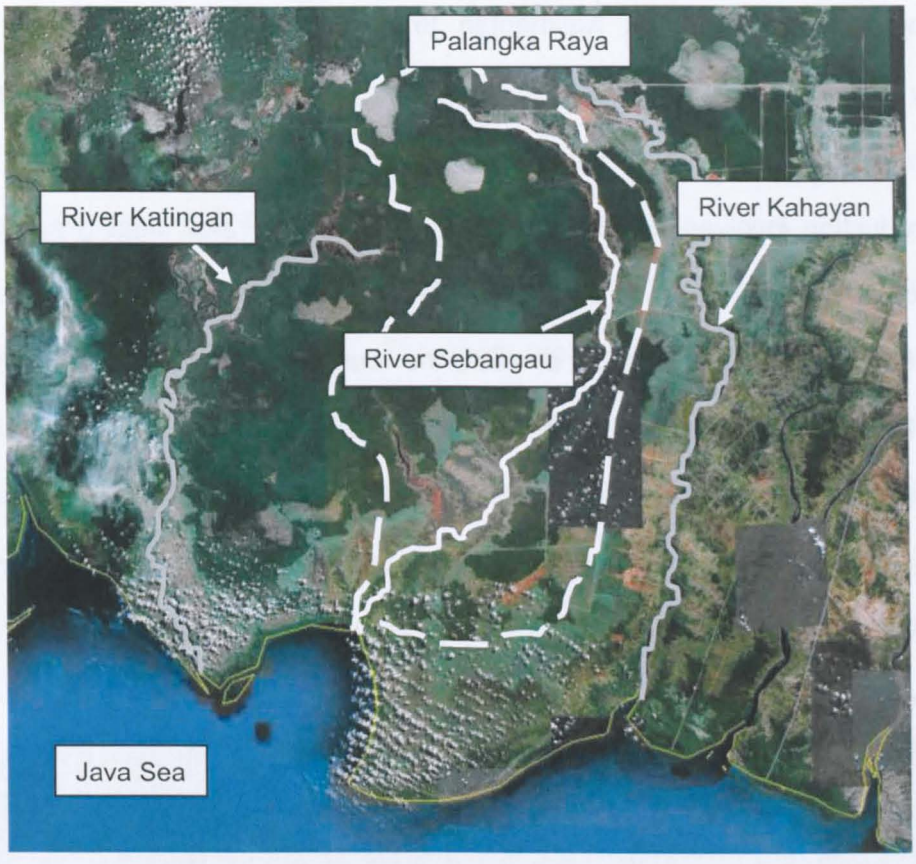


Figure 2.3: The Sebangau River basin (dashed white line) situated in Central Kalimantan drains into the Java Sea and is located between the River Kahayan to the east, the River Katingan to the west (grey lines; source: Google Earth, 2011).

2.2.1 Experimental site description

Three PSF land-cover classes that differed in their recent disturbance history, located in or near to the Sebangau River basin were identified and selected as sampling sites (figure 2.4): (1) an intact peat-swamp forest (IPSF) catchment in Sebangau National Park was selected as a reference/control site and provided a basis for comparison; (2) a moderately disturbed peat swamp forest (DPSF1) catchment in Tubangnusa; and (3) a severely disturbed peat swamp forest (DPSF2) catchment in Kalampangan. All three sites are located within 20 km of each other and were classified as part of the same ecosystem, pre-disturbance. This ecosystem was composed of the same belowground (thick peat dome) and aboveground (primary PSF) components which, in the case of DPSF1 and 2, were severely modified as a result of the Mega Rice Project (MRP; Vries, 2003). The

MRP (1995-1999) was a one million hectare peat reclamation project with the aim of establishing new rice fields in Kalimantan to meet the country's demand for self-sufficiency in rice production. The entire project area was split into five regional blocks, simply named 'Block A', 'B', 'C', 'D' and 'E'. Converting these peatlands into land suitable for rice production involved clearing the land of intact PSF and digging approximately 4,500 km of drainage channels in order to artificially control the water table levels (Hooijer *et al.*, 2008). It is estimated that as a result, the total land area covered in PSF around Palangka Raya reduced by more than 50% from 24,000 km^2 in 1991 to 11,000 km^2 in 2000 (Boehm & Siegert, 2001; Boehm *et al.*, 2001; 2002). The IPSF site lies outside the boundaries of 'Block C' and was therefore unaffected by the MRP. DPSF1 and DPSF2 however are both situated within 'Block C' and as such, were subject to anthropogenic disturbance during the MRP.

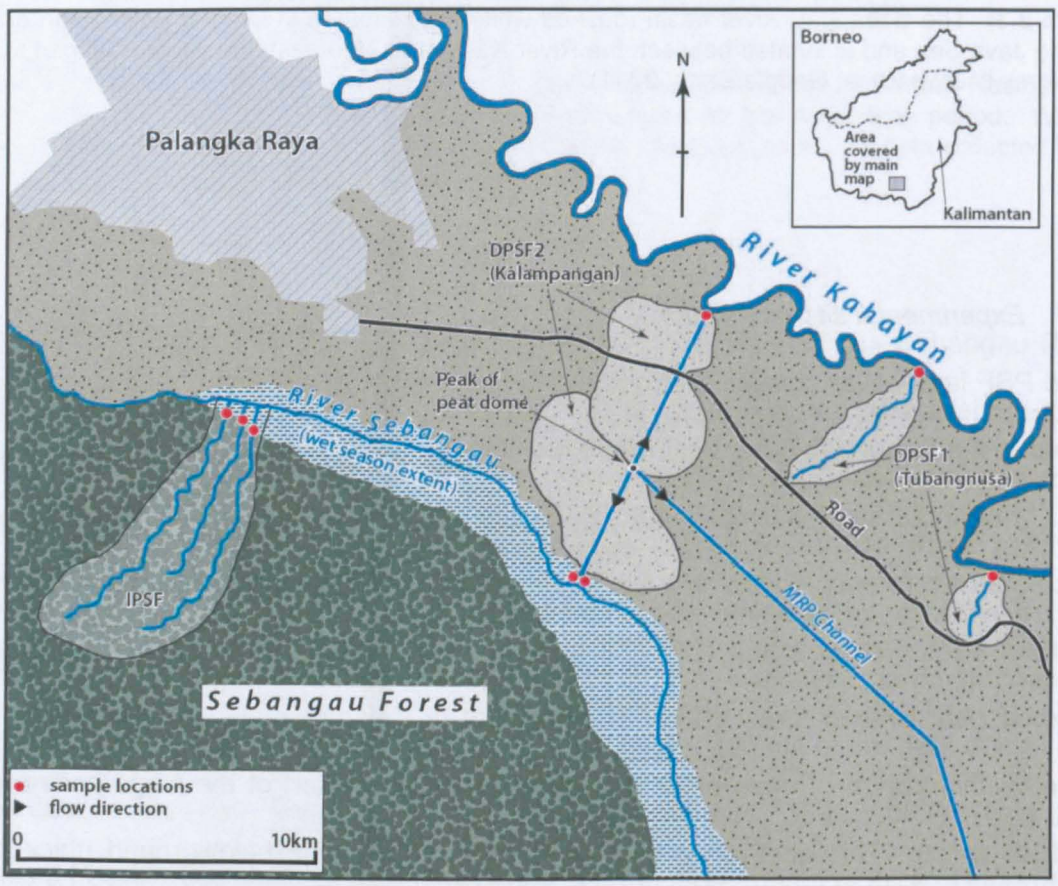


Figure 2.4: Location of study sites in Central Kalimantan, Borneo, Indonesia (inset). All sites lie within 30 km of Palangka Raya, the provincial capital of Central Kalimantan. IPSF (three channels) drains into the River Sebangau. DPSF1 (two channels) drains into the River Kahayan. DPSF2

(three channels): two channels drain into the River Sebangau and one channel into the River Kahayan.

2.2.2 *Intact peat swamp forest (IPSF) - Sebangau*

IPSF is situated within the borders of the Sebangau National Park, approximately 12 km south of Palangka Raya (figure 2.5). The study area extends southwest from the River Sebangau and consists of a continuum of forest types from the river (riverine forest) to the centre of the peat dome (tall interior forest; see Chapter 1.2.6; Page *et al.*, 1999). The peat dome of which IPSF forms a part ranges in thickness from less than 1 m at the edge to more than 11 m in the centre, averaging 7.8 m over the whole dome (Page *et al.*,

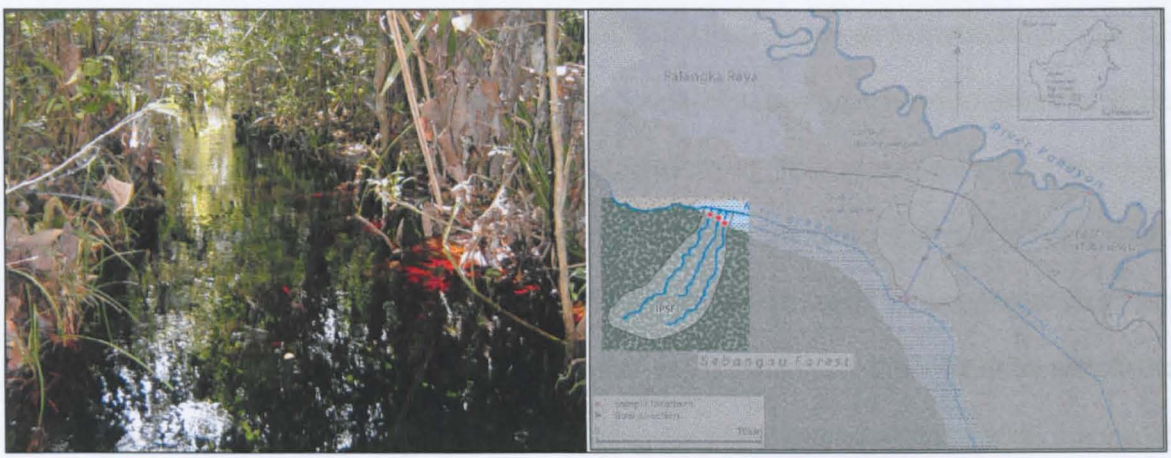


Figure 2.5: An example of a logging access channel in IPSF, approximately 1.5 m wide and 0.6 m deep (left) and the location of IPSF within study site map (right).

1999). Despite its National Park status, this study area cannot be termed pristine due to small-scale, selective logging that took place in the 1990s which was unrelated to the MRP. The loggers dug access channels to transport felled trees out of the forest and onto boats in the River Sebangau. Three channels that drain 34.2 km^2 of IPSF and discharge into the River Sebangau were monitored. These channels penetrate the forest approximately 15 km perpendicular to the forest edge and range in size. All channels are 1.5 to 2.0 m wide and do not exceed 1.0 m in depth, but the actual volume of water within

them varies depending on the time of year. In an average rainfall year, they dry out at distances greater than 1 km inside the forest, but remain wet all year closer to the forest edge. In drier years, they may dry out completely for a short period of time during the peak of the dry season, between July and September, when the water table reaches a maximum depth of -40 cm (Takahashi *et al.*, 2003). For the majority of the year, the water table is above the peat surface and the channels' flow is at capacity. The highest water tables during the peak of the wet season, between February and April, result in overland flow as well as channel flow at levels exceeding the channels' maximum capacity. Therefore the influence of these channels on the actual drainage of the peat dome is considered to be negligible.

2.2.3 Disturbed peat swamp forest 1 (DPSF1) - Tubangnusa

DPSF1 is one of two disturbed land-cover classes investigated and refers to an area of land that encompasses the village of Tubangnusa (figure 2.6). It is situated southeast of Palangka Raya in between the main road south to Banjarmasin and the River Kahayan, within what is termed 'Block C' of the MRP. The peat is slightly shallower in DPSF1 compared to IPSF and ranges from less than 1 to 5 m in depth. DPSF1 looks very different to IPSF, primarily due to the lack of overlying PSF (figure 2.6).

Figure 2.6: An example of a drainage channel in DPSF1, approximately 4.5 m wide and 2.8 m deep (left) and the location of DPSF1 within study site map (right).

The area was clear-felled of all PSF and the remaining vegetation was burned in preparation for the MRP in the late 1990s. In addition, two drainage channels approximately 3 to 6 m wide and 2 to 3 m deep were dug so that the water table could be artificially controlled during rice production. Today, the land-cover consists largely of shrubs and ferns with small clusters of trees that generally do not exceed 5 m in height. The limited regeneration of the land is due to a number of reasons; first and foremost, the drainage channels result in continuous artificial drainage of the surrounding peatland, drying it out. Since the channels were dug the water table has been significantly lowered. This leads to subsidence of the peat and significant gaseous carbon loss via continual oxidation (Couwenberg *et al.*, 2010).

Lower water tables, resulting in drier peat surfaces which are highly combustible, greatly increase the risk of fire (Page *et al.*, 2009a). Fires, many of which are started by local farmers to clear shrubs and ferns from deforested areas in preparation for agricultural use, spread very quickly out of control and ignite what is remaining of the surface vegetation as well as the underlying carbon-rich peat. Tubangnusa is particularly fire prone and has been subject to fires every year since the initiation of the MRP. The most severe fires often correlate with extended dry seasons during El Niño events, which have occurred in 1997, 2002, 2006 and most recently in 2009. During the El Niño years of 1997 and 2002, over 60,000 fire hotspots were detected across Borneo by satellite, many of them within the boundaries of the MRP, and in particular 'Block C' (Tansey *et al.*, 2008). The fires spread quickly across the peat and due to a lack of fire-fighting resources and personnel, often remained burning for months at a time. The fires burn fresh vegetation that has grown since the previous fire event, only ever allowing a thinly spread ground covering of 1 to 2 year old shrubs and ferns. This relentless fire cycle gives very little opportunity for more extensive re-growth to occur. Consequently, any sort of substantial regeneration at this site will only be possible if the fire cycle is broken for at least several continuous years.

The total drainage area of the two channels monitored in DPSF1 is 13.2 km^2. The first of these two channels in DPSF1 is located 5.2 km southeast of the large Kalampangan Canal. It runs for 6.1 km northeast from the main north-south road where it discharges into the Kahayan River. The second channel is located a further 9.4 km southeast along the main road and 14.6 km southeast of the Kalampangan Canal. This channel is shorter than the first, running only 2.8 km from the northeast of the road before discharging into the Kahayan River. The entire area within DPSF1 was also affected by the significant fires in the El Niño years of 1997, 2002, 2006 and 2009.

2.2.4 Disturbed peat swamp forest 2 (DPSF2) - Kalampangan

DPSF2 is the second disturbed land-cover class investigated and refers to an area of land close to a village named Kalampangan (figure 2.7). It is situated southeast of Palangka Raya within the most northerly part of 'Block C', between the River Sebangau and the River Kahayan. The peat dome here varies in depth from less than 1 m at the edges to a maximum of 8 m at the summit of the dome. The Kalampangan Canal drains this peat dome. The Kalampangan Canal was dug during the MRP and is the most recognisable feature of the area. It measures 15 to 25 m wide and 4 to 7 m deep. It is approximately 12 km in length and drains the peat dome into the River Sebangau to the southwest and the River Kahayan to the northeast (figure 2.7).

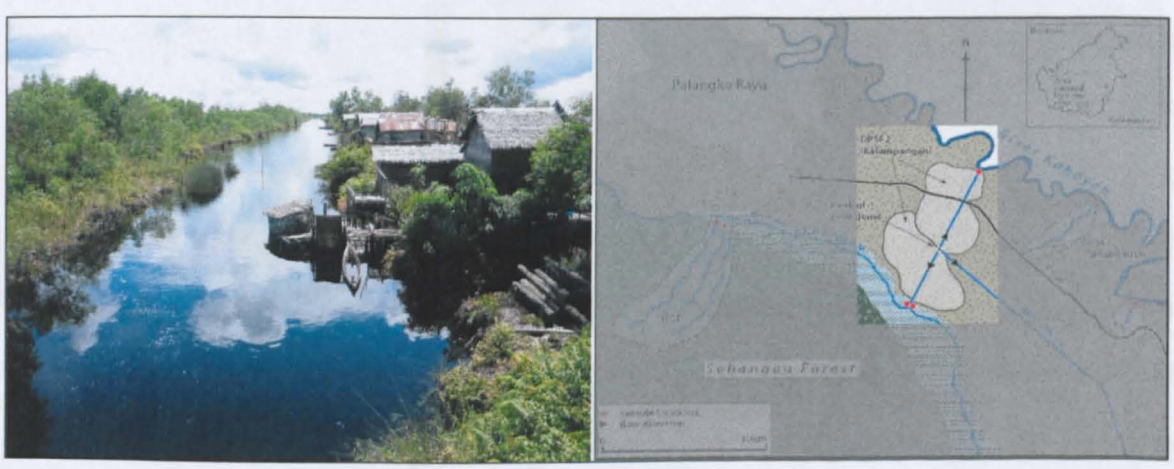


Figure 2.7: The Kalampangan Canal in DPSF2, approximately 23 m wide and 6 m deep (left) and the location of DPSF2 within study site map (right).

DPSF2 was also cleared of all its PSF during the MRP years. DPSF2 is subject to more severe drainage than DPSF1, induced by the Kalampangan Canal and the MRP channel that runs for 150 km south from the Kalampangan Canal where it discharges into the Java Sea. Water tables fluctuate according to rainfall but as a consequence of severe artificial drainage they remain below the peat surface for most of the year, reaching maximum depths of -140 cm in drier years (Hooijer *et al.*, 2008). The effect of such extreme drainage can extend into peatlands over large distances with high rates of subsidence, indicative of aerobic decomposition of the peat, concentrated in the first few hundred meters from the larger drainage channels (Hooijer *et al.*, 2008). The resulting landscape in DPSF2 is similar to DPSF1, consisting primarily of shrubs and ferns. Like DPSF1, DPSF2 experiences regular human-induced fire events. Due to its proximity to local villages however, it is more accessible to small fire-fighting teams who have had more success in controlling some of the fires in Kalampangan, as opposed to in Tubangnusa. Nonetheless, large areas within DPSF2 burned in the same post-MRP El Niño years of 1997, 2002, 2006 and 2009. Some areas within DPSF2 contain small stands of trees that reach up to 10 m in height, but these are uncommon as most woody re-growth is restricted by regular fire events.

In an attempt to limit further drainage, increase the water table and begin to re-wet the surrounding peatlands, dams of different designs and sizes have been constructed on many of the MRP drainage channels. In 'Block C', these damming projects have been implemented by the Centre for Integrated Management of Tropical Peatlands (CIMTROP) based at Universitas Palangka Raya (UNPAR), and are funded by international charities and non-governmental organisations. At present, the Kalampangan Canal is dammed at five locations, but due to a lack of significant funding and the resulting lack of resources, the dams regularly collapse during the wet season when the water table is at its highest, as illustrated in figure 2.8. Increasing the water table is commonly viewed as the only

long-term answer to reducing aerobic peatland decomposition, subsidence and the risk of fire.

Figure 2.8: An example of a broken dam on the Kalampangan Canal. These dams are constructed of locally sourced materials and installed by hand. With no machinery to assist, the foundations are shallow which invariably leads to them collapsing during times of high water flow.

The Kalampangan Canal runs up, over and down the Kalampangan peat dome. As a result, water flows in three directions away from the summit of the peat dome; towards the River Sebangau, the River Kahayan and down the MRP channel towards the Java Sea, as illustrated in figure 2.4 and 2.7. There is no outward flow of drainage water from within the DPSF2 catchment into the MRP channel, in the same way that there is no inward flow of drainage water from outside the DPSF2 catchment into the Kalampangan Canal. To the southwest, the Kalampangan Canal stops 200 m short of the River Sebangau where it splits into two smaller channels that discharge into the River Sebangau, as illustrated in figure 2.9. At the opposite end, to the northeast, the canal discharges directly into the River Kahayan. All three channels which drain an area of 42.9 km^2 in DPSF2, were individually monitored.

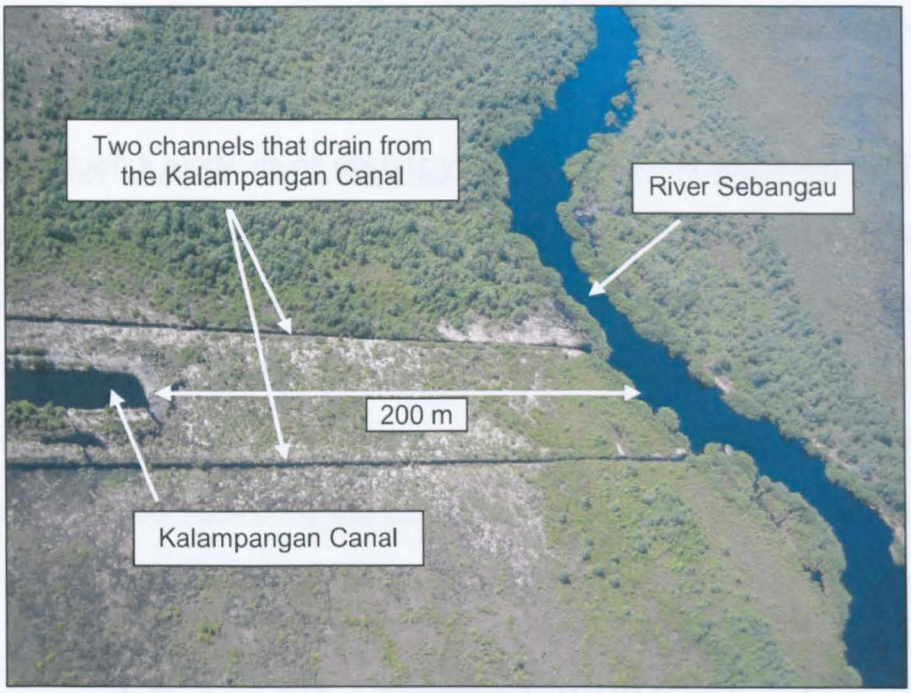


Figure 2.9: Aerial photograph of DPSF2 where the Kalampangan Canal discharges into the River Sebangau via two smaller channels (Photo: V. Boehm, 2006).

2.2.5 The Sebangau River basin

The Sebangau River basin is approximately 5,200 km^2. Of this, 3,400 km^2 is covered in intact PSF, the vast majority of which (3,040 km^2) is found to the northwest of the River Sebangau and forms Sebangau National Park. To the west of the southern stretches of the River Sebangau is a small transmigration settlement area which experienced deforestation and land use change in the 1970s through to the 1990s. The remaining 1,800 km^2 is a mix of degraded and secondary PSF, ferns and shrubs, cleared and burnt areas and small-holder areas. The vast majority of this (1,200 km^2) is found within 'Block C' to the east of the River Sebangau. A combination of peatland drainage and fires has created a much changed and degraded ecosystem on the eastern side of the river basin (Page *et al.*, 2002; 2009; Wösten and Ritzema 2007; Ballhorn *et al.*, 2009).

Aboveground vegetation aside, the Sebangau River basin is composed almost exclusively of peatlands, resulting in a high concentration of humic substances in the drainage water entering the River Sebangau. The River Sebangau is therefore commonly termed a

blackwater river and has a background pH of 3.5 to 4.0 (Haraguchi, 2007). Kya, the source of the River Sebangau is approximately 20 km west of Palangka Raya. From here, the River Sebangau flows approximately 150 km south where it discharges into the Java Sea (figure 2.10). The height above sea level at its source is 12 m (Page *et al.*, 1999). Averaged over the entire course of the river, there is, therefore, only a 1 m change in elevation for every 12.5 km of river length. Such a low relief gradient leads to low water flow rates within the river throughout the year.

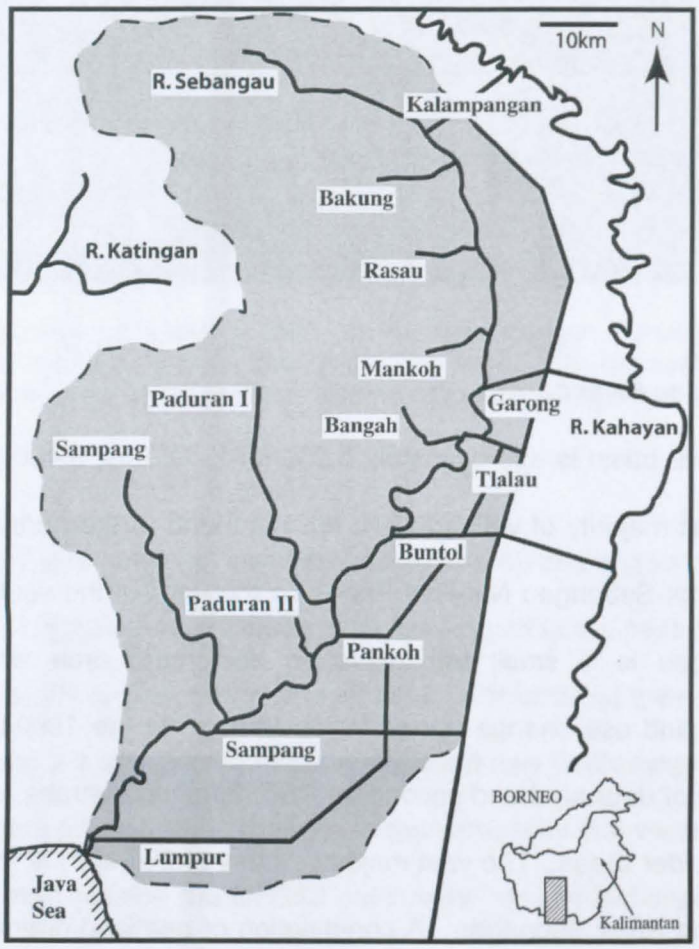


Figure 2.10: Map of the Sebangau River basin in Central Kalimantan, Borneo (inset). The Sebangau River basin is shaded grey and outlined by the dashed line to the west and south and the straight solid line (north-south canal) to the east. Fourteen named channels drain the Sebangau River basin into the River Sebangau (centre) which runs from north to south draining into the Java Sea.

2.3 General methods

2.3.1 Sample collection

All surface water samples were collected from channels (artificial canals or natural streams and rivers) using the same method. Where the objective was to quantify the loss of fluvial carbon from a specific channel, samples were collected at a point immediately upstream from where the channel discharged its load into a natural riverine system. The sampling location was marked with GPS and visually defined with rope tied over the width of the channel to ensure sampling was carried out in exactly the same location every time the site was revisited. Within each channel, five replicate samples were collected to represent the entire cross sectional area (figure 2.11). When collecting water samples from the wider channels, physically entering the water was sometimes necessary. In these instances, the sample location was always approached from downstream to ensure that access disturbance did not affect the sample taken.

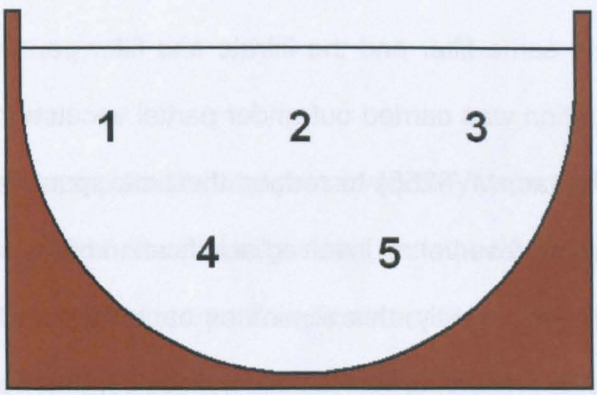


Figure 2.11: Channel cross-sectional area to illustrate the five replicate sampling locations.

All samples were collected in pre-rinsed (with sample) polypropylene 60 ml Nalgene wide-neck bottles. Polypropylene bottles have been recommended for sample collection and storage when DOC analysis is required (Norrman, 1993). The sample bottle was kept inverted under the water so as not to let any water in until it reached the desired sample collection depth, whereupon it was angled to allow water to slowly enter. Once the bottle

was full, the screw-cap was fastened under water to ensure only water from the desired depth was collected.

2.3.2 Sample preservation

Having collected the sample and taken in-situ measurements (see Chapter 2.4.1), a two-step processing technique was used: (i) to separate the POC fraction from the DOC fraction; and (ii) to preserve or 'fix' the DOC concentration, minimising any potential difference in concentration between the time of sample collection and sample analysis. The first stage of preservation involved filtering the water sample, the function of which is two-fold. Firstly, this serves to separate the DOC fraction from the POC fraction and secondly, it removes biologically active particles that could alter the concentration of DOC in the sample, post-collection (Sharp & Peltzer, 1993). To reduce the possibility of organic contamination, excess sample water was filtered through the cellulose acetate membrane filters (0.45µm) and the filtrate disposed of. A known volume of the sample (60 ml) was then passed through the same filter and the filtrate and filter paper retained for analysis (see Chapter 2.4). Filtration was carried out under partial vacuum (10 psi) using a hand-held vacuum pump (Mityvac, MV8255) to reduce the time spent waiting for samples to filter. The second stage of preservation involved acidification of the sample to pH 2, which also has a two-fold function. Firstly, this eliminates bacterial activity and denatures the majority of enzymes, while preserving the organic molecules, thus reducing the possibility of the DOC concentration being altered. Secondly, it removes any DIC present in the sample. Alkali-titration analyses were conducted in the field before the addition of acid to examine the proportion of carbon present in the inorganic form, the results of which indicated that no DIC was present. Given the very low water pH, this was consistent with expectations.

A solution of dilute sulphuric acid (20%) was used to acidify the samples. Water samples to be analysed for DOC that have been preserved with certain acid types have been

reported to show slight decreases in concentration with time (Kaplan, 1994). By using sulphuric acid, however, this decrease in concentration can be kept to a minimum and is undoubtedly a more efficient preservation technique than no addition of acid at all (Kaplan, 1994). The most desirable protocol would be to analyse samples immediately following collection. Due to the remote sampling location and the lack of laboratory instrumentation, this was not possible. For the same reasons, nor was it possible to create a DOC 'decay curve' and apply a correction factor to the data. To do this, the sample would have had to have been analysed immediately post-collection, acidified and analysed again, upon returning to the UK in order to show the decrease, if any, in DOC concentration over this time. Alternative preservation techniques such as the addition of biocide (e.g. mercury) and/or freezing were not viable options given the location of my study sites, and therefore preservation by addition of acid was considered the best available option. Despite these limitations, it should be noted that the only possible change in DOC concentration (when acid is used as a preservative) is a decrease and therefore the results, if anything, should only be considered as conservative estimates as opposed to overestimates.

Once the samples had been collected and preserved they were transported back from the field site in a cool box, out of direct sunlight and stored at 2 to 5°C at the University of Palangka Raya soil science laboratory. Samples were stored in this manner until the end of each field campaign when they were couriered back to the UK for analysis at the Department of Earth and Environmental Sciences laboratories, The Open University.

2.3.3 Flux calculations

To calculate a carbon flux from a channel, the channel discharge and the carbon concentration within the channel are required. Channel discharge rate (Q) was calculated as described in equation 2.1.

$$Q\ (m^3\ s^{-1}) = FR\ (m\ s^{-1}) \times CSA\ (m^2) \qquad \textit{(Equation 2.1)}$$

Where *FR* is the channel flow rate and *CSA* is the cross-sectional area of the channel. The flow rate was calculated using a handheld impeller flow meter (Geopacks Adv.). Five replicate flow rate measurements were taken from the same five locations that the water samples were taken from in order to represent the entire cross-sectional area of the channel. The flow meter is submersed in the channel at the sampling location for one minute and the number of impeller counts recorded. These impeller counts are converted into flow rates as described in equation 2.2.

$$FR\ (m\ s^{-1}) = 0.000854C + 0.05 \qquad \textit{(Equation 2.2)}$$

Where *C* is the number of impeller counts in one minute. Precision for this method was better than ±5%. The cross-sectional area was calculated by mapping the channel profile by taking water depth measurements at regular intervals (intervals varied with the size of the channel) across the channel width. These measurements were recorded every time the site was revisited as the water levels can vary over short time scales.

The DOC/POC flux (DOC/POC_{flux}) from individual channels was calculated as described in equation 2.3.

$$DOC/POC_{flux}\ (mg\ s^{-1}) = DOC/POC_{conc}\ (mg\ l^{-1}) \times Q\ (m^3\ s^{-1}) \qquad \textit{(Equation 2.3)}$$

Where DOC/POC_{conc} is the DOC/POC concentration of the channel water and *Q* is the channel discharge. This flux is assumed to stay at a constant rate when it comes to temporally up-scaling to calculate the total flux for that week (weekly time point resolution). The site is then revisited and the flux recalculated for the following week. The weekly flux data are presented in larger units (tonnes $week^{-1}$) and these were calculated by multiplying up accordingly. Where DOC/POC/TOC data are presented as a quantity

per unit area, this is referred to as a yield in grams of carbon, per meter squared, per year (g C m^{-2} yr^{-1}). This was calculated by dividing the total flux from a known area of land by that total land area. All land areas were quantified through combined use of aerial photography, a digital elevation model and a geographic information system (ArcGIS, 9.3).

2.4 Sample analysis

2.4.1 In-situ measurements

Samples were subject to a range of analyses in the field immediately post-collection and in various laboratories within the UK upon their return. Immediately following the collection of a water sample from a channel, water temperature, pH and electrical conductivity (EC) were recorded using portable pH (Hanna HI9024D) and EC (Hanna HI8633) meters. The wide-neck polypropylene bottles allowed these probes to be used without transferring the sample into another container, thereby reducing the risk of contamination.

2.4.2 Dissolved Organic Carbon

Samples were analysed for DOC by high-temperature catalytic oxidation (680°C) using a Total Organic Carboniser (Shimadzu, TOC-V_{CPN}) complete with a platinum catalyst and auto-sampler (Shimadzu, ASI-V). All samples were analysed against three 8-point calibrations for non-purgeable organic carbon (NPOC) analysis which covered the range of values produced from the samples. These NPOC calibrations consisted of the following concentration ranges: 0-50 mg l^{-1}; 0-75 mg l^{-1}; and 0-100 mg l^{-1}. The calibration curve with the most appropriate range for every individual sample was automatically selected by the instrument software to ensure the highest possible accuracy. Figure 2.12 shows an example of a NPOC calibration curve used during one of the sample runs. The calibration correlation co-efficient was never below r^2=0.99 (usually r^2=1.00).

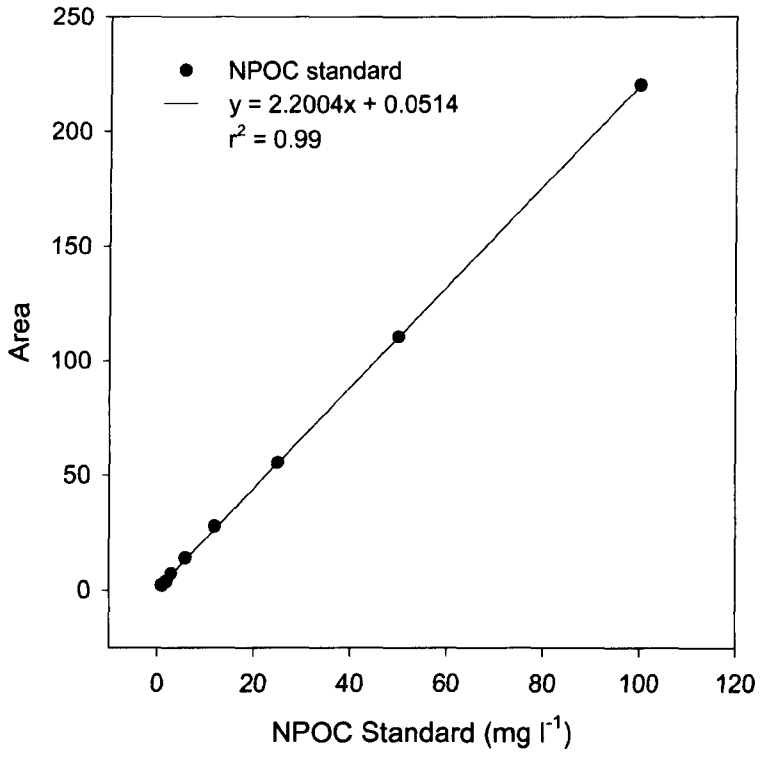


Figure 2.12: An example of a NPOC calibration curve (0-100 mg l^{-1}) used during a sample run.

The instrument was re-calibrated every two weeks or when any changes were made to the instrument. Calibration standard checks of 50 mg l^{-1} and 100 mg l^{-1} were run at the beginning, after every 15 samples and at the end of every sample run to check the precision of the calibration being run. Deionised water samples were also processed at the beginning of every run as blank controls.

2.4.3 Particulate Organic Carbon

Once a known volume of the water sample has passed through a 0.45 µm filter, the DOC fraction is in the filtrate and the POC fraction is retained by the filter. To derive POC concentration, the filter was retained following filtering and oven dried (24 h at 40°C). This quantifies particulate matter which is thought to be equal to particulate organic matter (POM; given the dominance of peat soil at all sites). POM was then converted to a POC value by assuming organic matter to be 50% carbon (Hope *et al.*, 1994). The resulting

data is the POC concentration with a unit of mg 60 ml^{-1} (volume of sample originally filtered). This data was then converted to standard POC concentration units (mg l^{-1}) by multiplying up accordingly.

2.5 Statistical analysis

Quantitative data were analysed using parametric statistical tests where appropriate (SPSS, 18.0). Assumptions for using parametric analysis (adherence to normality and homogeneity of sample variance) were tested using Kolmogorov-Smirnov and Levene tests.

Where Kolmogorov-Smirnov $p>0.05$, parametric statistics such as ANOVAs were used and where $p<0.05$, log transformations were attempted. Where these failed, non-parametric statistics such as Kruskal-Wallis were used. In testing for homogeneity, where the levene statistic was $p>0.05$, parametric statistics were used and where the levene statistic $p<0.05$, log transformations were attempted with those variables still $p<0.05$ being subject to non-parametric tests. Parametric correlations were also used such as Pearson's correlation, and non-parametric correlations such as Spearman's correlation to test for correlation between variables.

Statistical methods that are more specific to individual chapters are discussed within those chapters.

Chapter Three

Fluvial organic carbon fluxes from intact and disturbed peat swamp forests

A version of this chapter was submitted as a manuscript and is currently under review, as: Moore, S., Gauci, V., Page, S.E., Evans, C.D., Garnett, M.H., Jones, T.G., Freeman, C. and Limin, S.H., 2011. Fluvial organic carbon fluxes reveal deep instability of deforested tropical peatlands. *(Nature, submitted manuscript)*

3.1 Introduction

Peatlands, by virtue of their high water table and consequent low decomposition rates form large carbon stores (Gorham, 1991). Tropical peatlands are poorly understood with respect to higher latitude peatland ecosystems yet they consist of vast and old carbon stores, many of which predate the last Glacial (Page *et al.*, 2004), which are vulnerable to some of the most rapid rates of land use change in the world (Page *et al.*, 2011). Globally, tropical peatlands store 82-92 Pg of carbon, of which Indonesia accounts for 65% (57Pg; Page *et al.*, 2011). Southeast Asia currently experiences extensive anthropogenic tropical PSF degradation in the form of deforestation, drainage and fire (which does not play a role in the natural forest carbon cycle), all of which are converting carbon stored in peat into CO_2 via direct combustion or through oxidation within the peat column as a result of water table drawdown (Page *et al.*, 2002; Hooijer *et al.*, 2010). As a result of fire alone, it is estimated that between 0.81 and 2.57 Pg of carbon were released to the atmosphere in 1997 as a result of burning peat and vegetation in Indonesia (Page *et al.*, 2002). This was equivalent to 13 to 40% of the mean annual global carbon

emissions from fossil fuels at the time. Unlike boreal and temperate forests (McDowell & Likens, 1988; Michalzik *et al.*, 2001), and higher latitude wetlands (Mulholland & Kuenzler, 1979), the loss of fluvial organic carbon from tropical peatlands has yet to be quantified. In one of the most comprehensive reviews to date, Laiho (2006) explores the effects of lowered water tables on losses of fluvial organic carbon in peatlands, but does not include any reference to tropical peatlands. In the UK it has been estimated that 15,000 km^2 of the country's 29,000 km^2 of peat has been drained (Stewart & Lance, 1991; Milne & Brown, 1997). The reasons for draining are commonly stated as being for the lowering of water tables in order to improve grazing, hunting or to develop forestry (Ratcliffe & Oswald, 1988). Such drainage invariably results in increases in DOC export. Higher DOC concentrations were reported from a drained blanket peat in the UK when compared with intact peat (Wallage *et al.*, 2006), increased DOC concentrations from Minnesota peat soils were reported upon drainage (Clausen, 1980) and Mitchell and McDonald (1995) showed that in a UK upland catchment, areas of the highest drainage density were the largest sources of DOC. Biogeochemical modelling based on processes known to act on DOC production in upland Britain also showed that drained catchments export more DOC with increases in the range of 15 to 33% over a 10 year period, depending on the drainage intensity (measured by drain-spacing; Worrall *et al.*, 2007).

In general, the drainage of tropical peatlands, and more specifically drainage that occurred as a result of the MRP in Central Kalimantan, is more severe in terms of depth as opposed to drain-spacing. Initiated in 1995, the MRP was a failed agricultural development project which aimed to convert 10,000 km^2 of peatland into rice fields and involved digging more than 4,500 km^2 of drainage channels (see Chapter 2.2.1; Hooijer *et al.*, 2008). The only studies to have investigated the effect of artificially lowering water tables in tropical peatlands have been with respect to emission of carbon gases (Hooijer *et al.*, 2006; 2010). To date, no study has investigated the effect such a disturbance has on losses of fluvial organic carbon. Therefore, this investigation aims to quantify fluvial

organic carbon fluxes from three different land-cover classes that vary in their degree and nature of anthropogenic disturbance (deforestation, drainage and fire).

3.2 Methods

To quantify the effect of peatland disturbance on fluvial organic carbon fluxes, DOC and POC concentrations and water discharge rates were monitored from channels draining areas of both intact and disturbed PSF in a portion of Central Kalimantan, Indonesia, Borneo. The disturbed PSF has experienced severe deforestation, drainage and fire associated with the implementation of the MRP. Three PSF land-cover classes that differed in their recent disturbance history (as described in Chapter 2.2.1-2.2.3), located in or near to the Sebangau River basin were selected (figure 3.1): (1) intact PSF (IPSF; 3 channels in the Sebangau forest); (2) moderately drained disturbed PSF (DPSF1; 2 channels in Tubangnusa); and (3) severely drained disturbed PSF (DPSF2; 3 channels in Kalampangan).

TOC (DOC + POC) fluxes were monitored from each channel outlet (as described in Chapter Two) at weekly intervals from June 2008 to June 2009. Rainfall gauges were also installed and monitored weekly at each of the three land-cover classes. Weekly monitoring was carried out during two 12 week sampling campaigns over the peak of the dry season (1st Jun to 23rd Aug '08) and the peak of the wet season (25th January to 18th April '09). During the remaining weeks in the year (24th Aug '08 to 24th Jan '09 and 19th Apr to 31st May '09), sampling was carried out by the staff at CIMTROP, Universitas Palangka Raya. During these periods, all channels were monitored on a fortnightly basis where discharge measurements and samples were taken. For the weeks that remain unaccounted for, rainfall data were recorded and used to estimate channel discharge rates using the unique rainfall/discharge relationship for each individual land-cover class. This means that data for 38 out of the 52 weeks in the year are based on actual discharge

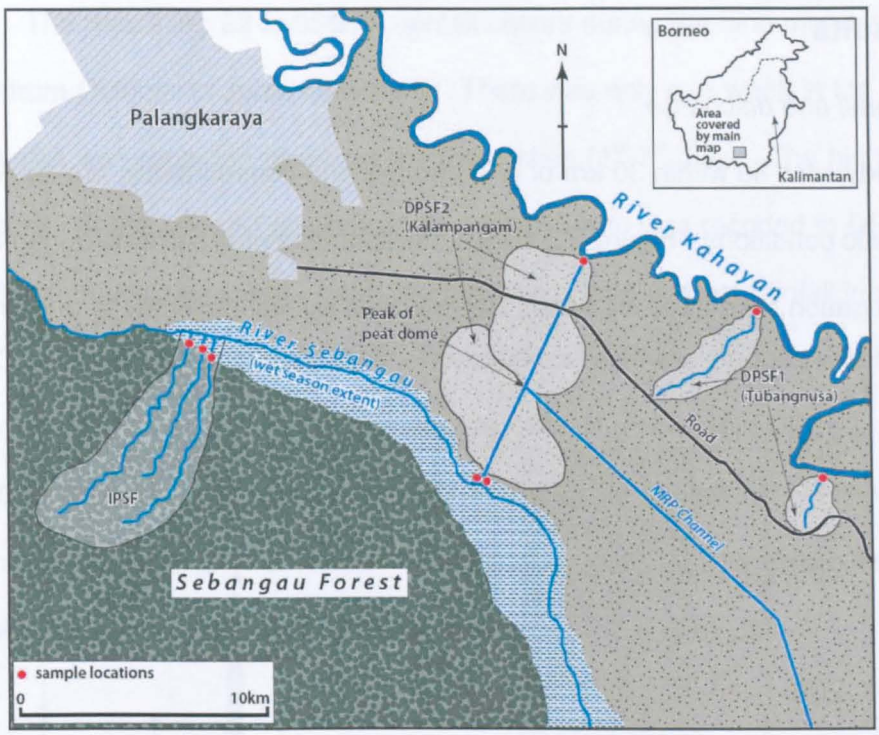


Figure 3.1: Location of study sites in Central Kalimantan, Borneo, Indonesia (inset). All sites lie within 30 km of Palangka Raya, the provincial capital of Central Kalimantan. IPSF (three channels) drains into the River Sebangau. DPSF1 (two channels) drains into the River Kahayan. DPSF2 (three channels): two channels drain into the River Sebangau and one channel into the River Kahayan.

measurements and the remaining 14 weeks are inferred from rainfall data that was collected weekly. Water samples were collected from channels in the same weeks as actual discharge measurements were taken, and sent to the UK for analysis. For the 14 weeks of inferred discharge data, no water samples were collected and DOC/POC concentration data were calculated as the mean of the preceding and following week's actual data. All land-cover class areas were defined through combined use of aerial photography, a digital elevation model and a geographic information system (ArcGIS, 9.3). This enables data to be presented per unit area (e.g. TOC yield in g C m^{-2} yr^{-1}) and in doing so, allows comparisons between catchments of varying sizes.

3.3 Results

3.3.1 Rainfall and discharge

All three study sites lie within 30 km of one another and consequently, are subject to very similar climatic conditions. Figure 3.2 shows the annual rainfall patterns during the course of the investigation from all study sites. Despite their spatial proximity to one another, the

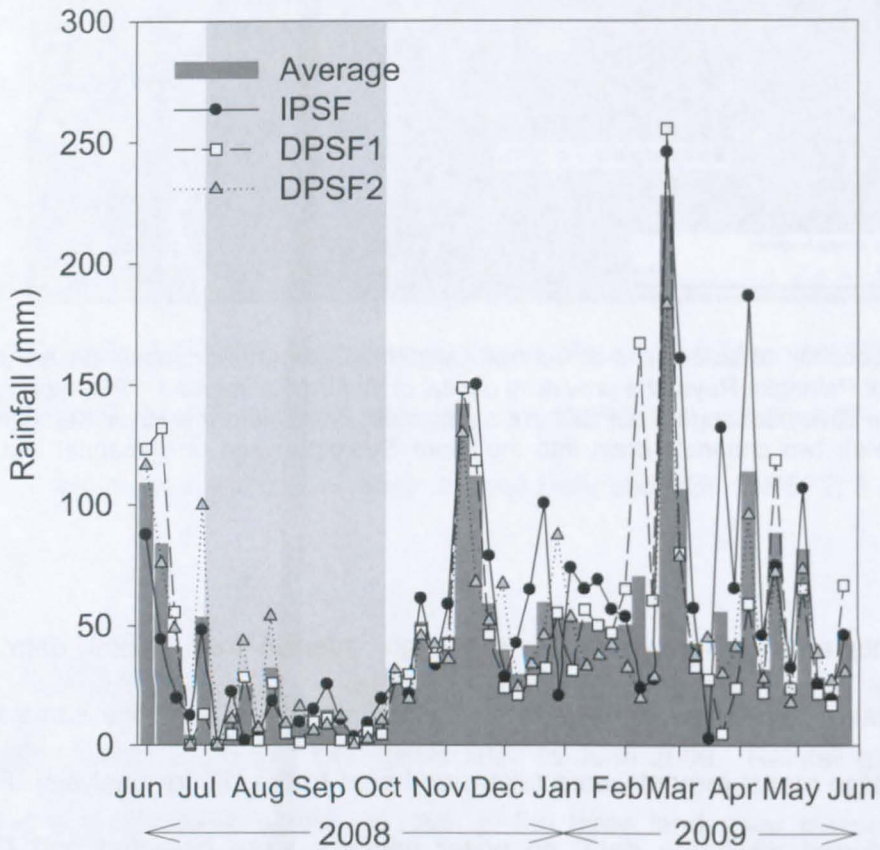


Figure 3.2: Weekly rainfall data (June 2008 to June 2009) taken from rainfall gauges within each land-cover class and average rainfall from all three sites. The light grey area indicates the timing of the dry season (July to September, inclusively).

total annual rainfall did vary somewhat between sites, totalling 2744 mm, 2356 mm and 2225 mm, at IPSF, DPSF1 and DPSF2, respectively. Higher rainfall over intact PSF compared to cleared land may be expected due to a more humid micro-climate created by a dense rainforest canopy. There is less than 20% difference between the site with the lowest annual rainfall (2225 mm) and the highest (2744 mm), and more notably, all three sites display the same seasonal trend. All sites receive only 5 to 8% of their total annual rainfall during the dry season which accounts for 25% of the year (July to September,

inclusively). The remaining 92 to 95% of rainfall occurs during the nine month wet season which lasts from October to June, inclusively. There was only one week in the entire year when no rainfall was recorded at any of the three sites (1st-7th July). The highest weekly rainfall occurred at the end of February when over 255 mm was recoded in DPSF1, most of which fell within one rain event. February also recorded the most rainfall in one month, averaging 386 mm across all study sites. The driest month was August, which averaged only 30 mm of rain across all sites and as little as 19 mm recorded in DPSF2. June 2008 to June 2009 was an unexceptional year in terms of annual rainfall (no El Niño or La Niña event) with the average annual rainfall from all three sites (2,325 mm) just below the reported mean annual rainfall for the region (2,700 mm; Page *et al.*, 2004).

Discharge data also show a strong seasonal trend across all study sites. This is to be expected since discharge is closely related to rainfall. Between 3% (IPSF) and 10% (DPSF2) of total annual discharge occurs during the dry season, with the remaining discharge occurring during the nine month wet season, which accounts for up to 97% of total annual discharge in IPSF. Total annual discharge was larger in DPSF2 compared to IPSF and DPSF1 and this is due to it having a larger total drainage area (42.9 km^2 compared to 34.2 km^2 and 13.2 km^2, respectively). However, despite IPSF being over 2.5 times larger in size than DPSF1, the latter discharged almost double the amount of water over the course of the year. Figure 3.3 displays the catchment size corrected weekly discharge data which allows for more meaningful comparison between the sites.

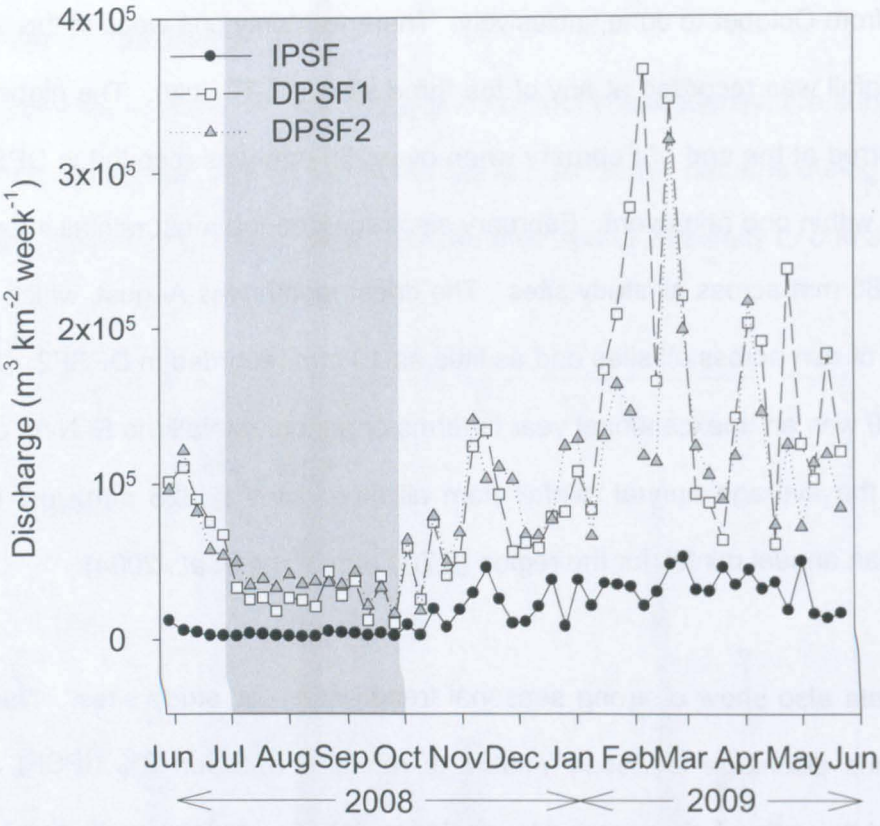


Figure 3.3: Weekly discharge data (June 2008 to June 2009) taken from all three land-cover classes (catchment size corrected). Data presented is the total discharge from each land-cover class (calculated by adding discharge from all channel outlets within each land-cover class). The grey area indicates the timing of the dry season (July to September, inclusively).

Total discharge rates are between two to three times greater in DPSF1 and 2 (1.8 and 2.7 × 10^6 m^3 km^{-2} yr^{-1}, respectively) compared to IPSF (0.9 × 10^6 m^3 km^{-2} yr^{-1}), when corrected to total catchment size (table 3.1). This is despite there being the highest annual rainfall recorded in IPSF and the lowest recorded in DPSF2. This implies that a large volume of water that enters the IPSF site as rainfall does not make it back to the discharge monitoring points at the mouth of the catchment (see Chapter 3.4).

Table 3.1: Land-cover class properties for IPSF, DPSF1 and DPSF2.

Land-cover class	Area (km^2)	Total annual rainfall (mm)	Total Discharge ($\times 10^6$ m^3 km^{-2} yr^{-1})	Mean DOC Conc (mg l^{-1})	Mean POC Conc (mg l^{-1})	Mean TOC Conc (mg l^{-1})
IPSF	34.2	2744	0.9	68.0 ± 0.3	1.4 ± 0.1	69.5 ± 0.4
DPSF1	13.2	2356	1.8	55.0 ± 0.7	5.3 ± 0.2	60.3 ± 0.8
DPSF2	42.9	2225	2.7	48.3 ± 0.5	3.6 ± 0.1	51.9 ± 0.5

Area (Total area of land-cover class), Rainfall (total annual), Discharge (total annual), DOC concentration (annual mean), POC concentration (annual mean), TOC concentration (annual mean).

The relationship between weekly rainfall and discharge across all sites is displayed in figure 3.4. A positive relationship is apparent in all three sites, but the strength of the regressions do vary between sites, most notably between the intact (IPSF) and disturbed sites (DPSF1 and 2).

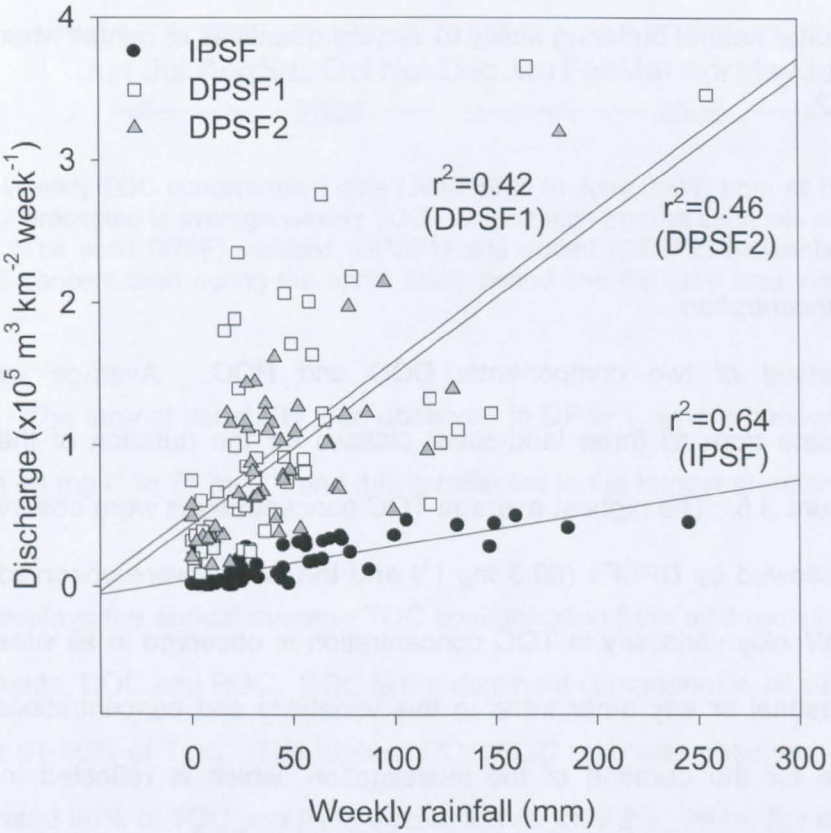


Figure 3.4: Relationship between weekly rainfall and weekly discharge data (catchment size corrected) from all three land-cover classes.

The strongest correlation between rainfall and discharge is in IPSF (r^2=0.64) with weaker correlations in DPSF1 and 2 (r^2=0.46 and 0.42, respectively). With discharge being directly linked to rainfall, one might expect these correlations to be stronger than the ones

observed. However, the relationship is somewhat complicated due to the lag time between rain falling and it reaching the mouth of the catchment where discharge is monitored. Figure 3.4 illustrates that although an increase in rainfall generally results in an increase in discharge in IPSF, an equally large increase in rainfall results in a larger increase in discharge in sites DPSF1 and 2. This is further evidence of a greater proportion of rainfall reaching the catchment outlets and being recorded as discharge in the disturbed land-cover classes. IPSF consists of a very different overlying vegetation composition to DPSF1 and 2, which may account for the different relationship observed between rainfall and discharge. Surface run-off from IPSF is slower and greatly reduced as a result of the surface micro-topography which consists of hummocks and hollows which are absent in DPSF1 and 2. Surface water collects in the hollows and can account for large volumes of stored surface water during the wet season. The data suggest that IPSF has a greater natural buffering ability to varying quantities of rainfall when compared to DPSF1 and 2.

3.3.2 TOC concentration

TOC is comprised of two components; DOC and POC. Average weekly TOC concentration data from all three land-cover classes for the duration of the study are displayed in figure 3.5. The highest average TOC concentrations were observed in IPSF (69.4 mg l^{-1}), followed by DPSF1 (60.3 mg l^{-1}) and the lowest were observed in DPSF2 (51.6 mg l^{-1}). Weekly variability in TOC concentration is observed in all sites, however, there is no seasonal or any other trend in this variability and concentrations remained relatively stable for the duration of the investigation, which is reflected in the small standard errors. There are hints of a downward trend in TOC concentration evident in DPSF2, but without a temporally expanded data set (of at least several years), it is difficult to say with any certainty that this is indeed a trend, as it may be part of longer term variability. Indeed, between the first and last data points in the series (52 weeks apart) there is only a 3 mg l^{-1} difference in concentration, which suggests low variability within the

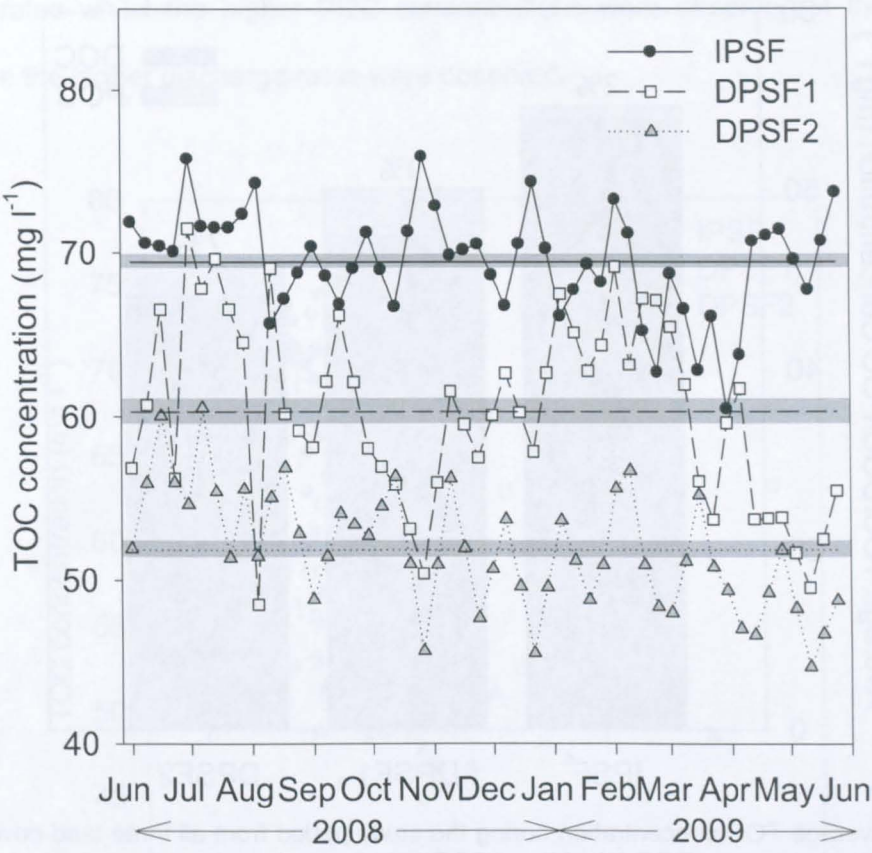


Figure 3.5: Weekly TOC concentration data (June 2008 to June 2009) from all three land-cover classes. Data presented is average weekly TOC concentration from all channels within each land-cover class. The solid (IPSF), dashed (DPSF1) and dotted (DPSF2) horizontal lines indicate average TOC concentration during the entire study period and the grey area indicates standard error.

data series. The largest variability was observed in DPSF1, where concentration values ranged from 48 mg l^{-1} to 71 mg l^{-1}, and this is reflected in the largest standard error.

Figure 3.6 displays the annual average TOC concentration from all three sites, split into its two components, DOC and POC. DOC is the dominant component in all sites, accounting for between 91-98% of TOC. The highest DOC:POC ratio was observed in IPSF where DOC comprised 98% of TOC and POC accounted for only 2%. Here, the annual average DOC and POC concentrations were 68.0 mg l^{-1} and 1.4 mg l^{-1}, respectively, resulting in a DOC:POC ratio of 48.6. In DPSF2, the average annual DOC and POC concentrations were 48 mg l^{-1} and 3.6 mg l^{-1}, respectively, which gives a DOC:POC ratio of 13.3. In DPSF1, the average annual DOC and POC concentrations were 55 mg l^{-1} and 5.3 mg l^{-1},

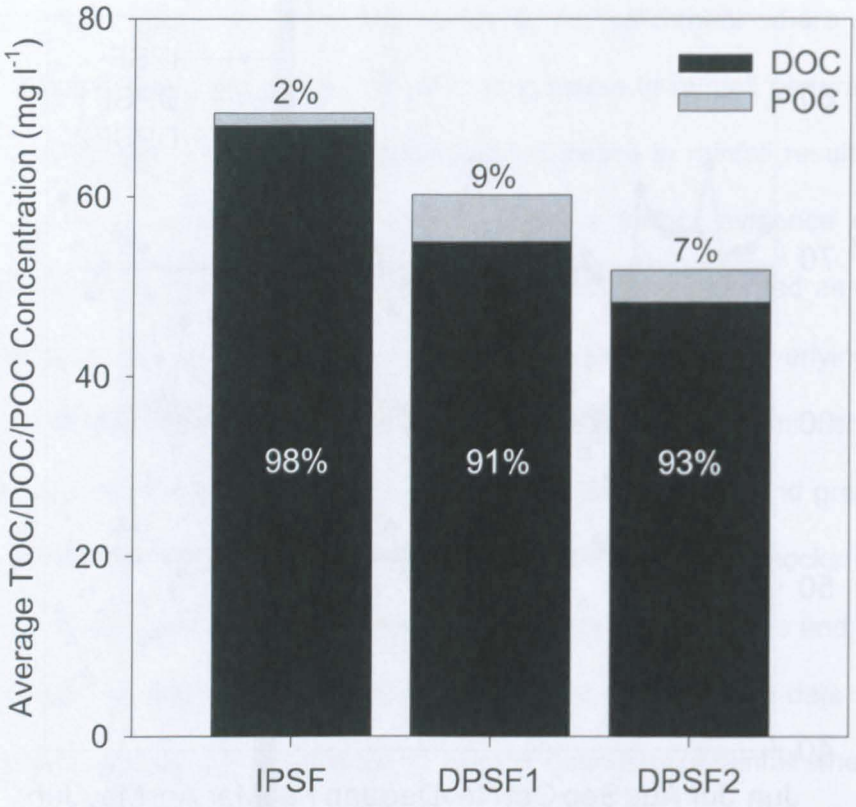


Figure 3.6: Average TOC concentration during the study period from all three land-cover classes, split into its two components; DOC (black) and POC (grey), as percentages.

respectively, which resulted in the lowest DOC:POC ratio of 10.4. Despite only ever accounting for a maximum of 10%, POC accounted for a greater proportion of TOC in both the disturbed sites compared to the intact site. This suggests that the drained and exposed peat in these disturbed land-cover classes is vulnerable to mechanical breakdown which may be associated with increased runoff and discharge.

There is no relationship between TOC concentration and discharge (figure 3.7), largely due to there being no relationship with DOC concentration (which accounts for more than 90% of TOC at all sites) and discharge (figure 3.8a). Due to the three land-cover classes having distinctly different TOC concentrations and discharge rates, it can be said that, in general, the intact sites have lower discharge rates and higher TOC concentrations. However, equally small discharge rates in the disturbed sites display much lower TOC concentrations, hence the lack of any broader correlation. There is a weak positive correlation (r^2=0.14) between POC concentration and discharge (figure 3.8b) where the

lowest POC concentrations were observed in the intact site which had the lowest discharge rates whilst the higher POC concentrations were observed in the disturbed sites, where the higher discharge rates were observed.

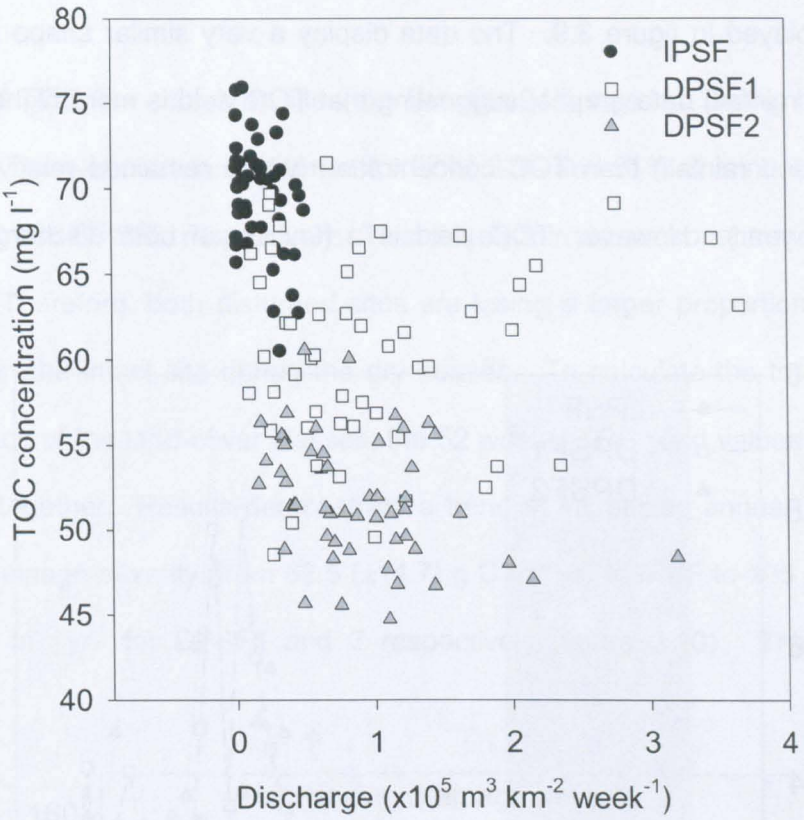


Figure 3.7: Weekly TOC concentration vs. discharge data (catchment size corrected) for all three land-cover classes.

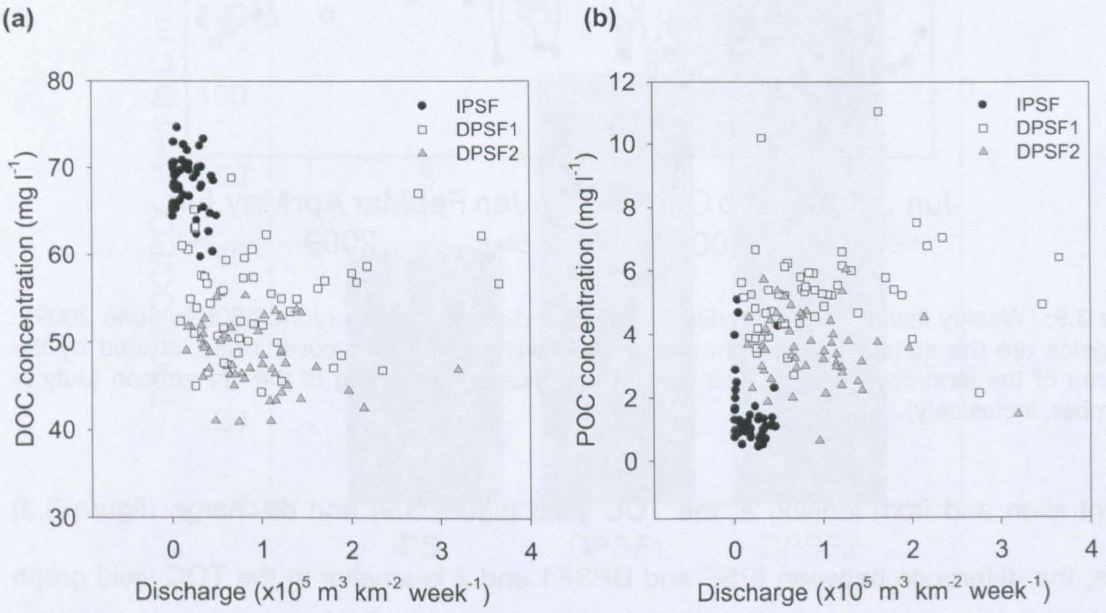


Figure 3.8: Weekly **(a)** DOC concentration vs. discharge data (catchment size corrected) and **(b)** POC concentration vs. discharge data (catchment size corrected) for all three land-cover classes. Note different y-axis scale.

3.3.3 *TOC yields*

Using both discharge and TOC concentration data, weekly TOC yields were calculated from all land-cover classes. Weekly fluxes from all channels within each land-cover class were added together and the sum divided by the total area of the land-cover class. The results are displayed in figure 3.9. The data display a very similar shape graph to the discharge (and rainfall) data graphs, suggesting that TOC yield is more highly dependent on discharge (and rainfall) than TOC concentration (which remained relatively constant throughout the year). However, TOC yield is a function of both discharge and TOC

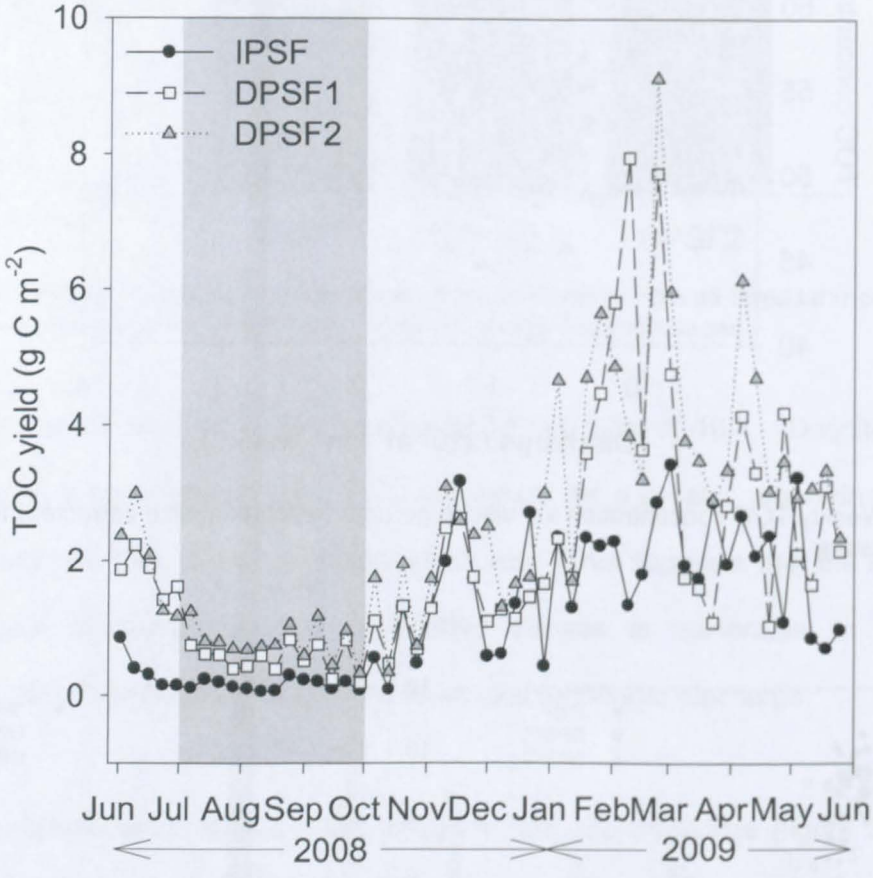


Figure 3.9: Weekly fluvial TOC yield data from all land-cover classes (June 2008 to June 2009). TOC yields are the sum of yields from all channels within each land-cover class, divided by the total area of the land-cover class. The grey area indicates the timing of the dry season (July to September, inclusively).

concentration and from looking at the TOC yield (figure 3.9) and discharge (figure 3.3) graphs, the difference between IPSF and DPSF1 and 2 is smaller in the TOC yield graph because TOC concentrations are 10-20 mg l^{-1} higher in IPSF than in DPSF1 and 2, making up for some, but not all of the difference in TOC yield. Despite the highest

average TOC concentrations in IPSF, the weekly fluxes here are almost invariably the smallest. In contrast, DPSF2 almost invariably has the largest weekly TOC fluxes despite having the lowest average TOC concentrations. This provides further support to the assertion that TOC fluxes are driven primarily by discharge over TOC concentration.

Of the annual TOC flux across all sites, on average 94% was lost during the nine month wet season. The wet season accounted for 97%, 92% and 91% of annual TOC flux from IPSF, DPSF1 and DPSF2, respectively. This closely mirrors seasonal trends in discharge at all sites. Therefore, both disturbed sites are losing a larger proportion of the annual TOC flux than the intact site during the dry season. To calculate the total annual TOC yield from each of the land-cover classes, the 52 weekly TOC yield values from each site were added together. Results demonstrate a trend of increasing annual TOC yield with increasing drainage severity, from 62.5 (±14.7) g C m^{-2} yr^{-1} in IPSF to 105 (±7.9) and 131 (±13.4) g C m^{-2} yr^{-1} for DPSF1 and 2 respectively (figure 3.10). This represents a

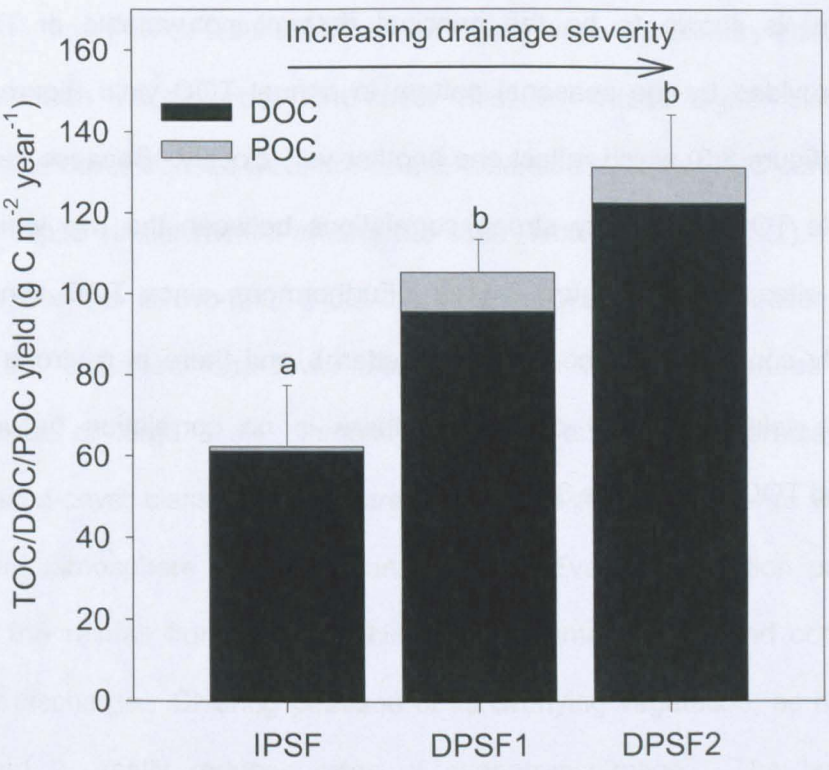


Figure 3.10: Cumulative annual TOC yield, DOC yield (black) and POC yield (grey) data from all three land-cover classes. 'a' and 'b' denote significant differences between land-cover classes ($p<0.01$, unpaired, two-sample t-test) and error bars indicate standard error.

108% increase in TOC export from the intact to the most severely disturbed land-cover class. Annual TOC yields from both disturbed sites were significantly larger than the yield from the intact site ($p<0.01$). However it was found that DPSF1 was not significantly different from DPSF2. When looking at the two components of TOC, the DOC and POC yields contribute exactly the same percentages to the yield as the DOC and POC concentrations do to the TOC concentration; 2%, 9% and 7% in IPSF, DPSF1 and DPSF2, respectively. This equates to a DOC and POC yield of 61.3 and 1.2 g C m^{-2} yr^{-1} in IPSF, respectively, 95.6 and 9.7 g C m^{-2} yr^{-1} in DPSF1 and 122 and 8.6 g C m^{-2} yr^{-1} of DOC and POC in DPSF2, respectively.

3.4 Discussion

Results of the investigation indicate that the annual TOC yield increases with drainage severity. TOC yield is the product of two components; discharge and TOC concentration. Given the lack of seasonal variation in TOC concentration, discharge, which does have a seasonal pattern, is shown to be the principal determining variable of TOC yield. Verification is provided by the seasonal pattern in annual TOC yield (figure 3.9) and discharge rates (figure 3.3) which reflect one another very closely. Because discharge is used to calculate TOC yield, very strong correlations between the two variables are observed at all sites ($r^2>0.94$; figure 3.11a). Furthermore, since TOC concentration remains relatively constant (with no seasonal pattern), and there is a strong seasonal pattern in TOC yield (driven by discharge), there is no correlation between TOC concentration and TOC yield (figure 3.11b).

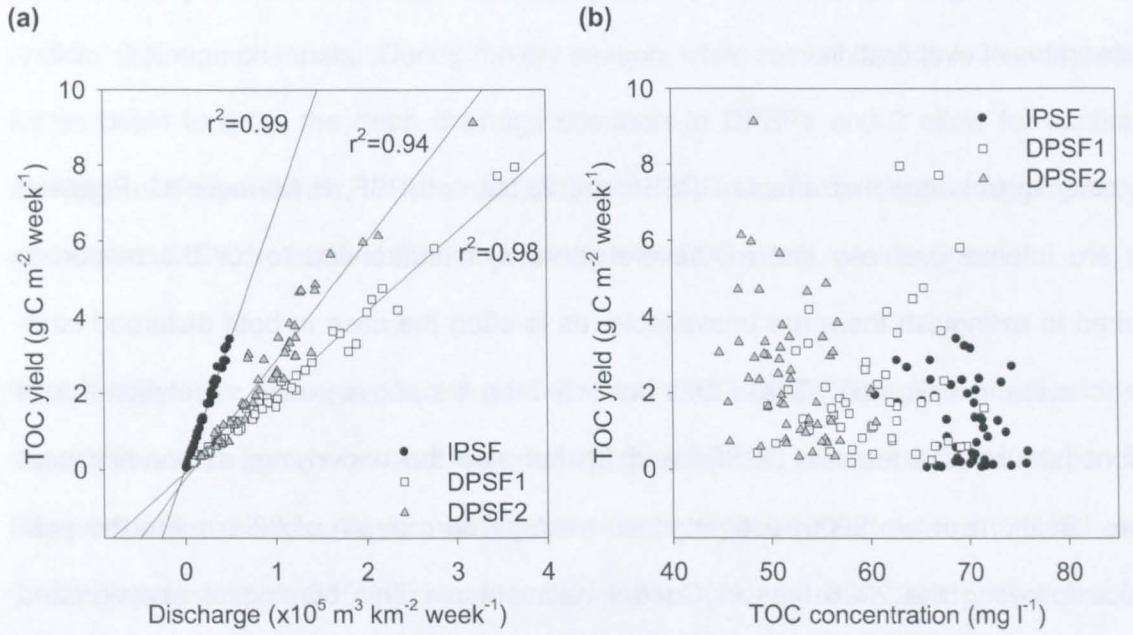


Figure 3.11: Relationship between **(a)** weekly discharge and TOC yields and **(b)** weekly TOC concentrations and TOC yields for all land-cover classes.

It follows then, that larger discharge rates in DPSF1 and 2 (1.8 and 2.7 x 10^6 m^3 km^{-2} yr^{-1}, respectively) than in IPSF (0.9 x 10^6 m^3 km^{-2} yr^{-1}) were the primary driver behind larger TOC yields from the disturbed land-cover classes. These higher discharge rates in disturbed land-cover classes were not counterbalanced by lower TOC concentrations, and occurred despite similar rainfall among the sites (table 3.1; figure 3.2). The most likely explanation for this is two-fold; a decline in rates of evapotranspiration and increased runoff in the disturbed land-cover classes. Both of these features are the direct consequences of large scale biomass loss, fires and artificial drainage in both the disturbed land-cover classes. Intact forest intercepts and returns large volumes of water back to the atmosphere via evapotranspiration. Evapotranspiration prevents a large portion of the rainfall from ever reaching the catchment outlet and contributing to the catchment discharge. Clearing peatland of its overlying vegetation, as has happened in DPSF1 and 2, vastly reduces rates of evapotranspiration. The lack of overlying vegetation also reduces the amount of rainfall interception, thus increasing the amount of water landing directly onto the peatland surface. Transversely, it could be argued that

clearing aboveground vegetation exposes the underlying peat to greater levels of solar radiation and higher temperatures, creating conditions from which one would expect greater rates of evaporation.

The other disturbance that affects DPSF1 and 2, but not IPSF, is fire events. Peatland fires are intense and can last for several months if unattended to, or the resources required to extinguish them are unavailable, as is often the case in both disturbed land-cover classes investigated. These fires not only burn the aboveground vegetation that is present (shrubs and ferns in DPSF1 and 2), but also the underlying, carbon-rich peat dome. Ballhorn *et al.* (2009) estimated an average burn depth of 33 cm into the peat surface following the 2006 fires in Central Kalimantan. This burning of aboveground vegetation and surface layer peat in both DPSF1 and 2 also influences discharge rates from the ecosystem. Fire destroys the binding of roots and reduces the water retention capacity of peat, which in its natural state is very high (Scott, 1989). Following a fire event, the peatland surface is left scorched and denuded. Due to the highly fibrous nature of tropical peat, large quantities of charcoal form on the peat surface during a fire event. Charcoal is hydrophobic in nature (Sander & Pignatello, 2005) and therefore repels water which has been reported to result in faster, increased runoff (Glasspool, 2000; Hoekman, 2009).

As well as increased runoff due to the fire effects mentioned above, drainage channels also present in DPSF1 and 2 artificially lower the water table and in doing so increase the efficiency of throughflow (during the dry season) and overland flow (during the wet season; Verwer *et al.*, 2008). This reduces the amount of standing water on the peat surface, unlike the situation in un-drained forests (IPSF), where large areas of surface water are common. The drainage channels in DPSF1 and 2 therefore increase the proportion of water that is returned to the catchment outlets that is then monitored and recorded as discharge.

It was also observed that the disturbed land-cover classes lost a greater proportion of their annual TOC yield than the intact site during the dry season. Again, this is due to the artificial drainage channels. During the dry season, when rainfall is at its lowest and water tables begin to drop, the deep drainage channels in DPSF1 and 2 allow for continued drainage of the peatlands. In contrast, during the dry season the shallow logging access channels in IPSF dry out and discharge, along with TOC yields, are negligible.

The relationship between discharge rate and TOC/DOC/POC concentration is an important one as these two variables combine to determine the overall fluvial carbon flux. Reports on the relationship vary widely from strongly positive correlations (Coynel *et al.*, 2005; Raymond *et al.*, 2007) to negative correlations (Aldrian *et al.*, 2008). The data from this investigation, as with other studies (Bilby & Likens, 1979) suggest that discharge is more closely correlated to POC flux than DOC flux (and TOC flux, as a result of DOC being by far the dominant component, as is the case in this study). Higher rates of discharge lead to greater physical erosion of the peat during runoff and channel flow which result in higher POC concentrations in channels draining the disturbed land-cover classes. Higher POC concentrations combined with higher discharge rates led to greater overall POC yields from both disturbed sites, DPSF1 and 2 (9.7 and 8.6 g C m^{-2} yr^{-1}, respectively) when compared with the intact site (1.2 g C m^{-2} yr^{-1}).

TOC concentration and composition varied between land-cover classes. Average DOC concentration was high across all sites, ranging from 48-68 mg l^{-1}. This is to be expected from water draining peatland catchments and supports the general assumption that soil carbon is a major source of DOC in drainage water (Hope *et al.*, 1997; Aitkenhead & McDowell, 2000; Alkhatib *et al.*, 2007). The DOC concentrations recorded exceed most other reported values from tropical peatland studies (Coynel *et al.*, 2005; Alkhatib *et al.*, 2007; Baum *et al.*, 2007; Aldrian *et al.*, 2008) and are up to an order of magnitude larger than some values reported from temperate peatland studies (Nilsson *et al.*, 2008; Billet *et al.*, 2010; Koehler *et al.*, 2011). DOC concentrations were consistently higher in IPSF

than in DPSF1 and 2. There are three possible explanations for this. Firstly, the intact land-cover class is a far denser store of carbon; it not only consists of a thick underlying peat dome, but also has a dense overlying PSF which provides the peat surface with a constant supply of fresh organic matter which decays over time into POC and DOC. Secondly, the water table is much higher in IPSF than it is in DPSF1 and 2. This creates anoxic conditions throughout the peat profile in IPSF which are known to constrain the activity of phenol oxidase, an enzyme which eliminates phenolic compounds in the presence of bimolecular oxygen (Freeman *et al.*, 2001). Anoxic conditions therefore lead to higher concentrations of phenolic compounds, substantially reducing the biodegradation of organic matter, resulting in high concentrations of DOC. Thirdly, the DPSF1 and 2 sites have both experienced fire events in recent history. Charcoal, which is generated on the peat surface during fire events exhibits many hydrophobic properties which make it well suited to the sorption of organic compounds (DeLuca & Aplet, 2008). Due to its large number of adsorption sites, charcoal has the capacity to adsorb a host of compounds, including organic carbon, which is why it is often compared to 'activated carbon' (Sander & Pignatello, 2005). This 'activated carbon' therefore has the potential to adsorb some of the DOC compounds in pore water which may result in decreased concentrations of DOC observed in both the disturbed sites.

POC concentrations generally contributed less than 10% of TOC concentrations, which is consistent with most peatland ecosystems where the vast majority of TOC is exported as DOC (Hope *et al.*, 1994). Reports on what effect deforestation has on POC concentrations invariably show that it increases them (Hobbie & Likens, 1973), which is consistent with the finding that both DPSF1 and 2 had higher POC concentrations than IPSF. Artificial drainage in DPSF1 and 2 lowers the water table which destabilises the peat structure and exposes a greater area of the peat to mechanical breakdown. Fire events, also affecting DPSF1 and 2 further destabilise the peat structure by breaking the larger fibrous components down into smaller particles of organic matter (Boehm & Siegert,

2001). The higher discharge rates observed in disturbed land-cover classes then facilitate in washing away this POC in drainage channels.

The findings of this investigation suggest that human-induced alteration and disturbance of intact PSF is responsible for the large increases in fluvial organic carbon yields that were observed from disturbed PSF. These large fluvial losses of carbon play an important role in altering the carbon balance of such ecosystems, yet because they are assumed to be small in comparison to gross primary productivity and ecosystem respiration, they are seldom measured. While measurements of net ecosystem exchange (NEE) for intact PSF are rare, a carbon accumulation rate of 94 g C m^{-2} yr^{-1} was estimated from a peat core within the IPSF site (Page *et al.*, 2004; figure 3.12). The NEE was estimated from

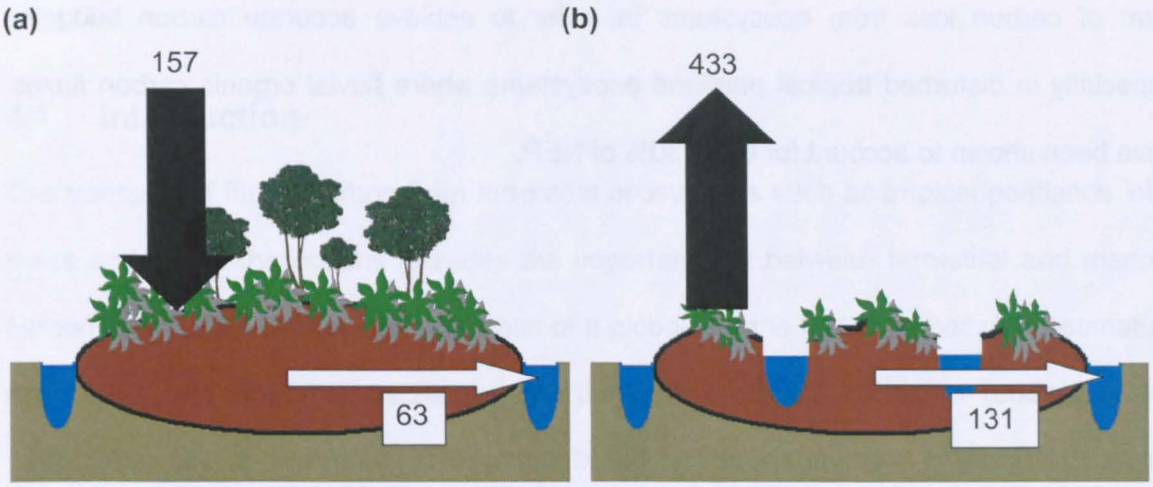


Figure 3.12: Schematic showing NEE (black arrows; g C m^{-2} yr^{-1}) and fluvial TOC loss (white arrows; g C m^{-2} yr^{-1}) estimates in **(a)** IPSF and **(b)** DPSF2 land-cover classes. Carbon gain of intact PSF estimated to be 94 g C m^{-2} yr^{-1} (-157 + 63 = -94). Carbon loss of disturbed DPSF2 estimated to be 564 g C m^{-2} yr^{-1} (433 + 131 = 564).

the average 500 year long-term apparent rate of carbon accumulation (LORCA). Including the IPSF fluvial carbon loss estimate of 63 g C m^{-2} yr^{-1} (from this study), suggests an approximation of a gaseous exchange based NEE of -157 g C m^{-2} yr^{-1} for IPSF (net carbon sink). Measured NEE within DPSF2 is +433 g C m^{-2} yr^{-1} (Hirano *et al.*, 2007) which results in an increased carbon loss of 564 g C m^{-2} yr^{-1} (net carbon source)

when including the fluvial carbon loss estimate from DPSF2 (131 g C m^{-2} yr^{-1}; from this study).

It follows then, that 30% more carbon is lost than previously assumed through gaseous exchange measurements alone. These calculations clearly illustrate the importance of including fluvial carbon losses if the impact of anthropogenic disturbance of tropical peatlands is to be fully realised and accounted for. Gielena *et al.* (2011) also demonstrate the importance of including losses of fluvial carbon from an ecosystem by calculating that the net ecosystem productivity (NEP) of a temperate Scots Pine forest in Belgium was overestimated by 11% as a result of not including the ecosystem's DOC yield (10 g C m^{-2} yr^{-1}). The DOC yield is clearly smaller in a Scots Pine forest compared to the tropical PSF sites monitored during this investigation and therefore changes the overall NEP to a lesser extent. However, it demonstrates the same principle of the importance of including this form of carbon loss from ecosystems in order to achieve accurate carbon budgets, especially in disturbed tropical peatland ecosystems where fluvial organic carbon fluxes have been shown to account for up to 30% of NEP.

Chapter Four

Fluvial organic carbon losses from the Sebangau River basin.

A version of this chapter is published in Biogeosciences: 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, doi:10.5194/bg-8-901-2011.

4.1 Introduction

The transport of fluvial carbon from terrestrial ecosystems such as tropical peatlands into rivers and out to the oceans provides the important link between terrestrial and marine carbon cycles (Meybeck, 1993). In terms of a global riverine flux of carbon, it is estimated that 1000 Tg of carbon is discharged into the world's oceans each year (Ludwig *et al.*, 1996). Globally, approximately 60% of this fluvial carbon is comprised of inorganic carbon and 40% organic carbon (Meybeck, 1993; Probst *et al.*, 1994). However, it is believed that fluvial carbon fluxes from peatland catchments are dominated by organic forms (Hope *et al.*, 1994). Two commonly accepted estimates put the annual figure of TOC discharged to oceans at somewhere between 330 and 370 Tg (Degens *et al.*, 1991; Meybeck, 1993). In most peatland ecosystems nearly 100% of TOC is exported in its dissolved form, DOC (Hope *et al.*, 1994). According to various modelling estimates, the global riverine DOC export to the oceans ranges from 170 (Harrison *et al.*, 2005) to 250 Tg C yr^{-1} (Ludwig *et al.*, 1996).

Despite tropical peatlands being one of the largest terrestrial carbon stores on earth, they have been shown to export more fluvial organic carbon per unit area than any other significant biogeographical land type in the world (Freeman *et al.*, 2001; Page *et al.*, 2002). Rivers that drain catchments composed almost entirely of peatlands are characterised by a low pH (highly acidic), low concentrations of suspended sediments (including POC) and sometimes undetectably low concentrations of dissolved inorganic nutrients (including DIC; Vegas-Vilarrubia & Rull, 1988). These rivers transport very high levels of DOC as humic substances which make them characteristically dark in colour and for this reason they are commonly called blackwater rivers. The South American Rio Negro and Caroni rivers are probably the most well known examples of blackwater rivers. They are large tributaries to two of the largest rivers in the world, the Amazon and Orinoco, and are extraordinary blackwater rivers in respect of their size. Most river basins that are composed entirely of peatlands are small in size, making most blackwater rivers small in size as well. Based on their size, blackwater rivers have consequently been considered quantitatively insignificant for carbon input into the ocean. It is however conceivable that blackwater rivers are more important for carbon cycling than previously thought and with regard to this, the existing knowledge on the biogeochemistry of these river types is inexplicably small.

Indonesia does not contain any of the major world rivers. Instead, its peatlands are drained by numerous small lowland rivers which contribute ~11% (135,000 $m^3 s^{-1}$) to the global freshwater export (Syvitski *et al.*, 2005). This is less than, but comparable with the Amazon River which, singlehandedly, accounts for ~15% of the global freshwater export (183,000 $m^3 s^{-1}$; Richey *et al.*, 1991). Indonesian rivers are, however, thought to account for significant export of DOC into the ocean. This is primarily due to high precipitation rates and large surface areas that are covered in peatlands (206,950 km^2; Page *et al.*, 2011), which are known to be an important source of riverine DOC (Hope *et al.*, 1997; Aitkenhead & McDowell, 2000). In a recent study, Baum *et al.* (2007) used data collected

from the River Siak, a blackwater river in Sumatra (Indonesia) to estimate a mean DOC flux of 0.32 Tg yr^{-1} for the Siak catchment alone. This estimate was then extrapolated to the entire land area of Indonesia (~1.9 × 10^6 km^2), taking into account the percentage peat area cover, and the annual fluvial DOC discharge was estimated to be 21 Tg yr^{-1}. According to the extrapolated estimate of Baum *et al.* (2007) and current global modelling estimates (170 to 250 Tg carbon yr^{-1}), Indonesian rivers account for approximately 10% of the global riverine DOC discharge into the ocean. The only other Indonesian blackwater river to be quantified with respect to organic carbon export to the ocean is the Dumai River estuary, also in Sumatra. This river is estimated to export 0.03 Tg DOC yr^{-1}, but no regional or national extrapolations were made, most likely due to its very small catchment size.

The reliability of the extrapolated estimate of 21 Tg yr^{-1} by Baum *et al.* (2007) is reduced by the limited availability of fluvial carbon data for other rivers in the region. This investigation aims to remedy this deficiency by providing the first quantitative fluvial organic carbon data set from a blackwater river in Central Kalimantan, the River Sebangau. This study aims to quantify the export of fluvial organic carbon in this river from the source (150 km inland) to the mouth, where it discharges into the Java Sea.

4.2 Methods

4.2.1 Study sites

The Sebangau River catchment lies in the southern part of Central Kalimantan, Indonesia. Central Kalimantan lies within the inter-tropical convergence zone (ITCZ) and experiences a tropical-monsoonal climate. The temperature remains relatively constant throughout the year (25-27°C) and annual rainfall averages 2700 mm yr^{-1} (Page *et al.*, 2004). Twenty two years of rainfall records from Central Kalimantan indicate that annually there is approximately 9 months of wet season (October to June) and 3 months of dry season

(July to September; dry months defined as periods of moisture deficit, i.e. when evapotranspiration exceeds rainfall; Hooijer *et al.*, 2008; figure 4.1).

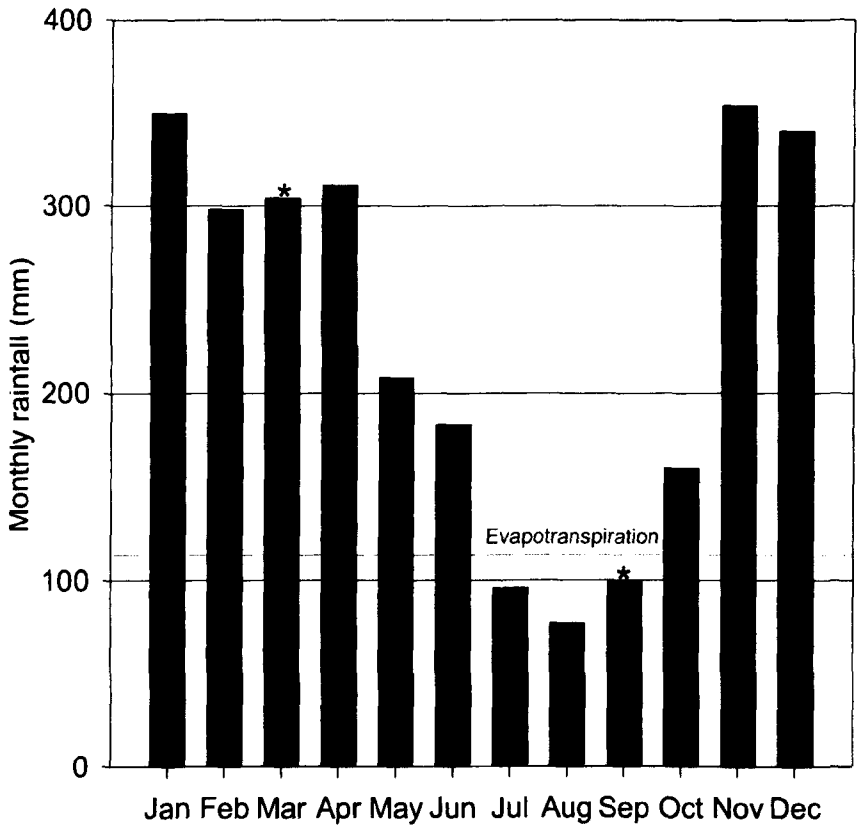


Figure 4.1: Average monthly rainfall over 22 year record (1984-2006) in Central Kalimantan. Dashed line represents the average evapotranspiration over the same time period. All data collected from Palangka Raya Meteorological Office (Hooijer *et al.*, 2008). * Denotes timing of the two sampling campaigns.

The Sebangau River basin lies between the River Katingan to the west and the River Kahayan to the east and has a total land area of approximately 5200 km^2 (figure 4.2). Kya, the source of the River Sebangau lies approximately 20 km west of Palangka Raya, the provincial capital of Central Kalimantan. Almost the entire catchment is composed of peatland resulting in a high concentration of humic substances in the water, giving the River Sebangau water it's characteristically dark orange-black colour and a background pH of 3.5 to 4.0 (Haraguchi, 2007; Haraguchi *et al.*, 2007; Tachibana *et al.*, 2007).

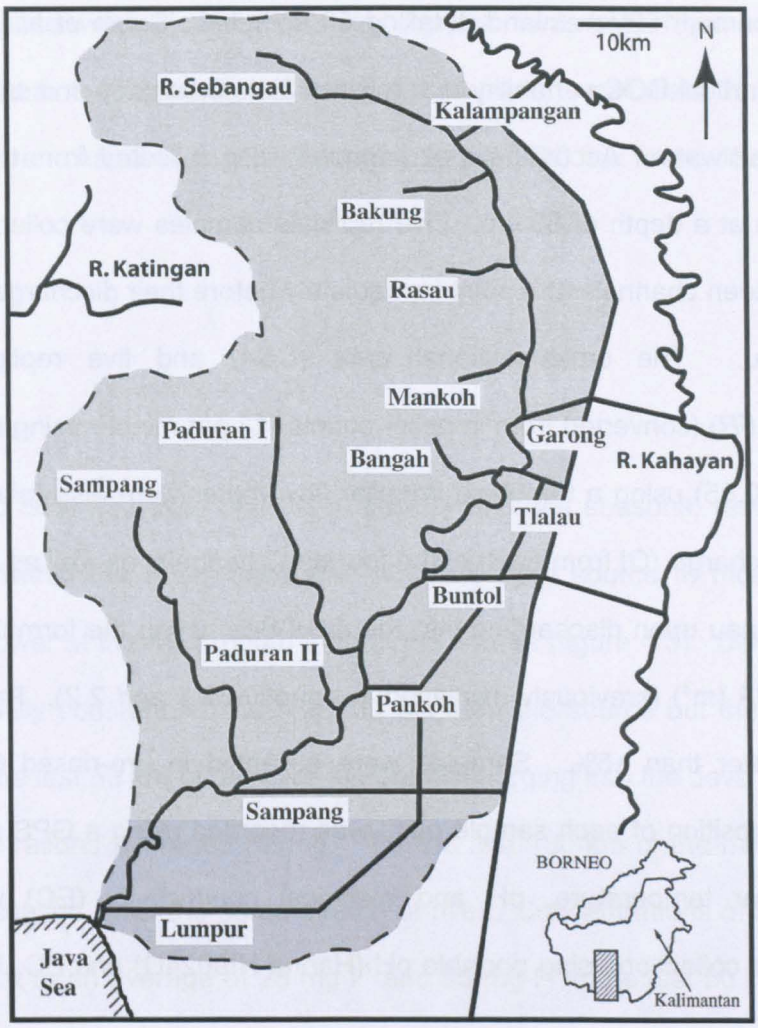


Figure 4.2: Map of the Sebangau River basin in Central Kalimantan, Borneo (inset). The Sebangau watershed is shaded grey and outlined by the dashed line to the west and the south and the straight solid line (north-south canal) to the east. Fourteen named channels drain the Sebangau catchment into the River Sebangau (centre) which runs from north to south draining into the Java Sea. To the west of the Sebangau River lies Sebangau National Park and to the east is 'Block C' of the MRP.

The maximum tidal range at the mouth of the River Sebangau is ~3 m (United Kingdom Hydrographic Office, 2008). Due to the low-lying nature of the Sebangau catchment, this mesotidal range has the potential to affect the river system over large distances inland.

4.2.2 Sample collection

Sampling was carried out on two separate occasions; the dry season in September 2008 (high tide) and the subsequent wet season in March 2009 (low-tide). River water samples were collected from the main channel of the River Sebangau at 3 km intervals from the

mouth to the source, 150 km inland, totalling 50 samples. Baum *et al.* (2007) reported horizontal and vertical DOC variability in the River Siak to be ±5% and ±3% respectively, due to well mixed water. Accordingly, all samples were collected from the centre of the River Sebangau at a depth of 50 cm. Five replicate samples were collected from within each of the fourteen channels at a point immediately before their discharge points into the River Sebangau. The cross-sectional area *(CSA)* and five replicate flow rate measurements (*FR*) (converted from impeller counts (*C*) per minute using the formula: $FR = 0.000854C + 0.05$) using a handheld impeller flow meter were also taken and used to calculate the discharge *(Q)* from each of the fourteen channels, as well as at the mouth of the River Sebangau upon discharging into the Java Sea, using the formula: Q (m^3 s^{-1}) = FR (m s^{-1}) × CSA (m^2) (previously displayed in equation 2.1 and 2.2). Precision for this method was better than ±5%. Samples were collected in pre-rinsed 60ml Nalgene® bottles and the position of each sample point was recorded using a GPS (Garmin, eTrex Venture). Water temperature, pH and electrical conductivity (EC) were recorded immediately after collection using portable pH (Hanna HI9024D) and EC (Hanna HI8633) meters.

4.2.3 Sample preparation and analysis

To derive POC concentration, a known volume of river water was filtered through a 0.45µm cellulose acetate membrane filter (Whatman), that had been pre-rinsed with excess sample, under partial vacuum (hand-held vacuum pump, Mityvac, Nalgene). The filter was retained and oven dried (24 h at 40°C) to quantify particulate matter which is thought to be equal to POM (given the dominance of peat soil in the catchment). POM was then converted to a POC value by assuming organic matter to be 50% carbon (Hope *et al.*, 1994). Samples of filtrate were acidified to pH 2.0 using a solution of dilute sulphuric acid (20%). The samples were then stored at 2 to 5°C and analysed for DOC after the samples were returned to the Open University. DOC was measured by high-temperature catalytic oxidation (680°C) using a Total Organic Carboniser (Shimadzu,

TOC-V_{CPN}) complete with a platinum catalyst. Precision was better than ±1%. DOC/POC concentrations were then combined with discharge rates to calculate the TOC flux from each of the fourteen channels and the River Sebangau TOC flux to the Java Sea.

4.3 Results

4.3.1 DOC

DOC comprised 88% and 94% of TOC in the dry and wet seasons, respectively. DOC concentrations within the River Sebangau fluctuate from source to mouth and in both seasons were lower at the river mouth than at the source (figure 4.3). DOC concentration remained relatively constant for the first 100 km from the source but then decreased as water entered the last 50 km of the river, before discharging into the Java Sea. In the wet season, concentrations averaged 52 mg l^{-1} for the first 100 km of the river and 44 mg l^{-1} during the dry season, over the same stretch of river. Concentrations of DOC decreased beyond this point to an average of 28 mg l^{-1} and 35 mg l^{-1} in the last 50 km of the river in the dry and wet seasons, respectively.

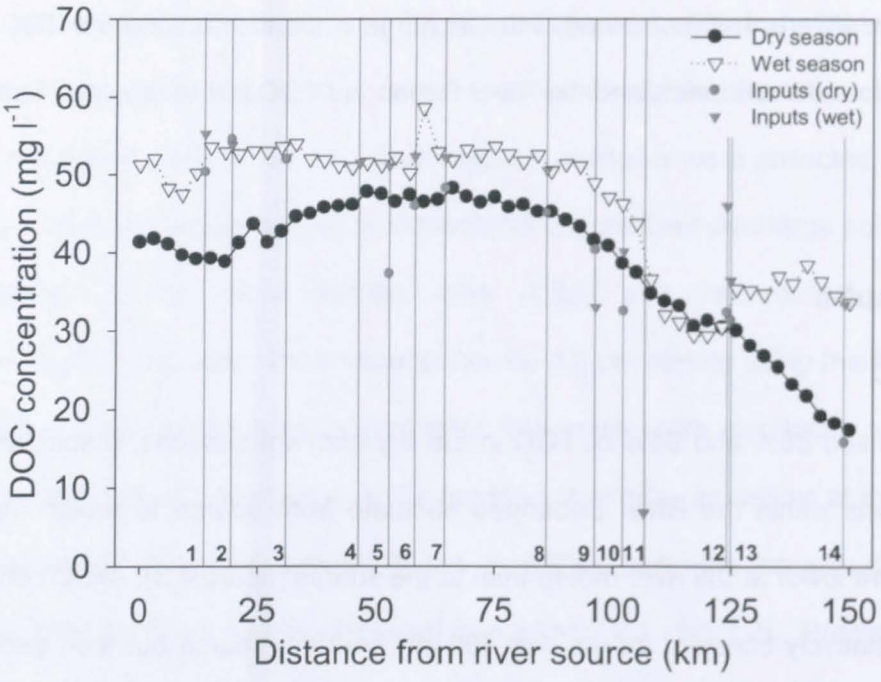


Figure 4.3: DOC concentration along the course of the River Sebangau during the dry and wet seasons. Vertical lines represent the confluences of fourteen channels that discharge into the River Sebangau. Each confluence has an identification number above the x-axis (see table 4.1). Single point data represent DOC concentrations in each channel prior to discharge into the River Sebangau.

Differences between the two sampling runs are partly attributable to differences in tidal conditions. The dry season sampling was undertaken at high tide, and some influence of sea-water (defined as electrical conductivity (EC) greater than 200 µS cm^{-1}) was observed in samples collected below 126 km from the source. Dry season samples above and below this point were therefore analysed separately. In the wet season, sampling was undertaken at low tide, and all samples had an EC value of less than 110 µS cm^{-1}, implying that all samples contained freshwater. All wet season samples were therefore analysed together. Figures 4.4a and 4.4c show that from 0 to 126 km from the source, the river follows a similar transition in both seasons; from stable (high DOC, low EC) peat-derived water (0 to 90 km), through to a more peat/mineral-derived mix of water with a higher EC and lower DOC concentration further downstream. In the dry season, below 126 km from the source, the river water becomes progressively mixed with seawater, which raises the EC and lowers the DOC concentrations. The EC vs. DOC relationship at

Table 4.1: Mean discharge, DOC, POC and TOC concentrations (± s.e.m) and fluxes (s.e.m <1%) from the confluences of 14 channels that discharge into the River Sebangau, during the dry and the wet season in 2008/09. The row titled River Sebangau represents concentrations and fluxes from the River Sebangau to the Java Sea. Total mean includes the 14 channels, but not the River Sebangau data.

Number on graph	Channel	Distance from river source (km)	Discharge ($m^3 s^{-1}$)		DOC concentration ($mg l^{-1}$)		DOC flux ($x10^3 kg day^{-1}$)		POC Concentration ($mg l^{-1}$)		POC flux ($x10^3 kg day^{-1}$)		TOC Concentration ($mg l^{-1}$)		TOC flux ($x10^3 kg day^{-1}$)	
			Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
1	Kalampangan	13.8	0.2	1.1	50.3 ± 0.3	55.3 ± 0.2	0.1	5.3	4.0 ± 0.2	1.8 ± 0.1	0.1	0.2	54.4 ± 0.5	57.1 ± 0.3	1.0	5.4
2	Bakung	19.5	2.7	5.5	54.5 ± 0.2	53.8 ± 0.3	12.6	25.6	4.9 ± 0.1	0.7 ± 0.1	1.1	0.3	59.4 ± 0.3	54.5 ± 0.3	13.8	25.9
3	Rasau	31.0	4.4	9.0	52.0 ± 0.1	52.3 ± 0.2	19.8	40.8	7.6 ± 0.2	4.2 ± 0.4	2.9	3.3	59.6 ± 0.3	56.4 ± 0.6	22.7	44.1
4	Mangkoh	46.5	dna	7.9	dna	51.5 ± 0.2	dna	35.2	dna	2.5 ± 0.5	dna	1.7	dna	54.0 ± 0.7	dna	36.9
5	Garong	52.8	0.7	5.4	37.3 ± 0.3	51.2 ± 0.1	2.4	23.9	4.7 ± 0.3	0.7 ± 0.1	0.3	0.3	41.9 ± 0.6	51.9 ± 0.2	2.7	24.2
6	Tlalau	58.1	0.2	3.7	46.0 ± 0.3	52.3 ± 0.4	0.8	16.9	3.7 ± 0.2	4.3 ± 0.2	0.1	1.4	49.6 ± 0.5	56.6 ± 0.6	0.8	18.3
7	Bangah	64.6	6.3	16.1	48.2 ± 0.3	52.1 ± 0.1	26.3	72.5	3.3 ± 0.4	4.5 ± 0.3	1.8	6.3	51.4 ± 0.7	56.7 ± 0.4	28.0	78.8
8	Buntol	86.0	2.9	11.3	45.0 ± 0.5	50.6 ± 0.2	11.1	49.5	2.4 ± 0.2	2.9 ± 0.2	0.6	2.8	47.4 ± 0.7	53.4 ± 0.4	11.7	52.4
9	Paduran I	96.3	59.4	235.0	40.4 ± 0.8	33.0 ± 0.3	207.2	669.9	6.7 ± 0.2	1.2 ± 0.1	34.2	23.7	47.0 ± 1.0	34.2 ± 0.4	241.4	693.6
10	Pankoh	102.2	8.8	10.6	32.5 ± 0.4	40.1 ± 0.4	24.8	36.8	7.1 ± 0.2	4.3 ± 0.1	5.4	3.9	39.6 ± 0.6	44.4 ± 0.5	30.2	40.7
11	Paduran II	106.5	dna	40.7	dna	6.8 ± 0.1	dna	24.0	dna	3.0 ± 0.2	dna	10.4	dna	9.8 ± 0.3	dna	34.4
12	Sampang	124.0	52.8	59.1	32.3 ± 0.3	45.9 ± 0.3	147.5	234.4	5.7 ± 0.2	0.1 ± 0.1	26.0	0.7	38.0 ± 0.5	46.0 ± 0.4	173.5	235.1
13	Sampang	124.8	25.0	29.8	31.3 ± 0.2	36.4 ± 0.4	67.6	93.6	6.6 ± 0.1	4.5 ± 0.2	14.3	11.5	37.9 ± 0.3	40.8 ± 0.6	81.9	105.1
14	Lumpur	148.9	43.6	38.6	15.8 ± 0.1	33.4 ± 0.1	59.4	111.4	4.1 ± 0.3	1.0 ± 0.3	15.4	3.4	19.9 ± 0.4	34.4 ± 0.4	74.8	114.8
	River Sebangau	150.0	445.8	460.8	17.3 ± 0.4	33.6 ± 0.1	667.9	1337.2	3.8 ± 0.8	1.5 ± 0.1	146.4	61.1	21.1 ± 1.2	35.1 ± 0.2	814.3	1398.3
	Total Mean		17.3	33.9	40.5	43.9	48.4	102.8	5.1	2.5	8.5	5.0	45.5	46.4	56.9	107.8

126-150 km from source (figure 4.4b) is not linear, and therefore cannot be explained by conservative mixing (see Chapter 4.5.1).

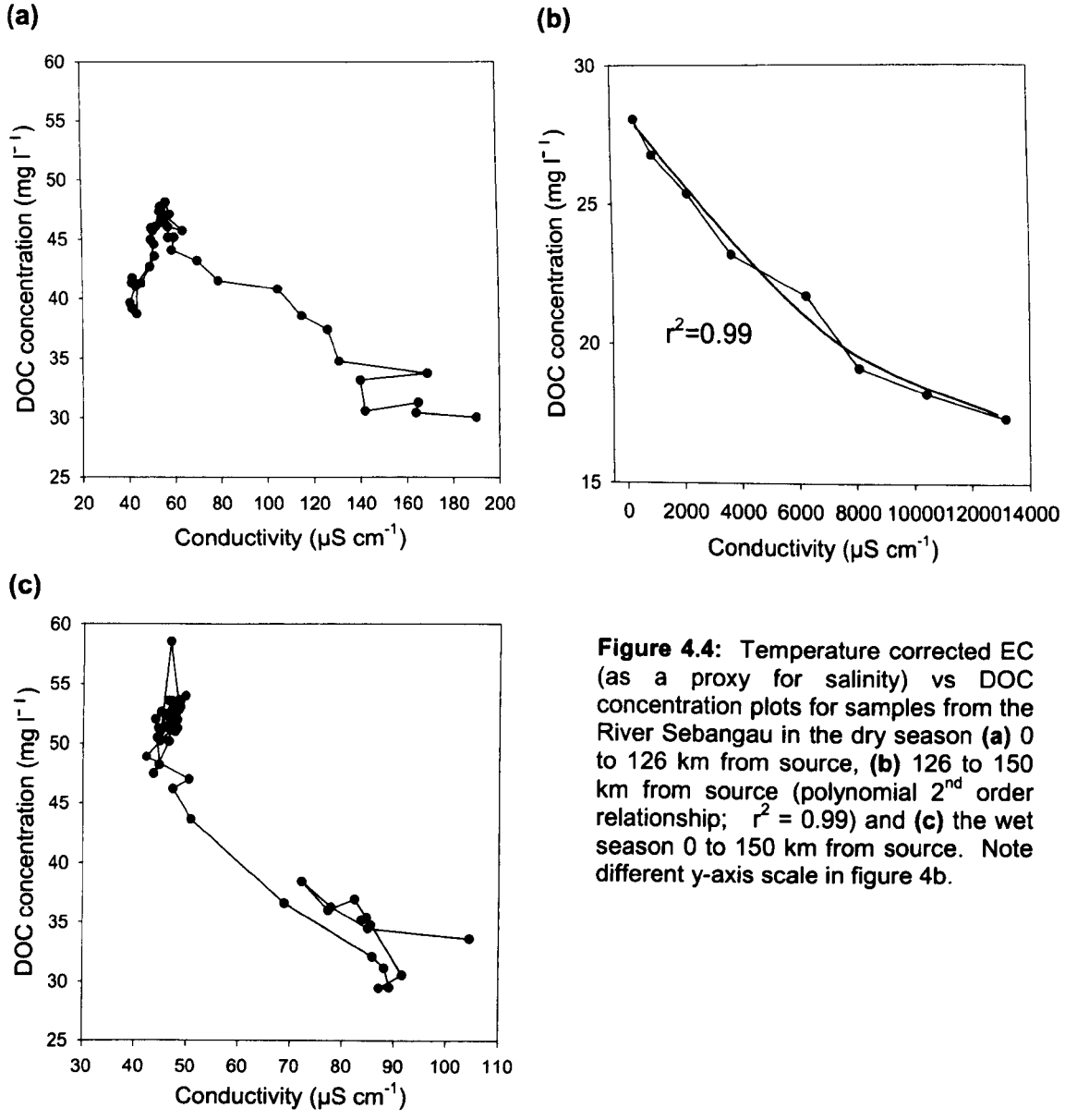


Figure 4.4: Temperature corrected EC (as a proxy for salinity) vs DOC concentration plots for samples from the River Sebangau in the dry season **(a)** 0 to 126 km from source, **(b)** 126 to 150 km from source (polynomial 2nd order relationship; r^2 = 0.99) and **(c)** the wet season 0 to 150 km from source. Note different y-axis scale in figure 4b.

4.3.2 POC

POC comprised 12% and 6% of TOC in the dry and wet seasons, respectively. Figure 4.5 shows that despite varying concentrations and high spatial variability, POC followed a similar trend in both the dry and wet seasons, namely a decrease in concentration from source to mouth. The increase (wet season) and decrease (dry season) in POC

concentration between 50 to 100 km from the source is perhaps attributable to the input of larger and smaller POC fluxes from channels 6 and 7 in the wet and dry seasons, respectively (table 4.1); channel 6 (Tlalau) discharged 100 kg day^{-1} in the dry season compared to 1,400 kg day^{-1} in the wet season. Similarly, channel 7 (Bangah) discharged 1,800 kg day^{-1} compared to 6,300 kg day^{-1} in the dry and wet seasons, respectively. Across both seasons, average POC concentrations 0 to 25 km from the source were ~4 times higher than average POC concentrations 125 to 150 km from the source. This difference is more pronounced in the wet season when the average POC concentration is ~7 times greater 0 to 25 km from the source (4.8 mg l^{-1}) than at 125 to 150 km from the source (0.7 mg l^{-1}).

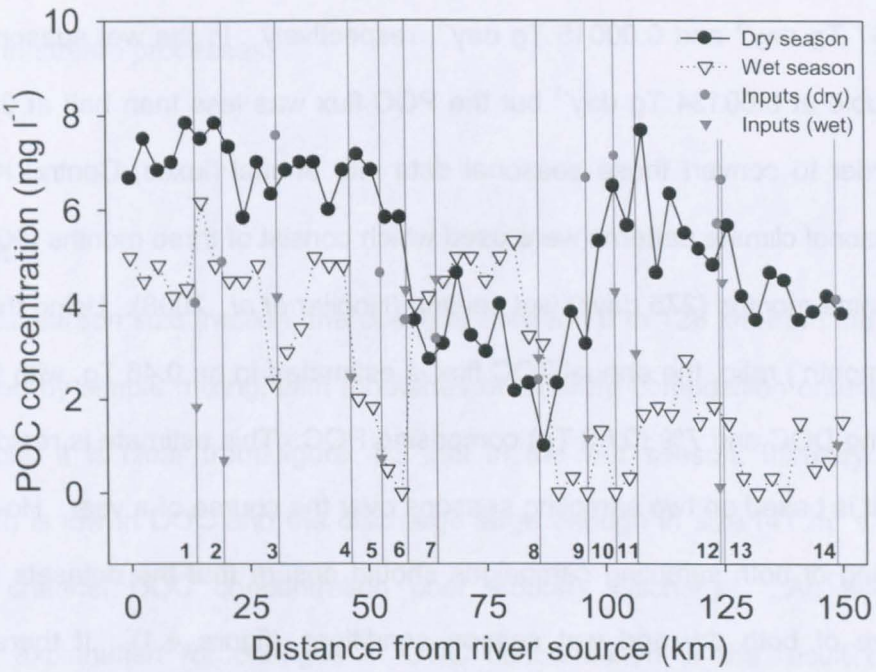


Figure 4.5: POC concentration along the course of the River Sebangau during the dry and wet seasons. Vertical lines represent the confluences of fourteen channels that discharge into the River Sebangau. Each confluence has an identification number above the x-axis (see table 4.1). Single point data represent POC concentrations in each channel prior to discharge into the River Sebangau.

4.3.3 Dry Season vs. Wet Season

Average water discharge from the fourteen channels in the wet season (34 m^3 s^{-1}) was double that observed in the dry season (17 m^3 s^{-1}), with the biggest interseasonal differences occurring in the upper reaches of the river, in channels 1 to 7.

Over the course of the entire river, mean DOC concentration in the wet season (46 mg l^{-1}) was slightly higher than in the dry season (39 mg l^{-1}). Conversely, average POC concentrations were higher in the dry season (5.2 mg l^{-1}) when compared to the wet season (2.7 mg l^{-1}). The fourteen channels display the same trend; DOC concentration being higher in the wet season (44 mg l^{-1}) than in the dry season (41 mg l^{-1}) and POC concentrations higher in the dry season (5 mg l^{-1}) compared to the wet season (3 mg l^{-1}).

4.3.4 TOC export to the Java Sea

In the dry season, the DOC and POC fluxes from the River Sebangau to the Java Sea were 0.00067 Tg day^{-1} and 0.00015 Tg day^{-1}, respectively. In the wet season the DOC flux was double at 0.00134 Tg day^{-1} but the POC flux was less than half at 0.00006 Tg day^{-1}. In order to convert these seasonal data into annual fluxes, Central Kalimantan average seasonal climate patterns were used which consist of three months (90 days) dry season and nine months (275 days) wet season (Hooijer *et al.*, 2008). Using the 3:9 ('dry month: wet month') ratio, the annual TOC flux is estimated to be 0.46 Tg, with 93% (0.43 Tg) comprising DOC and 7% (0.03 Tg) comprising POC. This estimate is restricted in its reliability as it is based on two sampling seasons over the course of a year. However, the strategic timing of both sampling campaigns should ensure that the datasets are highly representative of both dry and wet season conditions (figure 4.1). If there are any inorganic particulates present, the POC fraction may be a slight overestimate (see POC methods, Chapter 4.2.3), however as this accounts for only 7% of the TOC, it would not greatly alter the overall flux.

Baum *et al.* (2007) estimate the River Siak's DOC flux into the ocean to be 0.3 Tg yr^{-1}. This figure places the River Siak at number 17 on the ranking list of DOC exports of major global rivers (Ludwig *et al.*, 1996). Baum *et al.* (2007) did not determine POC flux and therefore the TOC flux cannot be estimated. Baum *et al.* (2007) also used dry and wet

season data with an even balance between the two to work out mean monthly DOC fluxes due to slightly different climate patterns in Sumatra (the meridional migration of the ITCZ). In Sumatra there is generally 6 months of dry season and 6 months of wet season (6:6 'dry month: wet month' ratio as opposed to 3:9 in Kalimantan). Using the respective climate ratios, the data imply that the River Sebangau discharges approximately 50% more DOC to the ocean per year than the River Siak.

4.4 Discussion

In this river basin scale study of fluvial organic carbon dynamics along the course of the River Sebangau, the observed trends can be explained through a combination of tributary inputs and in-stream processes.

4.4.1 DOC

In this fluvial carbon size fraction, the changes between 0 to 126 km from the source can be explained by simple mixing, with tributaries of different composition entering the river. For example, it is clear from figure 4.3 that in the wet season, tributary number 11 (Paduran II) is low in DOC and the discharge large enough in size (41 $m^3 s^{-1}$) to reduce the main channel DOC concentration post tributary discharge. An alternative, or additional, explanation for changes in DOC concentration is the result of in-stream processes such as microbial respiration and oxidation which results in DOC removal and appears to be a significant biotic mechanism in blackwater rivers (Meyer, 1986). Several studies have shown that in-stream production of DOC (for example from POC degradation) is small in comparison to that which is derived from terrestrial sources (Worrall *et al.*, 2007).

The non-linear relationship observed (polynomial 2nd order; r^2=0.99) within a stretch of the river without major tributary inputs, suggests that some form of DOC removal is also

taking place (figure 4.4b). Percent estuarine DOC removal at high tide (dry season) was estimated by extrapolating linear regressions between DOC and EC for samples collected at the lower end of the estuary, following the method of Spencer *et al.* (2007). This method permits an estimate of the DOC concentration of a freshwater end-member, assuming conservative mixing, with the difference between this estimate and the observed DOC concentration of the last freshwater sample (EC less than 200 µS) providing an indication of the amount of DOC removal that has occurred within the estuary. Linear regression lines were derived using the last three samples at the seaward end of the estuary (150 to 144 km) and for the last four samples (150 to 141 km). These data suggested a removal of DOC in the Sebangau estuary of 27% and 12% respectively. It therefore appears that significant DOC processing is occurring in the estuary, reducing the flux into the ocean. It can be implied, therefore, that the carbon flux measured from the river mouth, at least during the dry season high tide sampling, is a smaller estimate when compared to the actual carbon loss from the peatland itself.

In the dry season, below 126 km from the source, the most likely DOC removal mechanism is via flocculation to become POC, or adsorption to existing POC or mineral particles, resulting from decreased DOC solubility with increasing salinity (Battin *et al.*, 2008). Studies of DOC transport through estuaries in temperate regions have shown varied evidence of conservative and non-conservative mixing in different systems (Spencer *et al.*, 2007). In the tropical Siak estuary, Baum *et al.* (2007) reported a negative linear relationship (r^2=0.97) between salinity and DOC concentration, suggesting conservative mixing during the period of observation.

4.4.2 POC

The movement of POC through river systems is very different to that of DOC. POC is subject to gravitational settling, hydrodynamic lift and drag forces which result in transport occurring as a series of discrete movements (Battin *et al.*, 2008). This accounts for the

larger in-stream variability and fluctuation of POC concentration down the river. The most likely cause for the overall decrease in POC concentration from source to mouth is gravitational settling onto the benthic layer of the river bed. River flow rates determine the proportion of the POC that is carried as suspended sediment within the water column and how much settles onto the river bed (Wainwright *et al.*, 1992). When flow rates drop below a threshold value (variable depending on the river system), particulates accumulate on the river bed, while at flow rates above the critical value particulates are re-suspended and transported downstream (Wainwright *et al.*, 1992). The source of the River Sebangau is 150 km inland, yet only 12 m above sea level. Averaged over the entire course of the river, there is, therefore, only a 1 m change in elevation for every 12.5 km of river length. Such a low gradient leads to low water velocities throughout the river. The water velocity at the source of the River Sebangau is higher than at the mouth in both seasons, varying from 0.49 m s^{-1} to 0.57 m s^{-1} at the source and dropping to 0.12 m s^{-1} and 0.15 m s^{-1} at the river mouth during the dry and wet seasons respectively. It is likely, therefore, that higher flow rates in the upper reaches of the river suspend more particulates which result in higher POC concentrations being recorded. Similarly, lower flow rates towards the mouth of the river result in more benthic accumulation of POC and less POC in the water column. It may therefore be the case that there is no regular overall loss of POC from the river system, but instead a relocation of the suspended POC in the more turbulent upper reaches of the river to the river bed through deposition due to slower flowing water in the lower reaches of the river. If this is the case, then it is likely that there is episodic re-suspension of organic sediment during high flows which transport a pulse of POC into the ocean. This repositioning is possible, given the extensive interchange that occurs between the suspended and deposited POC fractions along the course of a river (Minshall *et al.*, 1983).

Another explanation for decreasing POC concentrations along the course of the River Sebangau is that there is a loss in total POC as a result of in-stream biological processes. Whilst very little research on invertebrate communities in PSF ecosystems has been

conducted (Wells & Yule, 2008) and in particular, no biotic assessment of the River Sebangau has ever been carried out, it is known that blackwater rivers in Kalimantan contain a large number of fungal and bacterial communities, the former best suited to degrading particulates and the latter to consuming smaller molecules released during fungal metabolism (MacKinnon, 1996; Dudgeon, 2000). It is therefore possible that some form of biological POC degradation occurs, as is reported from temperate streams (Monaghan *et al.*, 2001).

Finally, the large within-river variability seen across both seasons may be attributed to the influence of the fourteen channels that discharge into the River Sebangau. The positioning of these discharge points is represented in figure 4.3 and 4.5 by vertical lines, and the 'inputs' denote the POC concentration of the channel prior to discharge into the River Sebangau. For example, in the dry season, River Paduran I (channel 9) discharges water with a high POC concentration (6.7 mg l^{-1}) relative to the River Sebangau. The effect of this POC input to the River Sebangau is seen in the next sample point immediately downstream. The influence of these inputs on the River Sebangau is also dependent upon the actual discharge rate (see table 4.1). For example, in the wet season, a high POC concentration (relative to the River Sebangau) of 4.3 mg l^{-1} from the Pankoh channel (channel 10) has no influence on POC concentrations in the River Sebangau. This is because the discharge rate of this channel is so low that the overall POC flux (table 4.1) is too small to have any effect on the concentration of the sample taken immediately downstream in the River Sebangau.

4.4.3 Dry season vs. Wet season

Most tropical regions only have two seasons; a wet season and a dry season, with the temperature staying relatively constant throughout the two seasons. This monsoonal climate is highly favourable for plant growth and results in large quantities of organic material being washed into rivers year round. As a result, it was speculated in this study

that DOC concentrations should be relatively constant throughout the year, without evidence of the summer/autumnal peak that is commonly reported in temperate regions owing to maximum ecosystem productivity or autumn leaf fall (Wetzel & Manny, 1977; Naiman & Sibert, 1978; Skiba & Cresser, 1991). To some extent this is reflected in the similar DOC concentrations between seasons. However, the effect that an increased flow rate (primarily due to increased rainfall) has on DOC concentration is still unclear and can differ according to ecosystem type. In peatlands, which are typically permanently waterlogged, throughflow at both high and low water levels is through an organic layer which has been shown to result in a negative relationship between stream flow and DOC concentration due to the 'dilution effect' (Schiff *et al.*, 1998; Clark *et al.*, 2007). The relationship in this study shows the opposite which may be attributed to the 'flushing effect' whereby water with a high DOC concentration (due to a long residence time in the soil/peat layer throughout the dry season) is washed into the rivers by the rising water level during the onset of the wet season (Pearce *et al.*, 1986; Hornberger *et al.*, 1994). A strong positive correlation between DOC concentration and discharge was also reported from the Congo basin which comprises evergreen forest, savannah and swamp forest (Coynel *et al.*, 2005). The 'flushing' process is enhanced when the previously dry or stagnant upper limits of the river bed/bank are inundated with large amounts of water as discharge rates increase (Casey & Farr, 1982). The effect seasonality has on POC concentrations is also uncertain. However it is clear that lower water tables during the dry season result in a larger area of peat drying out compared to during the wet season. It is this drying of the peat and the resulting increased rate of aerobic decomposition that destabilises the peat dome structure leading to denudation and increased amounts of POC being released during the dry season.

4.5 Conclusion

In summary, the data suggest that given its relatively small catchment size, the River Sebangau is a significant contributor of organic carbon to the ocean. DOC concentrations

in the River Sebangau are amongst the highest ever recorded, exceeding most of those reported for other tropical rivers as well as all of the 'major world rivers' mentioned by Ludwig *et al.* (1996). The Dumai River estuary in Sumatra, is the only other study to report such high concentrations of DOC (greater than 60 mg l^{-1}) which compare to those found in the River Sebangau (Alkhatib *et al.*, 2007). However, due to its small size (discharge at river mouth of 16 m^3 s^{-1} as opposed to 450 m^3 s^{-1} from the River Sebangau), its estimated annual export of DOC (0.03 Tg) is approximately 15 times smaller than that from the River Sebangau.

High DOC concentrations within the River Sebangau can be attributed to the large expanse of peatlands within the Sebangau catchment. High DOC concentrations may also be explained by the anoxic conditions in waterlogged peatlands, which are known to constrain the activity of phenol oxidase, an enzyme which eliminates phenolic compounds in the presence of bimolecular oxygen (Freeman *et al.*, 2001). Anoxic conditions therefore lead to higher concentrations of phenolic compounds, substantially reducing the biodegradation of organic matter which results in high concentrations of DOC. Soil carbon is also thought to be the main source of riverine POC (Hedges *et al.*, 1986). POC concentrations are generally only a tenth of the DOC concentrations in the River Sebangau, largely because of the low topography in the Sebangau River basin which results in a slower runoff and a likely depositional environment throughout the river's course. Differences in DOC and POC concentrations do occur between the dry and wet season, but the most pronounced interseasonal differences are between DOC and POC fluxes because these incorporate discharge which is strongly correlated with rainfall. TOC flux from the river to the ocean was nearly twice as large during the wet season, despite there being considerably higher POC concentrations in the dry season.

The TOC flux from the River Sebangau to the Java Sea is estimated to be 0.46 Tg yr^{-1}, comprised of 93% (0.43 Tg) DOC and 7% (0.03 Tg) POC. This equates to a fluvial TOC yield over the whole catchment (5,200 km^2) of 88 g C m^{-2} yr^{-1}, a value which far exceeds

those reported for northern peatlands (10-30 g C m^{-2} yr^{-1}; Nilsson *et al.*, 2008; Koehler *et al.*, 2009; Billet *et al.*, 2010). The entire land area of Indonesia is ~1.9 x 10^6 km^2 of which over 10% (206,950 km^2) is covered by peat soils (Page *et al.*, 2011). On extrapolating the Sebangau catchment TOC flux to the total peat covered area of Indonesia a TOC loss of 18.2 Tg yr^{-1} is estimated. Extrapolation from one river basin to the entire peat covered land area of Indonesia has its limitations, which are duly noted. These limitations, however, are somewhat reduced by the similarities between other river basins that have been studied in Indonesia (Alkhatib *et al.*, 2007; Baum *et al.*, 2007); most are made up of similar land use types (intact/disturbed PSF and agriculture) and the biogeochemistry of the rivers that drain the peatlands are highly comparable (DOC/POC concentration, pH, EC). Further confidence in our extrapolated result is that it closely approximates that of the Baum *et al.* (2007) estimate based on the River Siak (~21 Tg C yr^{-1}) and therefore provides some validation to the conclusion that Indonesian rivers account for approximately 10% of the global annual riverine DOC discharge into the ocean.

Chapter Five

Qualitative analysis of fluvial organic carbon

Radiocarbon data from this chapter are included in a manuscript that is currently under review, as: Moore, S., Gauci, V., Page, S.E., Evans, C.D., Garnett, M.H., Jones, T.G., Freeman, C. and Limin, S.H., 2011. Fluvial organic carbon fluxes reveal deep instability of deforested tropical peatlands. *(Nature, submitted manuscript).*

5.1 Introduction

One of the most pertinent questions that arises following a study that quantifies the loss of fluvial organic carbon is, "where does it all go?" A number of analytical tools are available to help gain further insights into the most likely fate of fluvial carbon and in doing so help to answer the above question. Having quantified the loss of fluvial carbon at small (sub-catchment) and large (river basin) spatial scales, samples were subject to a number of qualitative analyses: (i) radiocarbon dating (^{14}C) was employed to help indicate the most likely source of the carbon, which in turn gives some indication into how labile/recalcitrant the carbon compounds are; (ii) Specific Ultra-Violet Absorbance (SUVA) gives further insights into the aromaticity of the DOC compounds; and (iii) tetramethylammonium hydroxide (TMAH) thermochemolysis of the DOC helps to identify the functional groups present, which help define the bioavailability of the compounds and ultimately the most likely fate of the fluvial organic carbon.

5.1.1 *Radiocarbon dating (^{14}C)*

By radiocarbon dating water samples ($DO^{14}C$) an indicative age of the carbon in the sample can be deduced, which is the composite signal obtained by mixing organic matter from a range of ages. Although this is conventionally represented by a single, indicative 'mean age', this observed value may be obtained by different combinations of old (pre-bomb, i.e. pre-1950s) and new (post bomb, i.e. post-1950s) material. Pre-bomb carbon (^{14}C less than 100% modern) is older in age and is generally sourced from within the peat column itself as opposed to post-bomb carbon (^{14}C greater than 100% modern) which is of recent origin probably fixed from the atmosphere via photosynthesis within the last 1 to 10 years (see Chapter 5.2.2; Raymond *et al.*, 2007).

Previous $DO^{14}C$ measurements from waters draining intact, peat-dominated catchments in North America (Schiff *et al.*, 1997), Siberia (Amon *et al.*, 2004; Benner *et al.*, 2004) and Europe (Palmer *et al.*, 2001; Evans *et al.*, 2007; Tipping *et al.*, 2010) commonly show enrichment of DOC with 'bomb' carbon (associated with above-ground nuclear testing in the 1950s to 1960s), suggesting that the bulk of DOC leached from these systems is of recent origin. For these intact northern peatlands, this implies that DOC export does not represent a major loss pathway for long-term stored carbon, but instead a turnover of recently fixed carbon from aboveground biomass (Evans *et al.*, 2007). However, none of these studies specifically examined disturbed peatlands, and there is no knowledge of any measurements of $DO^{14}C$ from tropical peatlands, either pristine or disturbed, previously reported.

Radiocarbon techniques were used to establish if there were any significant differences in the mean age of the fluvial organic carbon being lost from intact and disturbed land-cover classes. The results help to indicate the most probable source of the lost carbon which, as well as having implications on the overall carbon balance of the ecosystem, will help to interpret the relative contributions from recently photosynthesised carbon from vegetation and older carbon from the peat column. Recently photosynthesised carbon from decaying

leaf litter on the forest floor is rich in lignin which is an integral part of plant cell walls. Structurally, lignin is a complex natural polymer, making it relatively hydrophobic and aromatic in nature. Consequently, it is very slow to decompose and upon reaching a point of stability, when decomposition only proceeds at a very slow rate (highly recalcitrant), it forms part of the humic layer on the forest floor.

5.1.2 Specific Ultra-Violet Absorbance (SUVA)

SUVA is an 'average' absorptivity for all the molecules that comprise the DOC in a water sample and can be used as a surrogate measurement for DOC aromaticity (Traina *et al.*, 1990). By definition, aromatic compounds contain a benzene ring and are highly reduced, making them recalcitrant compounds. The more aromatic a compound, the more recalcitrant that compound is considered to be and vice-versa. $SUVA_{254}$ is defined as the ultra-violet (UV) absorbance at 254 nanometres (nm) measured in inverse (reciprocal) meters (m^{-1}), divided by the DOC concentration measured in milligrams per litre (mg l^{-1}) and is reported in l mg-C^{-1} m^{-1}. Weishaar *et al.* (2003) tested the usefulness of $SUVA_{254}$ as an indicator for DOC aromaticity by plotting the $SUVA_{254}$ values of 13 organic matter isolates versus percent aromaticity that had been pre-determined using quantitative, liquid state carbon nuclear magnetic resonance (^{13}C NMR), which is the most accurate measurement of aromaticity of natural organic matter. They found that a strong correlation between the data existed (r^2=0.97), and in doing so provide strong support for the use of $SUVA_{254}$ as an indicator of aromaticity of aquatic humic substances and DOC as a whole. This is further supported by the findings of several other studies (Traina *et al.*, 1990; Chin *et al.*, 1994). $SUVA_{254}$ is therefore a useful tool for assessing the nature and general composition of DOC because it provides an integrated estimate of aromatic content across functional classes. This estimate of aromatic content indicates how labile or recalcitrant the DOC is and in turn, how likely it is to be consumed by microbes and thus converted into gaseous carbon.

When DOC is utilised by microbes in this manner, metabolic products of cellular respiration such as water (H_2O) and CO_2 are produced. This is an important step in the carbon cycle because it represents the stage at which fluvial carbon is converted into gaseous carbon. Therefore, $SUVA_{254}$ data can give a broad indication of how likely it is that the DOC will be converted into gaseous carbon through microbial respiration within the water body; high $SUVA_{254}$ = high aromaticity = recalcitrant compounds = less likely to be converted to gaseous carbon. If the DOC is not subject to metabolic conversion, it will most likely end up as a long-term carbon store as benthic sediments in a river or the ocean following physical or biological conversion to POC.

5.1.3 Tetramethylammonium hydroxide (TMAH) thermochemolysis

Having looked at the source (using $DO^{14}C$) and absorptivity of the DOC (using $SUVA_{254}$), a technique called TMAH thermochemolysis gas chromatography (GC) - mass spectrometry (MS; GC-MS), or TMAH GC-MS was used to investigate the DOC quality on an even smaller, functional group scale. Fluvial organic carbon is derived from a variety of different sources and can be subject to a number of transformations which affect the molecules in the DOC. As a result of this, DOC can become an extremely complex mixture of organic molecules spanning a great range of molecular weights (Frazier *et al.*, 2003). A technique called pyrolysis GC-MS has previously been used successfully for structural studies of organic matter (Schulten, 1999), but this process produces large quantities of carbon monoxide (CO) and CO_2, which result from the polar functionalities that are important structural features of organic matter (Saiz-Jimenez, 1994). The TMAH GC-MS technique, first implemented by Challinor *et al.* (1995), is able to retain CO and CO_2, otherwise lost through the simple pyrolysis GC-MS technique. This is achievable because sub-pyrolysis temperatures are used (300°C), a technique which is often referred to as thermally assisted chemolysis, hence its name, thermochemolysis. This technique was used to identify any differences in the structural composition of DOC within water samples draining intact and disturbed peatlands.

Whilst $SUVA_{254}$ data are useful as an indicator of aromaticity, TMAH GC-MS analysis gives information about the structural composition by providing a breakdown of the actual compounds that make up the DOC. It is a far more detailed analysis which also incorporates semi-quantitative measurements of the ensuing products, shedding light not only on the most probable source of the DOC, but also the bioavailability of the DOC. A combination of these three qualitative investigative techniques will help to build on our current knowledge about the fate of this fluvial organic carbon, which is currently poorly understood (Cole *et al.*, 2007; Battin *et al.*, 2009; Tranvik *et al.*, 2009).

5.2 Methods

5.2.1 Sample collection

Samples for radiocarbon analysis were collected from the three land-cover classes (IPSF, DPSF1 and DPSF2) during the dry season in August 2008. All samples were collected within 24 hours of one another to ensure similar water table levels and flow conditions. This is important as these hydrological conditions determine the runoff flow paths which in turn can influence the composition of DOC within the sample collected. Due to the large financial cost involved in analysing water samples for $DO^{14}C$, we had an allocation of nine samples. Therefore, three samples from each land-cover class were collected; one sample from each of the three channels draining IPSF and DPSF2, two samples from opposite ends of the first (longer) channel and one sample from the second channel draining DPSF1. Samples were collected from the centre of each channel at a depth of 20 cm at a point immediately before the confluence with the river. All sampling locations are shown in figure 5.1.

For $SUVA_{254}$ analysis, one sample per week was collected for ten consecutive weeks during the peaks of the dry season and the wet season from each of the three land-cover classes. Samples were taken from all channels within each land-cover class to ensure

equal representation. All samples were taken from the same sample locations as described in Chapter 3.2. In total, 30 dry season and 30 wet season samples were collected. Additionally, samples were collected at 5 km intervals during the peak of the wet season from the mouth to the source of the River Sebangau (150 km), totalling a further 30 samples. Samples were also collected from six of the channels that drain the largely disturbed eastern side of the Sebangau River basin ('Block C') and six channels that drain the largely intact western side of the Sebangau River basin (Sebangau), contributing a further 12 samples to the final total.

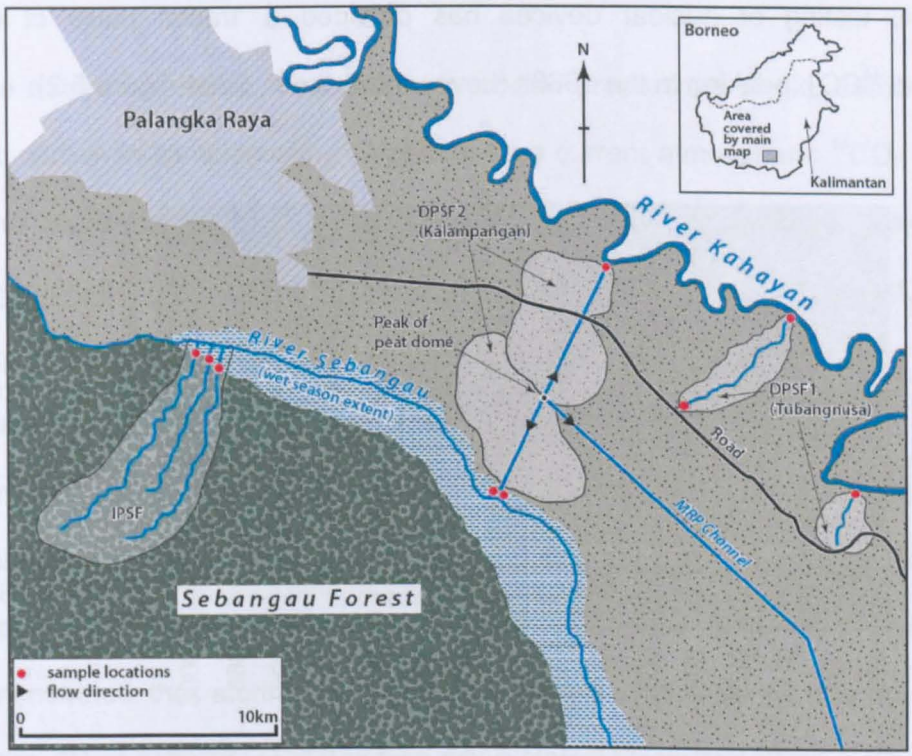


Figure 5.1: Map of study area to show the location of radiocarbon sampling points (red dots). Three samples were collected from three different sample locations in each land-cover class.

For TMAH GC-MS analysis, two samples from each of the three land-cover classes were collected over both seasons, totalling six samples. Samples were collected from two of the three channels in IPSF and DPSF2 and from both channels in DPSF1 to ensure equal representation. All samples were taken from the same sample locations as described in Chapter 3.2. Additionally, a further three samples were taken from the mouth, the middle

and the source of the River Sebangau at 150, 75 and 0 km from the source, respectively, during the peak of the wet season.

5.2.2 *Radiocarbon dating (^{14}C)*

The ^{14}C content of organic matter reflects the isotopic composition of atmospheric CO_2 at the time it was absorbed and 'fixed' by photosynthesis. Carbon fixed prior to 1950 can be 'radiocarbon dated', based on the rate of radioactive decay of cosmogenic ^{14}C, where zero years before present (BP) = AD 1950 (Evans *et al.*, 2007). Since the 1950s, atmospheric testing of nuclear devices has provided a 'tracer' pulse of enhanced atmospheric $^{14}CO_2$, peaking in the 1960s (Levin and Kromer, 2004; figure 5.2).

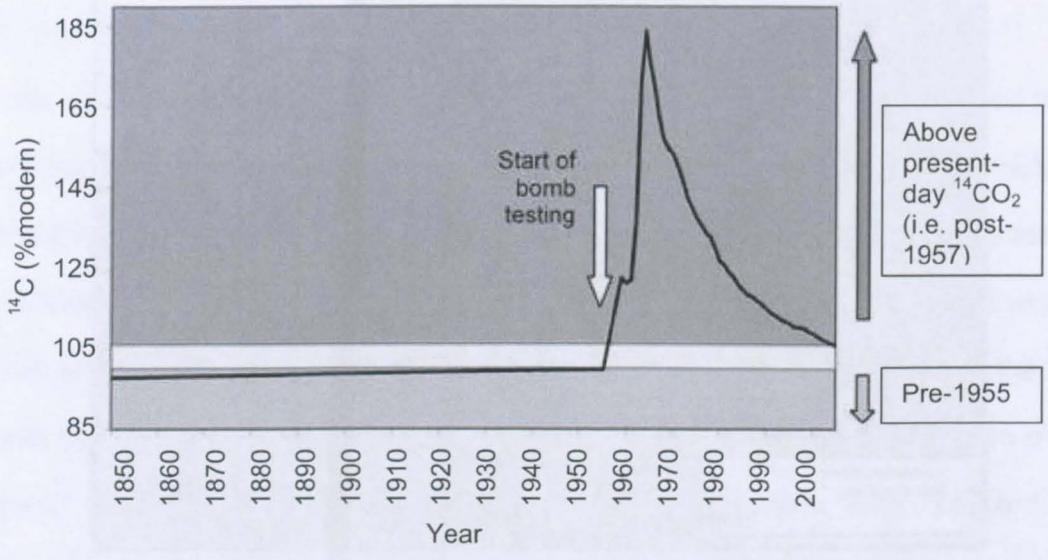


Figure 5.2: Approximate present-day ^{14}C level of organic carbon photosynthesised from atmospheric CO_2 in a single year, since 1850. Lower shaded area and arrow represent 'dateable' (pre-1955) carbon. Upper shaded area and arrow represent bomb-enriched carbon, fixed between 1957 and the present day. Bomb $^{14}CO_2$ reconstruction from Levin and Kromer (2004).

Since soil and dissolved organic matter generally represent a mix of compounds of varying ages, no single age can be ascribed to any one sample, but the following general statements can be made (Evans *et al.*, 2007):

(1) Samples with ^{14}C less than 100% 'modern' (i.e. atmospheric $^{14}CO_2$ before 1955) must contain predominantly pre-bomb carbon, and an average age can be assigned.

(2) Samples in the range 100 to 106% modern (just below atmospheric $^{14}CO_2$ levels when samples were collected) must contain a substantial fraction of carbon fixed before 1957 (the last time atmospheric $^{14}CO_2$ was this low).

(3) Samples with ^{14}C greater than 106% modern must contain a substantial fraction of carbon fixed since 1957.

Due to the nature of historic ^{14}C variations, precise proportions of old, bomb-peak and post-bomb carbon in samples with ^{14}C greater than current atmospheric $^{14}CO_2$ cannot be determined. However, the most probable explanation for a DO^{14}C value above 106% (the higher the value, the greater the probability) is that most of this DOC is derived from plant material formed since 1957 (Evans *et al.*, 2007).

Water samples were collected in pre-rinsed 250 ml polypropylene bottles, immediately passed through a 0.7 µm glass fibre filter (GF/F, Whatman), left un-acidified, refrigerated and transported to the NERC Radiocarbon Laboratory, Scotland, for ^{14}C analysis. It has been demonstrated that storing freshwater samples in this manner has no significant effect on the ^{14}C or delta ^{13}C ($\delta^{13}C$) values when stored for up to 180 days (Gulliver *et al.* 2010). Upon arrival, samples were acidified to pH 4 with 2M Hydrochloric acid (HCl) and purged with high purity nitrogen (carbon-free), then neutralised to pH 7 with 1M potassium hydroxide (KOH), rotary evaporated, frozen and freeze-dried. Weighed aliquots were combusted to CO_2 at 900°C in an elemental analyser (Costech ECS 4010, Cernusco). The gas was converted to graphite by Fe/Zn reduction (Slota *et al.*, 1987). ^{14}C content was determined by Accelerator Mass Spectrometry at the Scottish Universities Environmental Research Centre (Xu *et al.*, 2004). ^{14}C results were normalised to a $\delta^{13}C$ of

-25 ‰ (CO_2 subsamples having been measured for ^{13}C) and expressed as %modern (Stuiver and Polach, 1977).

5.2.3 Specific Ultra-Violet Absorbance at 254 nanometers ($SUVA_{254}$)

All samples were collected, preserved and transported back to the UK as described in Chapter 2.3. The preservation of samples by acidification down to pH 2.0 has no effect on UV absorbance measurements and yield the same results as measurements made on un-acidified samples (Weishaar *et al.*, 2003). Analysis was carried out at the School of Biological Sciences, Bangor University, UK. Samples were allowed to warm to room temperature before measurement. UV-visible absorbance measurements were performed on a Molecular Sciences plate reader (model M2e) and a Milli-Q blank reading was taken to subtract from each sample. A quartz cell with 1.0 cm path length was used. Samples were analysed for DOC at the Department of Environmental Sciences laboratories, The Open University as described in Chapter 2.4.2. $SUVA_{254}$ values were calculated according to equation 5.1:

$$SUVA_{254}\ (\text{l mg-C}^{-1}\ \text{m}^{-1}) = ((UV_{254} - UV_{blank}) * 100) / DOC_{conc} \quad \textit{(Equation 5.1)}$$

Where UV_{254} is the UV absorbance of the sample measured at 254 nanometers (nm), UV_{blank} is the UV absorbance of the Milli-Q blank measured at 254 nm and DOC_{conc} is the DOC concentration of the sample.

5.2.4 Tetramethylammonium hydroxide (TMAH) thermochemolysis

Preparation for TMAH GC-MS analysis involves extracting the actual DOC from the water sample first. Solid phase extraction (SPE) of DOC from water was carried out using SPE cartridges (IST Isolute C_{18}, Biotage). The SPE cartridges were pre-conditioned with hexane, dichloromethane (DCM), methanol (MeOH), and 0.01 M HCl. The sample was

then allowed to pass through the conditioned SPE cartridge with minimal forcing. Once the DOC had absorbed onto the cartridge, any mineral salts remaining in the cartridge were removed by flushing with 4 ml 0.01 M HCl followed by an air flush to dry the cartridge. The DOC was then eluted from the SPE cartridges into clean vials with 4 ml MeOH and stored in refrigeration until TMAH GC-MS analysis.

Following the SPE of DOC from water, the refrigerated samples in MeOH were absorbed onto quartz wool in a quartz pyrolysis tube. After drying overnight, 10 µl of 25% TMAH in MeOH were added and again, allowed to dry overnight. An alkali environment (pH 14) for the reaction is ensured by adding TMAH to excess. Thermochemolysis was carried out under the following conditions: heated to 300°C (held for 15 s) at 20°C ms^{-1} in a flow of helium (He) using a CDS Pyroprobe 5000 fitted with a 1500 valve interface (CDS Analytical, Oxford, PA) and coupled to a GC-MS instrument. GC-MS was carried out using an Agilent Technologies 6890 gas chromatograph coupled to a 5973 mass spectrometer. Separation was performed with a S.G.E. (UK) BPX-5 column (30 m x 0.25 mm i.d., 0.25 µm film thickness). He, at a flow rate of 1.1 ml min^{-1} was used as a carrier gas. Injection was at a 5:1 split and injector temperature was 270°C. The GC oven temperature was held for 1 min at 50°C and then programmed at 5°C min^{-1} to 310°C (held for 9 minutes).

TMAH GC-MS is a one-step reaction that is principally a degradative technique (decomposition of a compound) and secondarily a derivatisation technique (transforms the compound into a product). Labile carbon-oxygen (C-O) bonds such as esters, amide bonds, some ether bonds (β-0-4 bonds in lignin), and to some extent glycosidic bonds, are broken by the TMAH thermochemolysis reaction and result in fragments. This degradation occurs mainly through a base catalysed hydrolysis reaction at elevated temperatures. Simultaneously, functional groups containing acidic protons, such as carboxylic acids and phenols, are methylated whereas esters are converted to the

corresponding methyl esters (Filley *et al.*, 1999). The resulting products are volatile enough to be separated by GC and analysed by MS (Frazier *et al.*, 2003).

Individual compound mass yields (thermochemolysis reaction products; table 5.1; figure 5.3) were evaluated and calculated to help assess the relative degradation dynamics in samples from the three different land-cover classes.

Table 5.1: Major lignin compound names (TMAH thermochemolysis products).

Label	Compound name
G4	3,4-dimethoxybenzaldehyde
G5	3,4-dimethoxyacetophenone
G6	3,4-dimethoxybenzoic acid methyl ester
S4	3,4,5-trimethoxybenzaldehyde
S5	3,4,5-trimethoxyacetophenone
S6	3,4,5-trimethoxybenzoic acid methyl ester
P18	trans-3-(4-methoxyphenyl)-3-propenoic acid methyl ester
G18	trans-3-(3,4-dimethoxyphenyl)-3-propenoic acid methyl ester

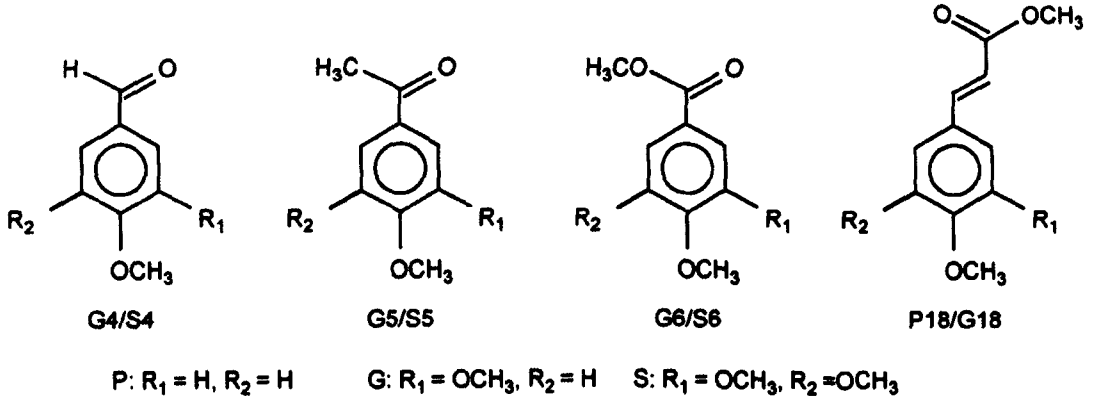


Figure 5.3: Structures of typical lignin compounds used to indicate degradation dynamics. P = *p*-hydroxyphenyl, G = guaiacyl, S = syringyl (see table 5.1 for compound names).

The syringyl/guaiacyl (S/G) ratio, used to assess vegetation type (angiosperm versus gymnosperm), was calculated as the sum of syringyl (S4 + S5 + S6) divided by the sum of guaiacyl (G4 + G5 + G6) phenols. The acid/aldehyde (Ad/Al) ratio which indicates the state of oxidation for guaiacyl components (G6/G4) was determined as the sum of the normalised amounts of 3,4-dimethoxybenzoic acid methyl ester (G6) divided by 3,4-

dimethoxybenzaldehyde (G4). The cinnamyl/guaiacyl (C/G) ratio is used to indicate the input of woody versus non-woody plant tissue and was calculated as the sum of cinnamyl (*p*-coumaric acid, P18 and ferulic acid, G18) divided by guaiacyl (G6 + G5 + G4) phenols.

5.3 Results

5.3.1 DOC radiocarbon ages

Due to samples only being collected at one time point in the dry season (August 2008), we cannot make inferences regarding the overall annual pattern of loss. However, the data do show clear between-site differences (table 5.2; figure 5.4). DOC from IPSF was ^{14}C-enriched with a mean ^{14}C of 109.1% modern. Because this is greater than 100% modern, the samples cannot be assigned an age and therefore are simply termed as 'modern'. In contrast, DOC from channels draining the two disturbed land-cover classes (DPSF1 & 2) was ^{14}C-depleted, ranging from 83.8 to 98.9% modern. This is equivalent to ^{14}C ages of 92 to 1417 years BP.

Table 5.2: ^{14}C (%modern) and DO^{14}C age (years BP) data for individual samples (± 1σ) and mean (± s.e.m) from all three land-cover classes.

Land-cover class	Sample ID	^{14}C (%modern)	DO^{14}C Age (years BP)
IPSF	SUERC-28121	109.8 ± 0.5	modern
	SUERC-28122	108.7 ± 0.5	modern
	SUERC-28123	108.8 ± 0.5	modern
	Mean	109.1 ± 0.3	modern
DPSF1	SUERC-28129	98.9 ± 0.5	92 ± 37
	SUERC-28130	97.2 ± 0.4	229 ± 35
	SUERC-28131	97.1 ± 0.4	239 ± 35
	Mean	97.7 ± 0.6	188 ± 47
DPSF2	SUERC-28126	83.8 ± 0.4	1417 ± 35
	SUERC-28127	85.5 ± 0.4	1259 ± 36
	SUERC-28128	85.6 ± 0.4	1249 ± 36
	Mean	85.0 ± 0.6	1308 ± 54

The mean ^{14}C in DPSF1 was 97.7% modern (range of 97.1 to 98.9% modern), which is equivalent to a ^{14}C age of 188 years BP (range of 239 to 92 years BP). DOC samples from DPSF2 had a mean ^{14}C of 85.0% modern (range of 83.8 to 85.6% modern), equivalent to a ^{14}C age of 1308 years BP (range of 1417 to 1249 years BP). ^{14}C data from all land-cover classes are significantly different from one another ($p<0.001$, unpaired, two-sample t-test), with the largest differences occurring between IPSF and DPSF2. The mean ^{14}C age is positively correlated with drainage severity, meaning that as drainage severity in a land-cover class increases, so does the mean age of the carbon in the drainage water lost from that land-cover class (figure 5.4). In IPSF, where the smallest channels are located and the effect of drainage is negligible, the carbon lost is classified as 'modern' and was most likely fixed from the atmosphere post 1957 (^{14}C greater than 106% modern). DPSF1, which is subject to moderate drainage, is losing carbon with a mean ^{14}C age of 188 years BP and DPSF2, which is subject to the most severe drainage is losing carbon with the oldest mean ^{14}C age of 1308 years BP.

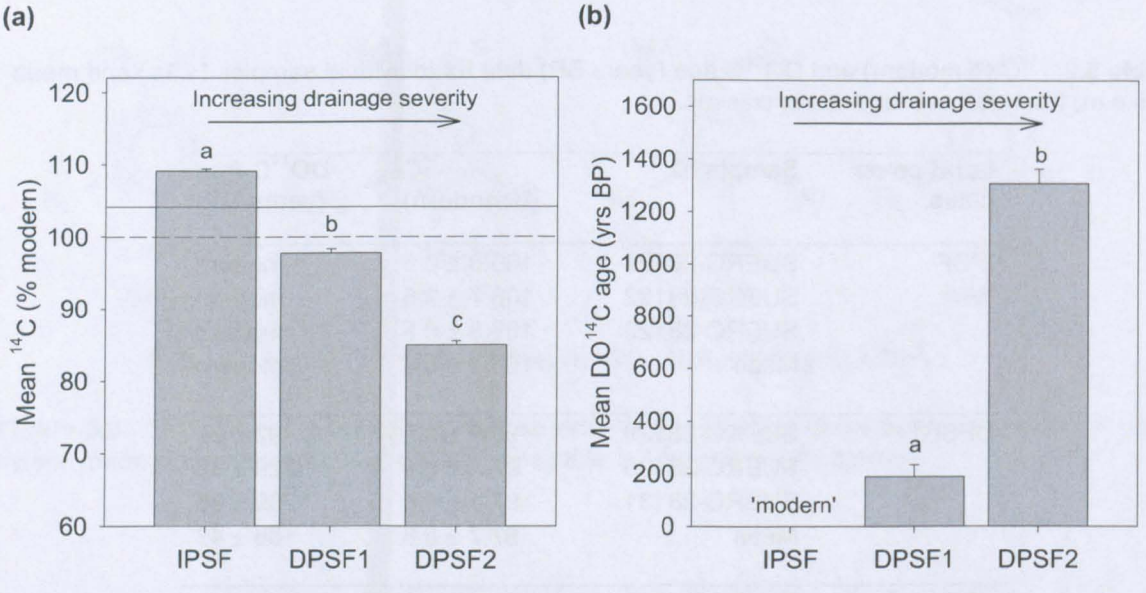


Figure 5.4: **(a)** Mean radiocarbon (^{14}C) levels (%modern) (± s.e.m) measured in DOC from all three land-cover classes, 'a', 'b' and 'c' denote significant differences ($p<0.001$, unpaired, two-sample t-test). Solid horizontal line (104% modern) represents the current atmospheric $^{14}CO_2$ level, dashed horizontal line (100% modern) represents the composition of the atmosphere in 1950, in the absence of any anthropogenic influences (i.e. fossil fuel burning and above-ground nuclear testing). **(b)** Mean radiocarbon age (DO^{14}C) in years BP (± s.e.m), 'a' and 'b' denote significant differences ($p<0.001$, unpaired, two-sample t-test). Mean ^{14}C levels are greater than 100% modern in IPSF samples and therefore cannot be assigned an age, instead they are termed 'modern'.

5.3.2 *Absorptivity and aromaticity*

$SUVA_{254}$ data for ten consecutive weeks during the peak of the dry and wet seasons had very little temporal variability (s.e.m <1%) and generally ranged between 3.00 and 5.00 l mg-C^{-1} m^{-1} (table 5.3).

Table 5.3: $SUVA_{254}$ data from ten consecutive weeks and the mean (± s.e.m) during the peak of the dry and wet season from all three land-cover classes.

Week	$SUVA_{254}$ (l mg-C^{-1} m^{-1})					
	IPSF		DPSF1		DPSF2	
	Dry	Wet	Dry	Wet	Dry	Wet
1	3.85	4.30	3.92	3.27	4.03	3.43
2	4.11	4.00	4.10	3.90	4.55	4.00
3	4.16	3.77	3.10	3.13	4.28	3.80
4	4.26	3.66	3.90	3.44	3.47	3.99
5	4.01	3.70	3.93	3.24	4.07	3.88
6	3.82	3.90	3.67	4.21	4.30	4.25
7	4.10	4.37	3.90	3.45	3.54	3.82
8	4.08	4.09	4.09	4.99	3.25	3.62
9	4.09	4.16	3.83	3.24	4.26	4.13
10	4.13	4.35	5.06	3.99	4.31	4.50
Mean	4.06 ± 0.04	4.03 ± 0.08	3.95 ± 0.15	3.69 ± 0.19	4.00 ± 0.14	3.94 ± 0.10

Across both seasons the mean $SUVA_{254}$ is consistently higher in IPSF than DPSF1 and DPSF2, with the largest differences occurring between IPSF and DPSF1. Within each land-cover class, $SUVA_{254}$ is consistently higher in the dry season compared to the wet season (table 5.3; figure 5.5). Figure 5.5 contains the same data displayed on two different y-axis units. $SUVA_{254}$ data (figure 5.5a) has been converted to percent aromaticity data (figure 5.5b) using the relationship found between the variables (Weishaar *et al.*, 2003). Because the relationship is based on a straight line equation (y = mx + c), the two datasets show the same trend but figure 5.5b illustrates that a difference in $SUVA_{254}$ of 0.37 l mg-C^{-1} m^{-1} is equivalent to a 2.5% difference in aromaticity (difference

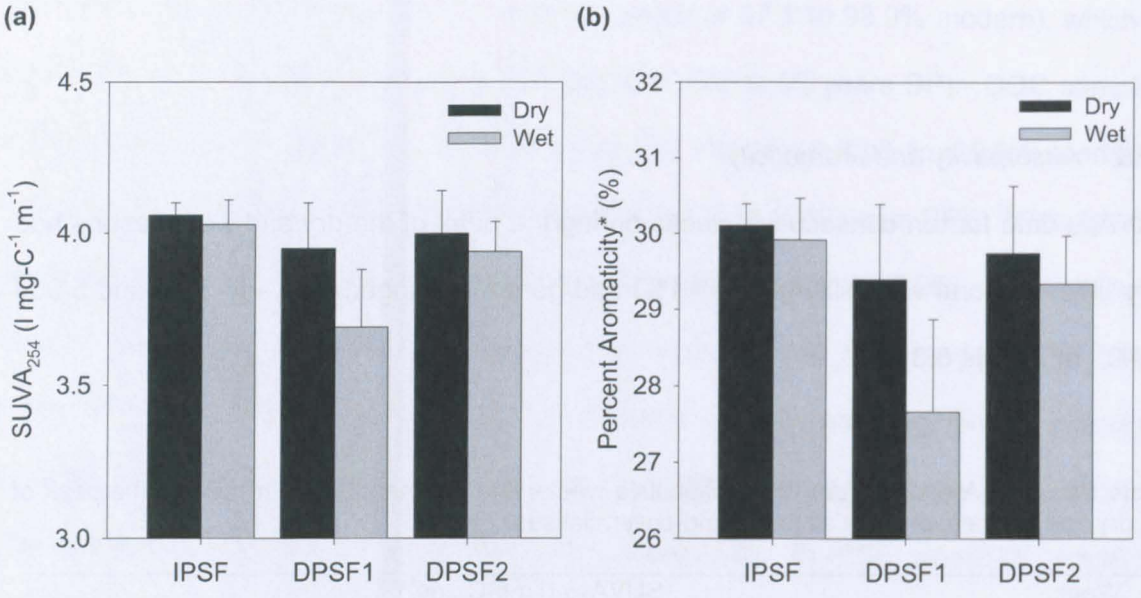


Figure 5.5: Mean **(a)** $SUVA_{254}$ data and **(b)** percent aromaticity data from all three land-cover classes during the peak of the dry (black) and wet (grey) seasons (± s.e.m). * Percent aromaticity is determined using the relationship between $SUVA_{254}$ and ^{13}C-NMR data as described in Weishaar *et al.* (2003), where percent aromaticity = $(6.52*SUVA_{254}) + 3.63$.

between IPSF dry season and DPSF1 wet season). It should however be noted that these differences between land-cover class and season are statistically non-significant.

Samples collected from the River Sebangau had a similar range in $SUVA_{254}$ values to those collected from the three land-cover classes in the wet season. There is a clear declining trend in $SUVA_{254}$ values from the river source to the mouth (figure 5.6). $SUVA_{254}$ values from within each of the channels that discharge into the River Sebangau are generally consistent with the $SUVA_{254}$ values from within the main channel of the River Sebangau. Channels 9 and 10 are the only exception to this, where high $SUVA_{254}$ inputs are followed by an increase in $SUVA_{254}$ values immediately downstream in the River Sebangau.

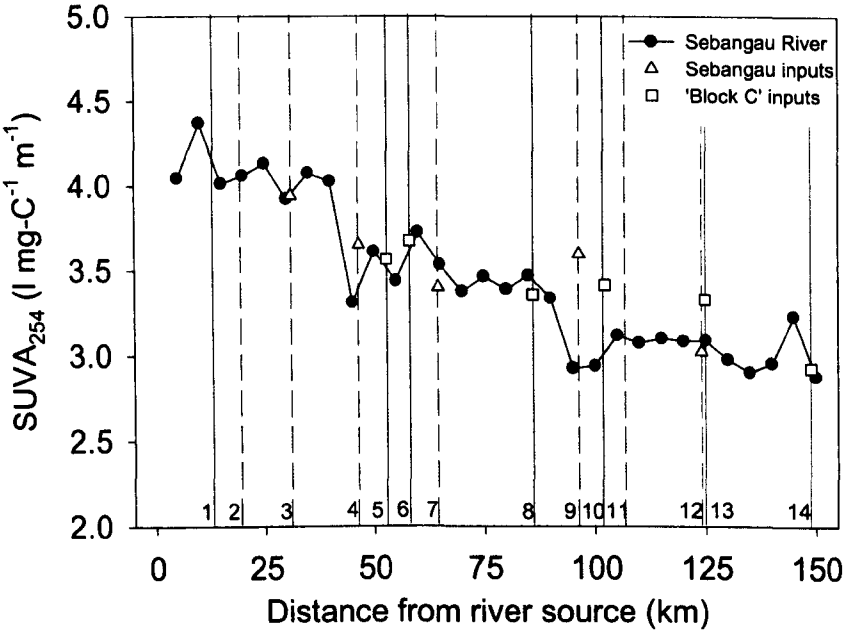


Figure 5.6: $SUVA_{254}$ along the course of the River Sebangau (5 km intervals) during the peak of the wet season. Vertical lines represent the confluences of fourteen channels that discharge into the River Sebangau from largely disturbed land-cover class 'Block C' (solid) and largely intact land-cover class 'Sebangau' (dashed). Single point data represent $SUVA_{254}$ in each channel prior to discharge into the River Sebangau. Data was not collected for channels 1 and 2 and an anomalous data point was obtained for channel 11 (8.3 l mg-C^{-1} m^{-1}) and omitted from the figure.

The mean $SUVA_{254}$ value of channels draining the largely disturbed land-cover class, 'Block C' is 3.38 l mg-C^{-1} m^{-1} (25.7% aromaticity) compared to 3.53 l mg-C^{-1} m^{-1} (26.6% aromaticity) from the channels draining the largely intact land-cover class, Sebangau. Despite this difference being small and statistically non-significant, the finding that water draining the intact land-cover class has higher $SUVA_{254}$ values/aromaticity than water draining the disturbed land-cover class is consistent with the datasets from sub-catchments IPSF, DPSF1 and DPSF2.

5.3.3 DOC functional groups

TMAH thermochemolysis GC-MS yielded the following methylated phenols from all samples (except one): guaiacyl (G), syringyl (S) and *p*-hydroxyphenyl (P) structures. All but one sample contained methyl esters of the *p*-courmaric acid (G18), while only three samples contained methyl esters of cinnamyl phenols, ferulic acid (P18). S/G and C/G

ratios were calculated, as described in Chapter 5.2.4, and plotted against each other as proxies for plant and tissue type found within the samples (figure 5.7). The plant and tissue type regions displayed in figure 5.7 are the traditional delineations used in Cupric oxide (CuO) oxidation analysis, and therefore may not be strictly appropriate for these samples analysed by TMAH, but nonetheless, is useful as a guide and has been applied to TMAH data in this manner before (Wysocki *et al.*, 2008). All but one sample fall within the woody angiosperm region, with only one ratio value falling within the woody gymnosperm region.

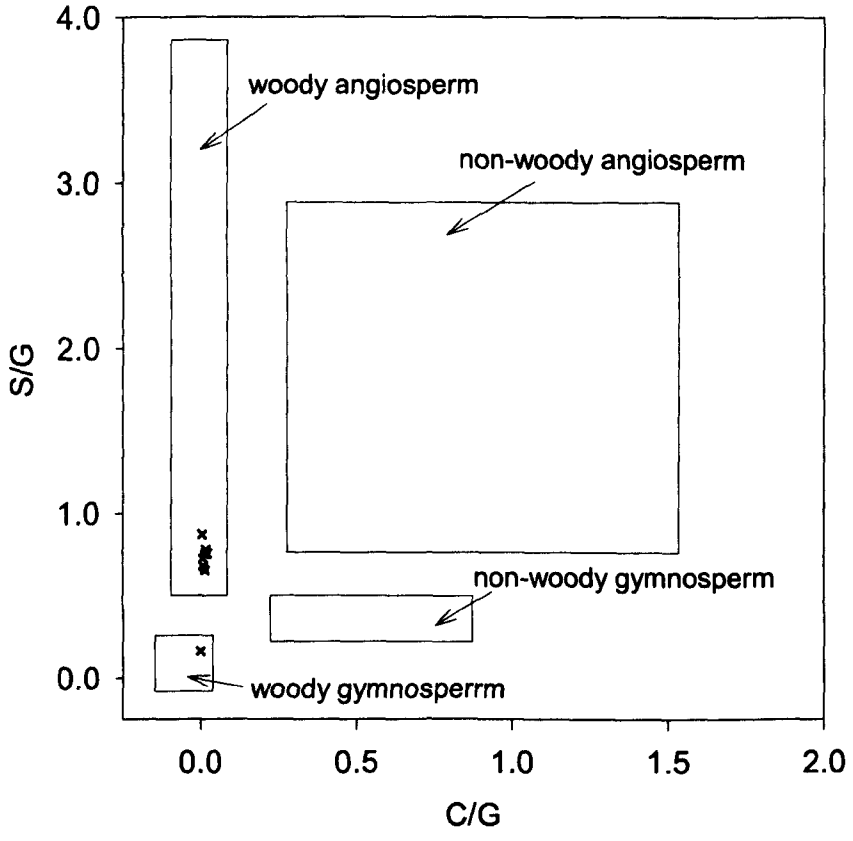


Figure 5.7: Compound ratio source identification plot for all DOC samples analysed by TMAH GC-MS. The labelled regions defining plant and tissue type are the traditional delineations used in CuO oxidation analysis (Wysocki *et al.*, 2008).

When tributary samples were grouped according to their broad land-cover classes (IPSF or DPSF), and S/G, C/G and Ad/Al ratios calculated, only the Ad/Al ratio was notably different between land-cover class (figure 5.8). All except one sample had an S/G ratio that ranged between 0.6 and 0.9 (angiosperm source). The lower average S/G ratio and

large standard error from IPSF sites is due to one very low S/G value of 0.2. This is the sample which falls within the woody gymnosperm region. The reason for this sample having a lower S/G ratio is a decline in syringyl compound inputs (S5 and S6). The C/G ratio, which is used to indicate the input of non-woody tissue of vascular plants varied very little between land-cover classes and was consistently low, never exceeding 0.03. The primary reason for this is the high guaiacyl compound inputs (G4, G5 and G6) and absence of methyl esters in some samples (P18 and G18). The consistently low C/G ratios indicate high levels of woody inputs within all samples.

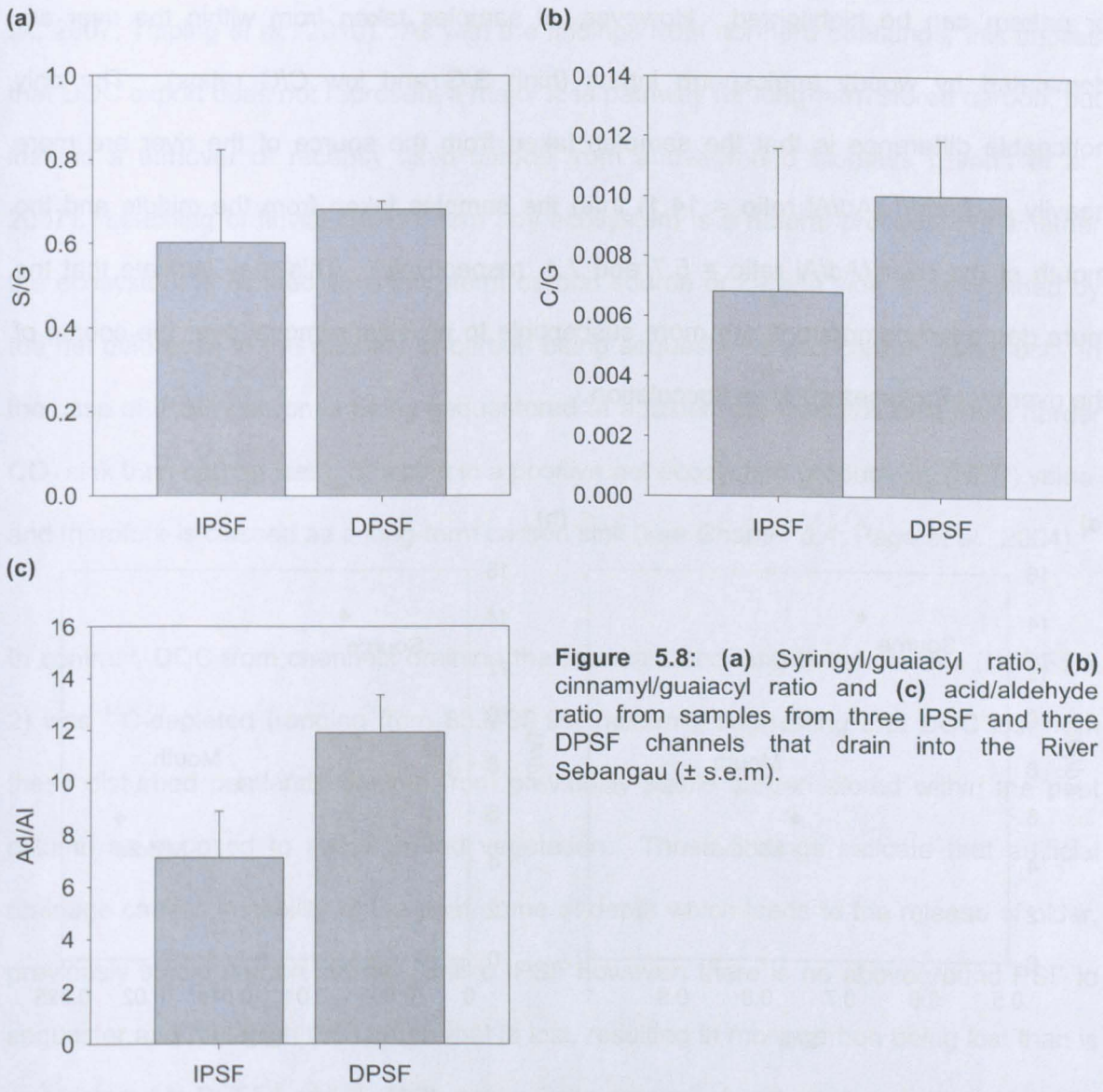


Figure 5.8: **(a)** Syringyl/guaiacyl ratio, **(b)** cinnamyl/guaiacyl ratio and **(c)** acid/aldehyde ratio from samples from three IPSF and three DPSF channels that drain into the River Sebangau (± s.e.m).

The Ad/Al ratio records the state of oxidation for guaiacyl compounds (G6/G4) and is used as an indicator for the degree of lignin degradation. Ratios can vary from less than one to

greater than ten, with higher Ad/Al ratios indicating a greater degree of oxidative degradation (Louchouarn *et al.*, 2006). All Ad/Al ratio values ranged between 4 to 14 and averaged 7.1 and 11.9 from IPSF and DPSF samples, respectively, indicating that samples from DPSF were more highly degraded than samples from IPSF. The primary reason for the higher Ad/Al ratios observed in DPSF samples is greater inputs (approximately double) of the G6 compound (3,4-dimethoxybenzoic acid methyl ester).

S/G, C/G and Ad/Al ratios of samples taken from the source, middle and mouth of the River Sebangau are presented in figure 5.9. Due to the small sample number, no trends or pattern can be highlighted. However, all samples taken from within the river are dominated by woody angiosperm inputs (high S/G and low C/G ratios). The only noticeable difference is that the samples taken from the source of the river are more heavily degraded (Ad/Al ratio = 14.1) than the samples taken from the middle and the mouth of the river (Ad/Al ratio = 5.7 and 7.1, respectively). This may indicate that the more degraded compounds are more susceptible to physical removal over the course of the river by processes such as flocculation.

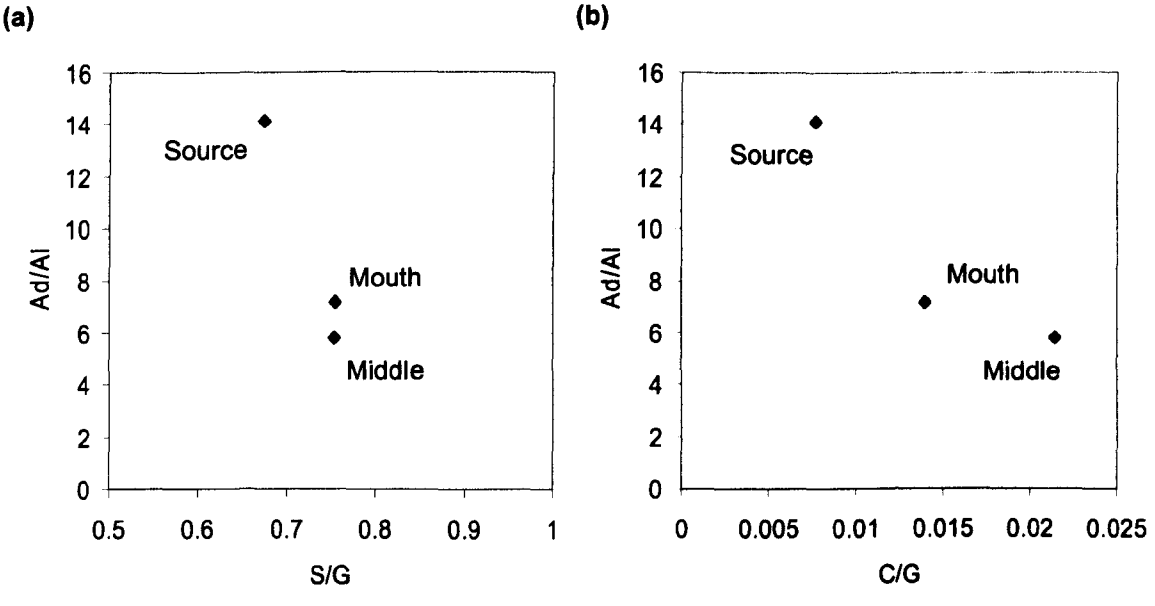


Figure 5.9: **(a)** Syringyl/guaiacyl vs. acid/aldehyde ratio, and **(b)** cinnamyl/guaiacyl vs. acid/aldehyde ratio for three samples from the source, middle and mouth of the River Sebangau.

5.4 Discussion

5.4.1 DOC age and likely source

Results from radiocarbon analysis showed that DOC from channels draining IPSF was ^{14}C-enriched with a mean ^{14}C of 109.1% modern. It is not possible to assign a radiocarbon age to this carbon because the sample is greater than 106% modern, however, it can be inferred that the majority of the DOC leaching IPSF is derived from plant material formed since 1957 (Evans *et al.*, 2007). This is consistent with existing evidence for the predominantly recent origin of DOC lost from intact northern peatlands (Schiff *et al.*, 1997; Palmer *et al.*, 2001; Amon *et al.*, 2004; Benner *et al.*, 2004; Evans *et al.*, 2007; Tipping *et al.*, 2010). As with the findings from northern peatlands, this implies that DOC export does not represent a major loss pathway for long-term stored carbon, but instead a turnover of recently fixed carbon from aboveground biomass (Evans *et al.*, 2007). Leaching of fluvial carbon from any ecosystem is a natural process, but whether the ecosystem is defined as a long-term carbon source or carbon sink is determined by the net difference in the quantity of carbon being sequestered and carbon being lost. In the case of IPSF, carbon is being sequestered at a faster rate than it is being lost (larger CO_2 sink than carbon loss), reflected in a positive net ecosystem productivity (NEP) value, and therefore is classed as a long-term carbon sink (see Chapter 3.4; Page *et al.*, 2004).

In contrast, DOC from channels draining the two disturbed land-cover classes (DPSF1 & 2) was ^{14}C-depleted (ranging from 83.8-98.9% modern), suggesting that DOC lost from these disturbed peatlands derived from previously stable carbon stored within the peat column as opposed to aboveground vegetation. These findings indicate that artificial drainage causes instability of the peat dome at depth which leads to the release of older, previously stable carbon stores. Unlike IPSF however, there is no aboveground PSF to sequester and replenish the carbon that is lost, resulting in more carbon being lost than is sequestered in DPSF1 and 2. With only a finite amount of carbon stored within the peat dome and large fluvial losses of peat-sourced carbon, as well as CO_2 emissions through peat decomposition, these drained ecosystems are destined not only to be long-term

carbon sources, but will also subside and eventually be altogether depleted of the peat that lies above the water table (Hooijer *et al.*, 2010). The data from the three land-cover classes display a positive relationship between the two variables; as drainage severity increases (using width and depth of drainage channel as a proxy) the mean age of the carbon that is lost also increases (using ^{14}C age as a proxy). This is because deeper drainage channels expose deeper/older layers of peat which leach fluvial carbon that was sequestered over one thousand years ago in the case of the most severely drained site (DPSF2).

Having used radiocarbon analysis to infer the source of the DOC (vegetation or peat), results from TMAH GC-MS analyses were used to indicate the most likely plant and tissue-type found within DOC samples. All samples (with one exception) were derived from woody angiosperm sources. Given that almost the entire Sebangau catchment is composed of highly fibrous peat which was covered in PSF (pre-disturbance), one would expect woody sources to dominate over non-woody sources. Like most tropical forests in Southeast Asia, large areas within the Sebangau catchment contain trees from the Dipterocarpaceae family such as *Shorea* which are all angiosperms. Only two species of gymnosperm are known to exist in Central Kalimantan (*Agathis dammara* and *Dacrydium pectinatum*). These species are quite rare, however, and are therefore unlikely to make a contribution to the DOC signature (S.E. Page, 2011, pers comm., 20th February). Accordingly, all but one sample fell within the woody angiosperm region in figure 5.7. In the case of DPSF1 and 2, where the source of the DOC is the peat column (as opposed to the aboveground vegetation), the DOC signature obtained is that from a past vegetation composition, when the dominant vegetation species could have differed to that of today. The data, however, would imply that angiosperm trees have dominated the PSF for the past ~1400 years (age of DOC from DPSF2). Interestingly, the one sample that indicated a woody gymnosperm source was taken from the River Paduran which drains an area that is dominated by pulp-wood plantations. The monoculture in this area has replaced the native tree/plant type and depending on the species grown, could account for the switch to

gymnosperm source dominance. However, if the pulp-wood plantation is composed of *Acacia* spp., as most in Indonesia are, this explanation is unlikely to account for the change in source dominance as this genera is also angiosperm.

5.4.2 DOC aromaticity and bioavailability

The $SUVA_{254}$ data do not highlight any significant differences between land-cover classes or between seasons. However, there is some indication of greater $SUVA_{254}$ values (higher DOC aromaticity) being lost from intact peatland compared to disturbed peatland, albeit statistically non-significant. This trend is apparent between the IPSF site and DPSF1 and 2 in both dry and wet seasons. From radiocarbon analysis, it is known that the source of DOC in the intact site is the aboveground vegetation whereas in the disturbed sites the source is the peat column. Therefore a combination of the radiocarbon and $SUVA_{254}$ data implies that the fresh input of DOC sourced from aboveground vegetation is more aromatic than DOC mobilised from the peat column. This may be a result of the overlying PSF present in IPSF feeding the forest floor with a diverse range of plant material, including large quantities of lignin that is highly aromatic in nature. This is because lignin-derived products are complex polymers of phenylpropane units, which are cross-linked to each other with a variety of different chemical bonds. Lignin is the most recalcitrant component of the plant cell wall, therefore the higher the proportion of lignin the lower the bioavailability of the substrate. Conversely, DOC sourced from within the peat column in both disturbed peatland sites is shown to be less aromatic in nature. Therefore, less aromatic, or more labile, DOC from disturbed peatland ecosystems has a greater potential to be mineralised and fed back into the atmosphere as CO_2, when compared with more aromatic DOC with a lower bioavailability that is leached from intact peatlands. This increases the carbon cost associated with anthropogenic disturbance of peatlands by further enhancing the potential source of carbon gases.

The second trend in $SUVA_{254}$ data is greater values (indicative of higher DOC aromaticity) during the dry season compared to the wet season, evident across all land-cover classes. Having established that DOC sourced from the peat column is less aromatic in nature than lignin-derived DOC from aboveground vegetation, one might expect to observe less aromatic DOC in the dry season. This would be because during the dry season when water tables are lower, a greater portion of the peat is exposed to aerobic decomposition and oxidation. Consequently, one might expect more (labile) DOC to be leached from the peat column resulting in a greater portion of the total DOC being less aromatic. However, with more aromatic DOC observed during the dry season, the opposite is observed, making the finding seem rather counter-intuitive. It should be noted that with an average difference across all sites in percent aromaticity between seasons of 4.4% (statistically non-significant), this trend in data perhaps ought not to be over-analysed. Of more interest is that less aromatic (albeit less than 5% difference) DOC is observed during the wet season which normally lasts for nine months of the year. This means that for three-quarters of the year, more labile DOC which has greater potential to be mineralised into gaseous carbon is leached from peatlands of all land-cover class types, increasing the indirect source of CO_2 from peatlands. Crucially, this additional source of CO_2 is generally unaccounted for in most tropical peatland carbon budgets that assess the impact of anthropogenic disturbance.

5.4.3 DOC aromaticity in the River Sebangau

The $SUVA_{254}$ data from the River Sebangau, is believed to be the first from a tropical Southeast Asian blackwater river and therefore the results cannot be placed in context with previous findings. The values obtained, however, are indicative of aromaticity within the range one might expect from a peat-dominated river basin (26-32%). The range observed from the River Sebangau encompasses reported values from the River Suwannee which drains a wetland swamp in Georgia (28% aromaticity), while exceeding several other rivers that drain temperate wetlands (12-30%; McKnight *et al.*, 2001).

The clear declining trend in $SUVA_{254}$ from source to mouth would appear to be the result of two processes occurring at different stretches along the River Sebangau: (i) in the upper reaches (0 to 100 km from source), input of DOC with lower $SUVA_{254}$ values from tributaries; and (ii) in the lower reaches (100 to 150 km from source), mixing with seawater with lower $SUVA_{254}$ values. From conductivity data (used as a proxy for seawater), we know that seawater regularly reaches up to 50 km inland as a result of the tidal cycle and has been recorded at greater distances inland during high tide. Figure 5.10 displays the $SUVA_{254}$ data from the source to the mouth of the River Sebangau on an expanded y-axis which helps to define a more detailed three-step decline instead of a steady decline as previously illustrated in figure 5.6. The data suggest that the source of the river consists of '100% peat-derived' water with the highest $SUVA_{254}$ values until about 40 km from the source (dark grey). The second step is a mixing transition stage with inputs of low-$SUVA_{254}$ DOC from tributaries (as a result of some mineral soil drainage water, lower in

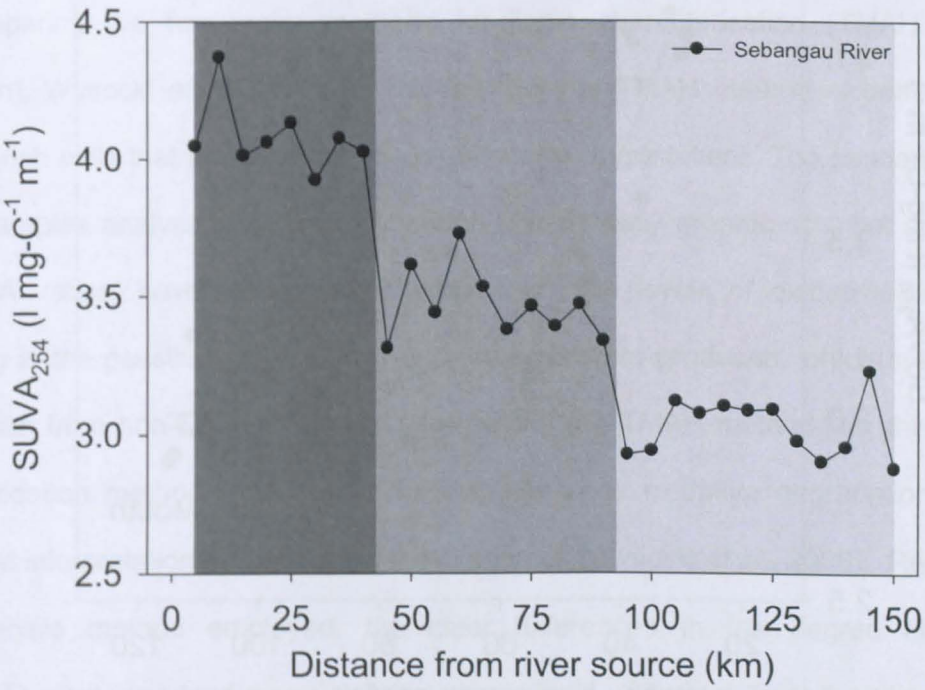


Figure 5.10: $SUVA_{254}$ along the course of the River Sebangau (5 km intervals) during the peak of the wet season at low-tide with an expanded y-axis. Different shades of grey define the three steps in $SUVA_{254}$ decline with distance downstream.

the Sebangau River basin) as well as some seawater influence, up to approximately 90 km from the source (grey). The third step represents 90 km from the source to the river mouth which consists of low-$SUVA_{254}$ DOC inputs, but primarily much higher concentrations of seawater, resulting in the lowest $SUVA_{254}$ values observed in the River Sebangau (light grey).

To check if the decline in $SUVA_{254}$ is the result of mixing with seawater, $SUVA_{254}$ data was plotted against conductivity data (EC; figure 5.11). If the decline in $SUVA_{254}$ values was the result of mixing with seawater, there would be a linear relationship between the two variables. The relationship displayed between these two variables is non-linear (polynomial 3rd order relationship, r^2=0.82) which is indicative of a qualitative change due to in-stream processing. This does not mean that there is no mixing with seawater, but it does mean that mixing with seawater cannot explain the observed trend on its own.

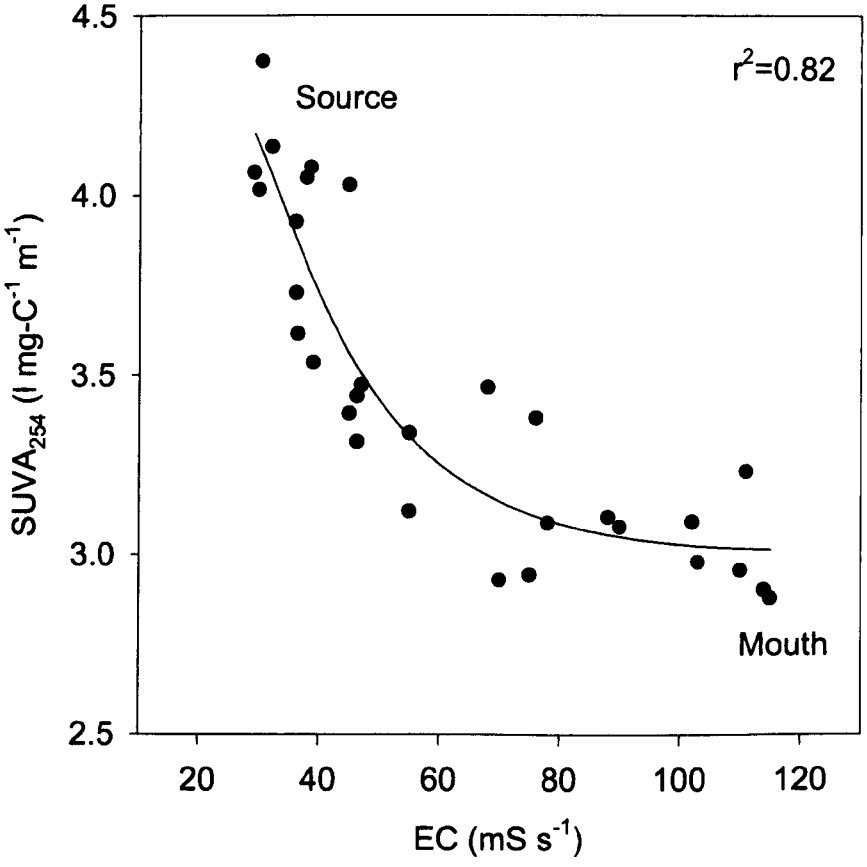


Figure 5.11: $SUVA_{254}$ vs. EC data from 30 samples taken from the mouth to the source of the River Sebangau (polynomial 3rd order relationship, r^2=0.82).

Some form of in-stream processing is occurring, but without additional accompanying datasets it is difficult to determine whether it is physical or biological. Biological processing could involve in-stream respiration, where consumption of the DOC leads to the release of metabolic products (CO_2 and H_2O). If the DOC is too recalcitrant for biological consumption, physical processing could account for the qualitative change through diagenetic alteration of the DOC, resulting in it being converted to particulate forms. These particulate forms either remain in the water column or are precipitated out as benthic sediments. Other explanations include photo-oxidation, where along the course of the river, absorption of ultraviolet radiation (sunlight) alters the chemical composition of molecules, breaking larger compounds down into smaller ones (see Chapter 6.6.1; Tranvik & Bertilsson., 2001) and reducing $SUVA_{254}$ values (Brooks *et al.*, 2007; Judd *et al.*, 2007).

5.4.4 DOC oxidative state and overall fate

By comparing the two major methods for lignin characterisation (TMAH and CuO oxidation), Wysocki *et al.* (2008) concluded that the TMAH method is better suited to organic-rich soils that had not undergone extensive degradation. The peatland drainage water samples analysed in this investigation are certainly organic-rich, but according to the Ad/Al ratios, have already been subject to high levels of oxidative degradation, resulting in the possibility that monomeric products were produced, which are difficult to distinguish from non-lignin molecules when using the TMAH method. In this case, the CuO oxidation method would be more suitable since oxidative degradation does not confound interpretation of the primary lignin sources (Wysocki *et al.*, 2008). Regardless of the analysis method employed, the clear differences in the degree of oxidative degradation between land-cover classes remain valid. Samples from the disturbed land-cover class were more highly degraded, which is consistent with the greater extent of decomposition one would expect from land that has been clear-felled and drained. When

the water table is artificially lowered, by drainage channels such as those present in DPSF1 and 2, the peat is exposed to aerobic decomposition and oxidation processes at greater depths down the peat profile. These processes result in greater quantities of more heavily degraded organic material being leached from the peat.

Wysocki *et al.* (2008) found that lignin yields analysed via TMAH (as opposed to CuO oxidation) tended to be skewed towards easily hydrolysed cinnamyl-based lignin and therefore remarked that this method may be biased against low-cinnamyl woody samples. All the samples in this investigation, however, were found to have a very low C/G ratio which is indicative of a woody source and therefore consistent with what one would expect from intact (IPSF) and recently deforested (DPSF1 & 2) PSF ecosystems. Until the same samples are run using the CuO oxidation method, it is not possible to comment fully on the findings, however, it is unlikely that the C/G ratios would decrease significantly when employing the alternative CuO oxidation method, given that the current C/G ratios are already very low.

Despite this theoretical understanding of lignin products, it is difficult to deduce what the TMAH data mean with regard to the overall fate of the DOC with absolute certainty. It has been found that DOC from disturbed peatlands is degraded to a higher oxidative state than DOC leaching from intact peatlands. More highly oxidised DOC is closer to being fully mineralised into CO_2 and H_2O. This oxidation process proceeds via alcohol groups, aldehyde/ketone groups to acids and finally, to ring cleavage of the aromatic units. In this respect, we can conclude that the DOC being lost from disturbed peatlands has a higher bioavailability and is more likely to fully mineralise into CO_2 and H_2O. The same data, however, may be interpreted differently which results in a conflicting conclusion to the previous one; DOC leaching from disturbed peatlands is already more heavily degraded, therefore it has reached a more stable, recalcitrant form (having already oxidised its more labile functional groups). This DOC is likely only to have the aromatic units left and is therefore no longer as labile as it once was, making it unlikely to ever be fully mineralised.

If this were the case, then despite only the recalcitrant aromatic units being left (which may never fully decompose), the majority of the organic matter will have already mineralised and contributed to emissions of gaseous carbon. If the first of the two interpretations above is considered, then the disturbed peatland ecosystems are losing fluvial carbon that is readily mineralised and more likely to be fed back into the atmospheric carbon cycle as CO_2 when compared with DOC that is less readily oxidised from intact peatland ecosystems.

In this chapter, three types of analyses have helped to depict qualitative differences in the nature of DOC that is lost from intact and disturbed peatland ecosystems. Radiocarbon analysis illustrates a fundamental difference between sites in the age of the DOC that is lost, which in turn indicates the different sources of DOC between sites. Whereas the intact site is losing younger carbon sourced from aboveground vegetation (PSF), the disturbed sites are losing much older carbon from the peat dome itself. The differing DOC sources between land-cover class help to explain the observed differences in results from $SUVA_{254}$ analyses. $SUVA_{254}$ data indicated that the vegetation-sourced carbon from IPSF was more aromatic than the peat-sourced carbon from the disturbed sites. This may be explained by inputs of lignin-rich carbon compounds that are recalcitrant in nature from the overlying PSF in IPSF. In contrast, less aromatic carbon sourced from the peat column in DPSF1 and 2 was found to be more highly oxidised than carbon lost from IPSF. This implies that a larger portion of the DOC from DPSF1 and 2 has already been mineralised into gaseous carbon.

These results mean that fluvial export of DOC from intact peatland systems does not represent a major loss pathway for long-term stored carbon, but instead a turnover of recently fixed carbon from aboveground biomass. This carbon is recalcitrant in nature, which is reflected in lower oxidative state levels, meaning that it is less likely to ever be fully mineralised into gaseous carbon. This contrasts with the more labile carbon that is lost from disturbed peatland ecosystems. Whilst previously contributing to a long-term

carbon store, this carbon is now being released in large quantities as a result of drainage and is more likely to be fully oxidised and contribute, indirectly, to yet further emissions of CO_2 from disturbed peatland ecosystems.

Chapter Six

General Discussion

Data from this chapter are included in a manuscript that is currently under review, as: Moore, S., Gauci, V., Page, S.E., Evans, C.D., Garnett, M.H., Jones, T.G., Freeman, C. and Limin, S.H., 2011. Fluvial organic carbon fluxes reveal deep instability of deforested tropical peatlands. *(Nature, submitted manuscript)*.

6.1 Introduction

Thus far this thesis has focused on three primary investigations: (i) quantifying the effects of ecosystem disturbance on fluvial organic carbon losses at a small (sub-catchment) scale (Chapter Three); (ii) validating these findings by applying them to larger, river basin scale flux estimates (Chapter Four); and (iii) examining the effects of ecosystem disturbance on the quality of fluvial organic carbon losses (Chapter Five). Here, a synthesis of the work from all three chapters is discussed and the results are extrapolated to the regional scale in order to understand their significance in a regional and global context.

6.2 Fluxes and ages

Data from Chapter Three indicate that fluvial organic carbon yields from all study sites investigated in the region are high when compared with previously published peatland fluvial TOC yields. The different land-cover classes investigated ranged in TOC yields

from 62.5 to 131 g C m^{-2} yr^{-1} and increased with increasing drainage severity (figure 6.1). The lowest TOC yield was observed in the intact PSF site, but at 62.5 g C m^{-2} yr^{-1} (DOC yield = 61.3 g C m^{-2} yr^{-1}), this is over four times larger than the average European (temperate) peatland DOC yield, which is estimated to be approximately 15 g C m^{-2} yr^{-1} (Nilsson *et al.*, 2008; Billet *et al.*, 2010; Koehler *et al.*, 2011). The intact PSF TOC yield is also more than double many reported values from tropical regions including Amazonia (Richey *et al.*, 1990; Waterloo *et al.*, 2006), Africa (Meybeck & Ragu, 1996; Coynel *et al.*, 2005) and other Southeast Asian regions (Baum *et al.*, 2007; Alkhatib *et al.*, 2007; Aldrian *et al.*, 2008). It should however be noted that the majority of catchments considered in these different studies are considerably larger than the catchments studied in this investigation and therefore they encompass a wider variety of land-cover classes. The yields obtained in this study were derived from catchments of uniform land-cover class that are between 5 to 35 km^2 and composed entirely of peatlands, which are known to yield high fluvial organic carbon fluxes (Hope *et al.*, 1997; Aitkenhead & McDowell, 2000).

The most severely drained land-cover class, DPSF2, had a TOC yield of 131 g C m^{-2} yr^{-1} which was over double the TOC yield from the intact site. The implications of these findings are highly significant for assessing the impact of anthropogenic disturbance of peatlands on fluvial carbon losses. However, TOC yield does not indicate the source of the additional carbon (i.e. new versus old peat). It is only when incorporating the radiocarbon dates of the DOC lost from the different land-cover classes that the significance of the finding is fully realised. In Chapter Five, radiocarbon analysis revealed that $DO^{14}C$ (% modern) was negatively correlated with drainage severity in the three land-cover classes (figure 6.1). In other words, the average age (years BP) of the DOC lost, increased with drainage severity. The DOC from the intact site had the highest ^{14}C (% modern; most modern carbon), which is consistent with evidence for the predominantly recent origin of DOC from intact northern peatlands (Schiff *et al.*, 1997; Palmer *et al.*, 2001; Amon *et al.*, 2004; Benner *et al.*, 2004; Evans *et al.*, 2007; Tipping *et al.*, 2010). No other known measurements of $DO^{14}C$ from tropical peatlands, either pristine or disturbed,

have previously been reported. This means that it is not possible to place the findings of this study in context, but nonetheless, the between-site differences are clear. The age of the DOC that is lost from a site can be used as a reliable indicator of the most likely source from which the DOC has been leached. The intact site leached 'modern' DOC (^{14}C = 109.1% modern) compared with the disturbed sites which leached DOC aged between 92-1417 years BP (^{14}C = 98.9-83.8% modern). This combination of quantitative and qualitative analyses demonstrates that the doubling of fluvial organic carbon lost from disturbed PSF is the result of inputs of old, peat-derived carbon. These findings suggest that instability and collapse of the peat column at depth in disturbed PSF ecosystems is responsible for the larger and older fluxes of fluvial organic carbon observed.

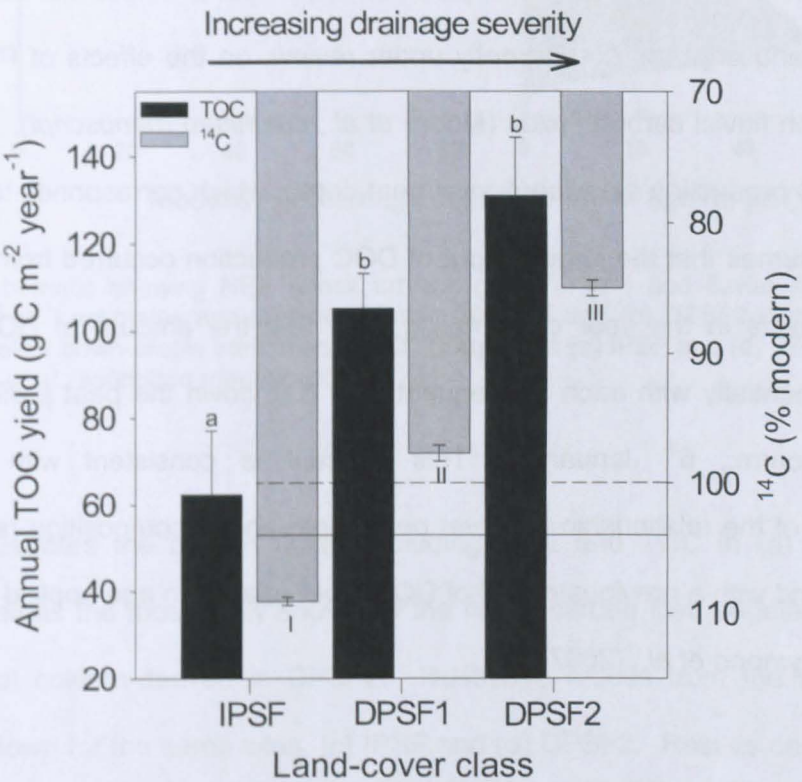


Figure 6.1: Cumulative annual TOC yield (± s.e.m), 'a' and 'b' denote significant differences between land-cover classes ($p<0.01$, unpaired, two-sample t-test) and mean radiocarbon (^{14}C) levels (± s.e.m) measured in DOC, 'I', 'II' and 'III' denote significant differences ($p<0.001$, unpaired, two-sample t-test). Solid horizontal line (104% modern) represents the current atmospheric $^{14}CO_2$ level, dashed horizontal line (100% modern) represents the composition of the atmosphere in 1950, in the absence of any anthropogenic influences (i.e. fossil fuel burning and above-ground nuclear testing).

6.3 $DO^{14}C$ age attribution

$DO^{14}C$ levels in water samples represent the composite signal obtained by mixing organic matter from a range of ages. Although this is conventionally represented by a single, indicative 'mean age', this observed value may be obtained by different combinations of old (pre-bomb, i.e. pre-1950s) and new (post-bomb) material. Samples dominated by bomb carbon (^{14}C greater than 100% modern) cannot be assigned a mean age using this approach.

In order to investigate in more detail the observed differences in mean DOC ages between land-cover classes, radiocarbon data from samples collected in this study were used to model the age distribution of DOC leached from each site, using a simple profile decomposition model (C. Evans, 2011, pers comm., 6th Jan). These will be included in a forthcoming manuscript, that is currently under review, on the effects of PSF clearance and drainage on fluvial carbon fluxes (Moore *et al.*, *submitted manuscript*). The model is based on DOC production as a function of peat depth, which corresponds to carbon age. The model assumes that the largest input of DOC production occurred from carbon fixed via photosynthesis in the year of sampling, and that the amount of DOC production declined exponentially with each subsequent year (i.e. down the peat profile; C. Evans, 2011, pers comm., 6th January). This concept is consistent with the general understanding of the relationship between peat depth and decomposition rates (Limpens *et al.*, 2008), and with a previous model of DOC input relative to age applied to Arctic river samples by Raymond *et al.*, (2007).

Having applied the age attribution model to all samples (three replicates from each of the three land-cover classes), the DOC was apportioned into age categories that ranged from 0 to 5000+ years. Samples from each land-cover class were then aggregated to give a mean modelled percentage of DOC within each age range and illustrative results for the two most contrasting sample sites (IPSF and DPSF2) are summarised in figure 6.2c and d.

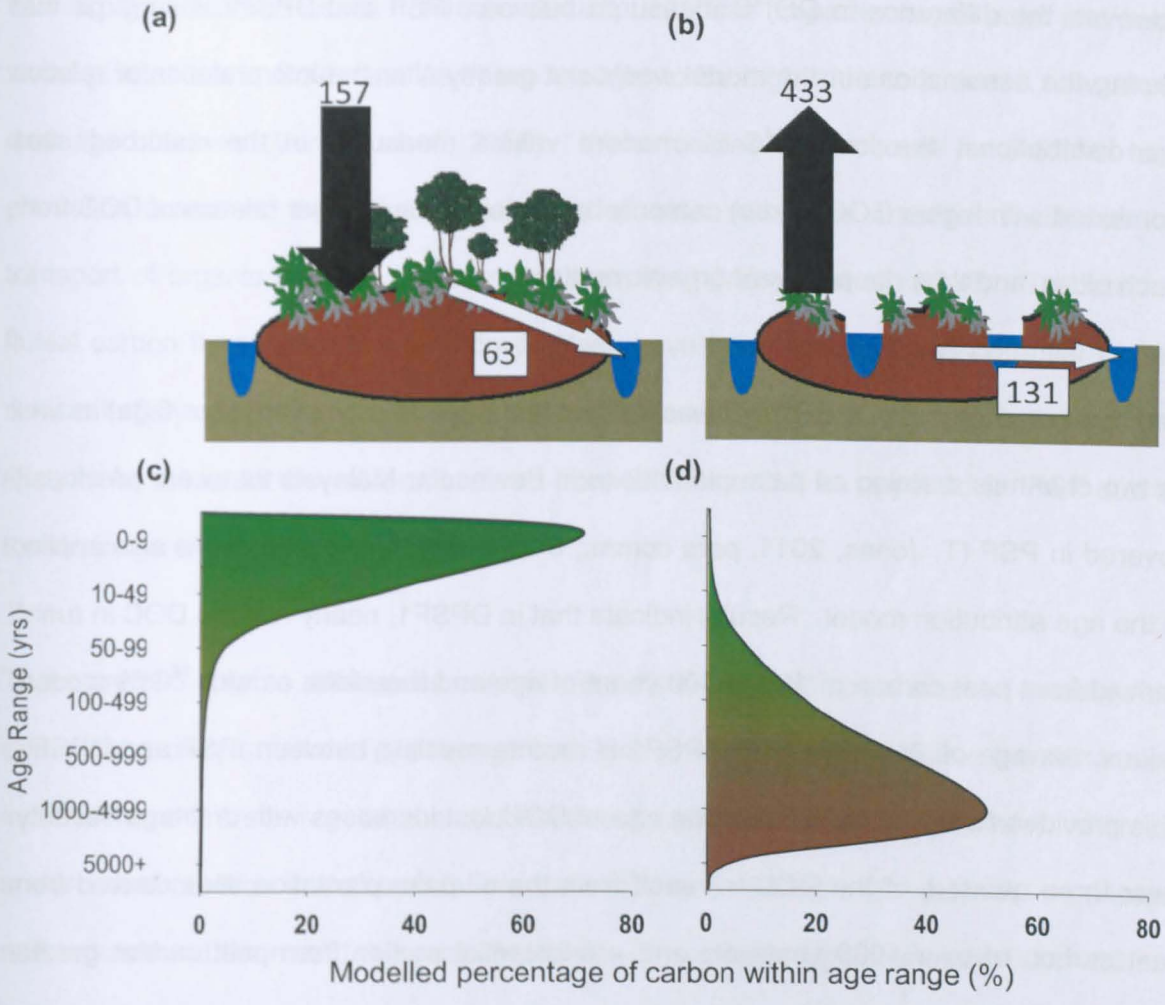


Figure 6.2: Schematic showing NEE (black arrows; g C m^{-2} yr^{-1}) and fluvial TOC loss (white arrows; g C m^{-2} yr^{-1}) estimates and likely sources in **(a)** IPSF and **(b)** DPSF2 land-cover classes. Illustrative modelled down-profile attribution of $DO^{14}C$ age from **(c)** IPSF and **(d)** DPSF2 land-cover classes (Moore *et al.*, *submitted manuscript*).

Figure 6.2 illustrates the carbon fluxes including NEE and TOC in (a) IPSF and (b) DPSF2, as well as the most likely source of the fluvial carbon lost; vegetation-derived in IPSF and peat column-derived in DPSF2. Illustrative results from the age attribution models are shown for the same sites, (c) IPSF and (d) DPSF2. Results demonstrate that almost all the DOC from the IPSF site is derived from carbon fixed from the atmosphere within the last 50 years (figure 6.2c). In contrast, the age attribution model suggests that two-thirds of DOC in runoff from the DPSF2 site is derived from peat carbon of 500-5000 years old (figure 6.2d). It is stressed that the age attribution model is only indicative, since different assumptions about the decrease in DOC production down the peat profile would alter the distributions obtained (as explained in Moore *et al.*, *submitted manuscript*).

However, the difference in $DO^{14}C$ measured between IPSF and DPSF2 is so large that altering the assumptions in the model would not greatly alter the interpretation of relative age distributions; the lower ^{14}C % modern values measured in the disturbed sites (combined with higher TOC fluxes) can only be explained by a larger release of DOC from much older, and thus deeper, peat organic matter.

Radiocarbon data from DPSF1 that was subject to moderate drainage (figure 6.3a) as well as two channels draining oil palm plantations in Peninsular Malaysia that were previously covered in PSF (T. Jones, 2011, pers comm., 6th January; figure 6.3b) were also applied to the age attribution model. Results indicate that in DPSF1, nearly half the DOC in runoff derived from peat carbon of 100 to 500 years of age and therefore, as with ^{14}C % modern values, the age of DOC lost from DPSF1 is an intermediate between IPSF and DPSF2. This provides further evidence that the age of DOC lost increases with drainage severity. Over three quarters of the DOC in runoff from the oil palm plantation sites derived from peat carbon of over 1000 years old and a substantial portion from peat carbon greater than 5000 years in age (Moore *et al.*, *submitted manuscript*).

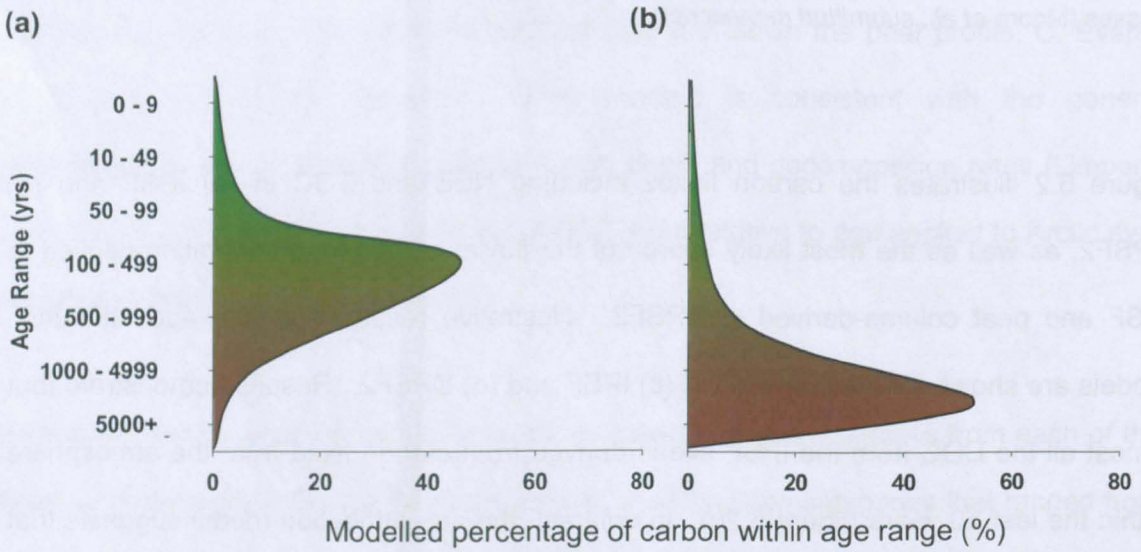


Figure 6.3: Illustrative modelled down-profile attribution of $DO^{14}C$ age from **(a)** DPSF1 and **(b)** ditches draining oil palm plantation sites in Peninsular Malaysia (Moore *et al.*, *submitted manuscript*).

Fluvial organic carbon losses from commercial plantations (in particular, oil palm and pulp-wood plantations in Southeast Asia) are thought to be high, due to a dense network of drainage channels (Verwer *et al.*, 2008). Water bodies can account for 3-5% of total plantation areas and the large surface area of water within the channels facilitates the transport of organic material out from the plantation (Verwer *et al.*, 2008). To date, no fluvial carbon fluxes from this land-cover class have been reported and potential values remain largely unknown. However, data from this investigation would imply that fluxes are likely to be closer to the values observed from DPSF1 and 2 as opposed to IPSF due to the drainage effect.

There are two notable differences between the disturbed land-cover classes investigated and commercial plantations: (i) although both land-cover classes are drained, water tables in DPSF1 and 2 are unregulated and consequently fluctuate according to rainfall, whereas under usual practice in commercial plantations, the water table is rigorously monitored and regulated at the most favourable depths for crop growth (approximately -60 to -80 cm for oil palm and pulp-wood); and (ii) DPSF1 and 2 have both been subject to several uncontrolled fire events. In comparison, land cleared in preparation for commercial plantations, is typically logged and burned in a controlled, isolated event for the purpose of removing any remaining vegetation from the peat surface. Despite these differences, results from the age attribution model imply that, much like DPSF1 and 2, older peat carbon from the peat column (as opposed to the overlying vegetation), is likely to be the dominant contributor to DOC losses from commercial plantations.

6.4 The River Sebangau in a global context

By conducting sampling campaigns in the wet and dry season, it was estimated that the River Sebangau discharges 0.46 Tg of fluvial organic carbon (TOC) to the ocean, annually. This comprised 93% DOC (0.43 Tg) and 7% POC (0.03 Tg). It is estimated that between 330 to 370 Tg of fluvial organic carbon is discharged via the world's rivers to the

oceans every year (Degens *et al.*, 1991; Meybeck, 1993). Based on these estimations, the River Sebangau contributes between 0.12 and 0.14% of the global annual fluvial organic carbon flux to the world's oceans. This translates to a rather more significant percentage however when considering that the Sebangau River basin only accounts for 0.005% of the world's exoreic (draining into oceans) drainage basin area (106,326,000 km^2; Ludwig *et al.*, 1996). The Sebangau River basin therefore clearly exports large quantities of fluvial organic for its size when compared to other rivers.

6.4.1 Climatic zones and organic carbon yields

Ludwig *et al.*, (1996) estimated that the wet tropical climatic zone covers 23,633,000 km^2 (22% of global drainage basin area) and contributes 90.2 Tg DOC to the oceans (44% of global DOC flux to oceans). This over representation of DOC fluxes from the wet tropical climatic zone is perhaps a function of high levels of rainfall and resultant discharge as well as high vegetation production. The findings from intact and disturbed land-cover classes in Chapter Three have already demonstrated that discharge is the most important factor in determining fluvial carbon fluxes. The Sebangau River basin accounts for only 0.02% of the total wet tropical climatic zone drainage basin area, yet it contributes up to 0.5% of the zone's total DOC flux. These percentages indicate that the Sebangau River basin over-proportionally contributes to DOC fluxes both within the wet tropical climatic zone as well as on a global scale. It follows that the Sebangau River basin is one of the highest contributors of fluvial organic carbon fluxes to the ocean per unit area within the climatic zone that contributes most significantly to fluvial carbon fluxes to the ocean. This is reflected in the annual TOC yield from the Sebangau River basin to the ocean which averages 88 g C m^{-2} yr^{-1}. This yield is considerably higher than all of the world's river basins reported in Ludwig *et al.* (1996) which, given that TOC yields take into account catchment size and discharge, is most likely due to the extremely high DOC concentrations within the River Sebangau (greater than 60 mg l^{-1}). These high concentrations are due to the Sebangau River basin being composed almost entirely of

carbon-rich peatlands. This is in contrast to larger drainage basins, which can encompass more than one climatic zone and consequently more than one land-cover class. For example, the Nile drainage basin, which is 1,874,000 km^2, encompasses five different climatic zones (temperate dry and wet, tropical dry and wet and desert), of which approximately 20% is desert, which, as an ecosystem not only contains very little organic matter, but also receives very little rainfall. As a result of lower TOC concentrations and discharges, the average TOC flux from the Nile river basin is 0.2 g C m^{-2} yr^{-1}, the majority of which is comprised of POC (Ludwig *et al.*, 1996). This is in contrast to wet tropical climatic zones where DOC is invariably the dominant component in TOC fluxes.

6.4.2 The Sebangau and other world rivers

DOC export versus catchment size for some blackwater rivers and other world rivers is presented in figure 6.4. The graph has been modified from the original, taken from Alkhatib *et al.* (2007), to include data from the River Sebangau. The overall trend illustrated in figure 6.4 is increasing DOC export with catchment size. The regression line between the two variables is for the existing set of data for blackwater rivers only (prior to addition of the River Sebangau data point) and approximates the data points more accurately before adding the River Sebangau data (r^2=0.81) than after (r^2=0.72). When the River Sebangau is included in the dataset, it is clear that it deviates from the existing trend to a greater extent than other blackwater rivers, by exporting more DOC than would be expected from its (relatively small) catchment size. Despite its smaller catchment, the River Sebangau exports more DOC annually than other blackwater rivers such as the Siak, Suwannee and Ogeechee. Of the four Indonesian blackwater rivers that have been quantified thus far, the Sebangau exports the most DOC annually. It is interesting to examine how the blackwater rivers (including the River Sebangau) compare with other world rivers. The Sebangau River basin is over 350 times smaller than the Nile river basin, yet the River Sebangau exports 1.2 times more TOC (and nearly 5 times more DOC) than the River Nile, annually. The Amazon, Congo and Mississippi river basins are

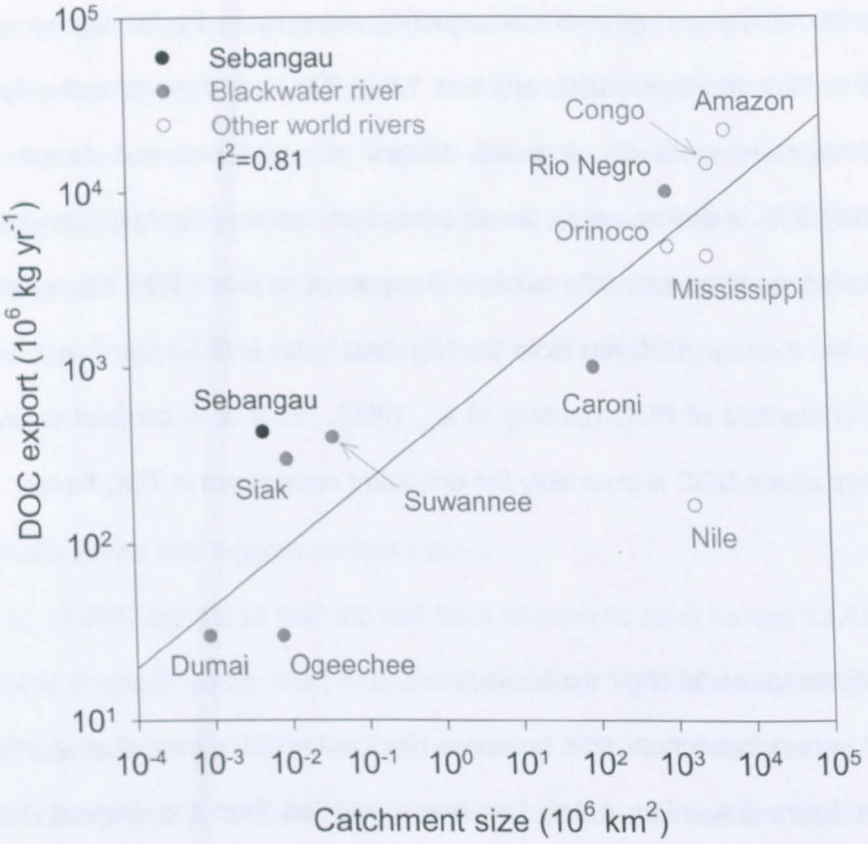


Figure 6.4: DOC export (log) vs. catchment size (log) for several blackwater rivers (black/grey circles) and other world rivers (white circles). Linear regression line is for the existing dataset for blackwater rivers only (prior to addition of the River Sebangau data point; r^2=0.81). Data are from Ludwig *et al.* (1996) and references within, Vegas-Vilarrubia and Rull (1988), Richey *et al.* (1990), Leff and Meyer (1991), Valentine and Zepp (1993), Hastenrath *et al.* (1999), McCallum and Hickey (2001), World Resources Institute (2003), Castillo *et al.* (2004), Coynel *et al.* (2005), Baum *et al.* (2007), Alkhatib *et al.* (2007) (catchment size is an estimate with high uncertainty) and Moore *et al.* (2011; Chapter Four).

the three largest river basins in the world. Their river basins are 5,903,000, 3,500,000 and 3,243,000 km^2 and annually they export 36.1 (Richey *et al.*, 1990), 14.4 (Coynel *et al.*, 2005) and 5.3 (Ludwig *et al.*, 1996) Tg TOC, respectively. These huge river basins are 1100, 700 and 600 times larger than the Sebangau River basin, respectively, yet annually they only export 80, 31 and 12 times more TOC to the ocean than the River Sebangau. This comparison in TOC export between small and large river basins illustrates the global significance and importance of quantifying TOC exports from small, peatland-dominated river basins because per unit area they account for much larger fluvial organic carbon exports. The Amazon, Congo and Mississippi River basins have average TOC yields of 6.9 to 8.5 (Coynel *et al.*, 2005; Richey *et al.*, 1990), 3.8 (Coynel *et al.*, 2005) and 1.0 to 1.6

(Coynel *et al.*, 2005; Ludwig *et al.*, 1996) g C m^{-2} yr^{-1}, respectively. These data demonstrate that the TOC yield of the Sebangau River basin (88 g C m^{-2} yr^{-1}) is approximately 10 times greater than the Amazon River basin and significantly more than 10 times greater than the other two largest river basins in the world.

6.5 Regional extrapolation

6.5.1 Sub-catchment vs. River basin scale

In order to verify the observed annual TOC yields from sub catchments of different land-cover classes (Chapter Three), the same yields were applied to the Sebangau River basin. The entire Sebangau catchment (5,200 km^2) was classified into two broadly defined land-cover classes (intact and disturbed) using satellite images, aerial photography and a geographic information system (ArcGIS, 9.3). The intact PSF yield of 62.5 g C m^{-2} yr^{-1} was applied to all areas defined as intact and an intermediate value of 118 g C m^{-2} yr^{-1} (which is the mean TOC yield value for DPSF1 and 2, given that there is no significant difference between them) applied to all areas defined as disturbed (table 6.1).

Table 6.1: Estimated TOC losses and yields from the Sebangau River basin based on sub catchment yields for intact and disturbed land-cover classes.

	Land-cover class	Area (km^2)	Actual TOC yield applied (g C m^{-2} yr^{-1})	Estimated total TOC loss (tonnes yr^{-1})	Estimated total land-cover class yield (g C m^{-2} yr^{-1})
Sebangau (western side of river basin)	Intact	3038.8	62.5	189,925	-
	Disturbed	567.0	118.2	67,019	-
	Total	3605.8	-	256,944	71.3
Block 'C' (eastern side of river basin)	Intact	361.4	62.5	22,588	-
	Disturbed	1202.6	118.2	142,147	-
	Total	1564.0	-	164,735	105.3
Total (Sebangau River basin)	Intact	3400.2	62.5	212,513	-
	Disturbed	1769.6	118.2	209,166	-
	Total	5169.8	-	421,679	81.6

Using these TOC yields, TOC losses were estimated to be 256,944 tonnes (0.26 Tg) and 164,735 tonnes (0.16 Tg) from the western (primarily intact - Sebangau) and eastern (primarily disturbed - 'Block C') sides of the river basin, which equated to TOC yields of 71.3 and 105.3 g C m^{-2} yr^{-1}, respectively. The annual TOC loss from the entire Sebangau River basin using the estimated yields from Chapter Three is estimated to be 421,679 tonnes, or 0.42 Tg, which equates to an estimated TOC yield of 81.6 g C m^{-2} yr^{-1}. These values are within 10% of the basin scale TOC loss (0.46 Tg yr^{-1}) and TOC yield (88.5 g C m^{-2} yr^{-1}) estimates based on data from Chapter Four and discussed in Moore *et al.* (2011).

Despite the estimated total TOC loss being within 10% of the actual observed value, the accuracy of the estimates did vary between land-cover classes. Table 6.2 compares the 'actual' values (from Chapter Four) with the 'estimated' values from the sub-catchment sites (from Chapter Three). The 'estimated' values are lower than the 'actual' values from the western side of the river basin (which is primarily intact PSF) by 0.08 Tg TOC yr^{-1}.

Table 6.2: Actual and estimated TOC fluxes from the western, eastern and total Sebangau River basin calculated from two river trip sampling campaigns and applying sub-catchment yields to the river basin, respectively.

	TOC flux					
	Sebangau - 'Intact' (western side of river basin)		Block 'C' - 'Disturbed' (eastern side of river basin)		Total (Sebangau River basin)	
	Actual	Estimated	Actual	Estimated	Actual	Estimated
Annual total (tonnes yr^{-1})	339,460	256,944	117,563	164,735	457,820	421,679
Annual total (Tg yr^{-1})	0.34	0.26	0.12	0.16	0.46	0.42

The same discrepancies are apparent from the eastern side of the river basin (which is primarily disturbed PSF), where the 'estimated' values are greater than the 'actual' values by 0.04 Tg TOC yr^{-1}. The difference in values is smaller on the eastern side of the

catchment primarily because this side accounts for a much smaller land area (30% of the total river basin). These inconsistencies mean that the TOC yield of 62.5 g C m^{-2} yr^{-1} for intact PSF is a slight underestimate and the mean value of 118 g C m^{-2} yr^{-1} for disturbed PSF is a slight overestimate.

There are two likely reasons for these discrepancies between the 'actual' and 'estimated' Sebangau River fluxes. The most likely reason is that the 'actual' data was based on two sampling campaigns in the year (wet and dry season) and extrapolated from these two datasets to give an annual loss. Extrapolating to an annual TOC loss based on two measurements is not without its limitations and it is likely that the 'actual' annual TOC loss is subject to high standard error. The sub-catchment yields for intact and disturbed land-cover classes that were used to calculate the 'estimated' values were based on weekly measurements throughout the year. Superior temporal resolutions result in them having far lower standard errors and are therefore likely to be more reliable than estimates based on only two datasets collected over the course of one year. The second reason is that in the larger river basin scale study, the land was classed into two broad categories, 'intact' and 'disturbed', when the reality is that there are many intermediate land-cover classes, such as secondary PSF within the Sebangau River basin. Should secondary PSF be classed as 'intact' or 'disturbed'? It is perhaps not as 'intact' as the IPSF site nor as 'disturbed' as the DPSF1 and 2 sites. Therefore assigning one of two possible TOC yields to the entire Sebangau River basin land area is likely subject to more error than the sub-catchment investigation in Chapter Three which investigated discrete areas of land subject to the same uniform disturbance (within each land-cover class). This is another reason as to why fluxes observed in Chapter Three should be considered as more reliable estimates of TOC yield than the basin scale derived estimates.

However, given these small differences, the broad agreement in flux estimates for the entire Sebangau River basin derived over contrasting scales provides confidence that the calculated yield estimates for sub-catchments are representative of fluxes occurring at

larger scales. It should also be noted that due to the 'estimated' values being smaller than the 'actual' values, all extrapolations performed should be considered conservative.

6.5.2 Sub-catchment vs. Regional scale

To quantify the impact peatland disturbance has had on regional long-term fluvial carbon loss, the TOC yields observed from the sub-catchments (Chapter Three) were applied to land areas of intact and deforested PSF prior to and after peatland disturbance. Industrial plantations were omitted from the calculations as there is no known quantitative data on fluvial organic carbon yield from this land-cover class available, although the $DO^{14}C$ data suggest that these ecosystems may also be highly unstable due to land use change. Given the exclusion of peatlands converted to plantations in the calculations, the estimated increase in regional fluvial organic carbon flux should be considered conservative. To quantify the impact the MRP has had on the long-term loss of fluvial carbon, the appropriate TOC flux estimates were applied to land areas of intact PSF (62.5 g C m^{-2} yr^{-1}) and disturbed PSF (118 g C $^{-2}$ yr^{-1}) both before and after ('pre' and 'post') the development of the MRP (table 6.3). It is estimated that the total area of intact PSF in the MRP area (defined as 'Blocks A to E' and the area between the River Sebangau and River Katingan) decreased from ~15,600 km^2 in 1991 (four years prior to the MRP) to ~11,100 km^2 in the year 2000 (post-MRP; Boehm & Siegert, 2001). It is therefore estimated that the conversion of intact PSF to disturbed PSF in the MRP area during this 9 year interval, resulted in a 25% increase in TOC loss, from 0.98 Tg yr^{-1} in 1991 to 1.23 Tg yr^{-1} in 2000.

The MRP forms part of the ~155,000 km^2 of peatlands that cover Borneo (Kalimantan, Sabah and Sarawak), Sumatra and Peninsular Malaysia (~60% of total peatlands in Southeast Asia). Mietinnen and Liew (2010) estimate that in 1990, approximately 50% (75,810 km^2) of this land area was classed as intact PSF, with 'minor

Table 6.3: Annual TOC fluxes pre and post disturbance at various spatial scales.

Region	Intact area 'pre' (km^2)	Intact area 'post' (km^2)	Disturbed area (km^2)	Total TOC flux 'pre' (Tg)	Total TOC flux 'post' (Tg)	Increase (Tg)
MRP	15,604	11,102	4,502	1.0	1.2	0.2
B, S and PM	75,805†	15,600	60,205	4.7	8.1	3.4
Southeast Asia	121,272††	49,344	71,928†††	7.6	11.6	4.0

MRP = Mega-Rice Project; B, S and PM = Borneo, Sumatra and Peninsular Malaysia; and Southeast Asia = Indonesia, Malaysia, Papua New Guinea, Brunei, Myanmar, Thailand, Vietnam, The Philippines. 'pre'/'post' dates for regions are as follows: MRP, 1991/2000; Borneo, Sumatra and Peninsular Malaysia, 1990/2008; and Southeast Asia, 1990/2008. †Area of remaining intact PSF in 1990 – 48.9% of 155,020 km^2 (data taken from Miettinen & Liew, 2010). ††Area of remaining intact PSF in 1990 – 48.9% of 248,000 km^2 (data taken from Miettinen & Liew, 2010 and Page *et al.*, 2011). †††Area of disturbed peatland (excluding industrial plantations) calculated using actual rates of PSF loss for individual regions (as reported in Miettinen & Liew, 2010 and Hooijer *et al.*, 2010).

or no sign of human activity'. They go on to estimate that in 2008, as a result of anthropogenic peatland disturbance, only 10% (15,600 km^2) of intact PSF remained, which equates to a PSF loss of 2.15% yr^{-1} for the years 1990 to 2008. It is calculated that this conversion of intact PSF to disturbed peatlands since 1990 has resulted in a ~70% increase in the fluvial TOC flux, from 4.7 Tg C yr^{-1} to 8.1 Tg C yr^{-1}.

Excluding Borneo, Sumatra and Peninsular Malaysia, the remaining peatland area in Southeast Asia comes to 93,000 km^2. If 50% of this land area is considered to be intact PSF in 1990, as Mietinnen and Liew (2010) estimate above, and the same rate of annual PSF loss is applied for the period 1990 to 2008, then the fluvial TOC loss (as a result of disturbance to intact PSF since 1990) is estimated to have increased by 5.3 Tg carbon (from 7.6 Tg C yr^{-1} to 12.9 Tg C yr^{-1}). Applying the rate of annual PSF loss observed in Kalimantan, Sumatra and Peninsular Malaysia to all of Southeast Asia, however, may overestimate the total PSF loss as rates are generally greater in these regions compared to elsewhere in Southeast Asia. By applying the actual observed rates of annual PSF loss (0.2 to 1.3% yr^{-1}; Hooijer *et al.*, 2006) to the remaining areas of Southeast Asia (Brunei, Papua New Guinea and the remaining regions in Indonesia) a more conservative increase

in fluvial TOC loss of 4.0 Tg is estimated (table 6.3). Therefore, by up-scaling the observed sub-catchment TOC yields, the annual fluvial TOC loss from peatland that has been subject to anthropogenic disturbance since 1990 in Southeast Asia is estimated to be 11.6 to 12.9 Tg C yr^{-1}. Scaled back to a carbon yield per unit area, this results in an average TOC yield from intact peatland that has been subjected to disturbance (drainage area of 121,272 km^2) of 95.5 to 106 g C m^{-2} yr^{-1}. The lower estimate is considered to be more reliable as this takes into account country-specific rates of PSF loss as opposed to applying one rate of loss to all countries. The 53% increase, alone, in TOC loss from 7.6 to 11.6 Tg (the lower estimate) approximates the entire annual European peatland fluvial TOC flux (4.3 Tg yr^{-1}), estimated using a European peatland area of 292,000 km^2 (Montanarella *et al.*, 2006) and an average fluvial carbon flux estimate of 14.6 g C m^{-2} yr^{-1} (Nilsson *et al.*, 2008; Billet *et al.*, 2010; Koehler *et al.*, 2011). It should be noted, however, that in general, a much larger portion of fluvial carbon is lost in its inorganic form (DIC) in Europe (greater than 60%) compared to Southeast Asia (less than 10%), which is not included in the above flux estimates.

Because the extrapolation carried out thus far only accounts for half of the peatlands in Southeast Asia (as a consequence of Miettinen & Liew (2010) only accounting for 50% in their estimates), it is important to note that 11.6 Tg is not the total annual Southeast Asia TOC loss. Due to the remaining 50% of land being unclassified in terms of land-cover class (simply defined as 'not intact'), it is difficult to apply one yield to these areas in order to estimate a total annual Southeast Asian TOC flux. In the same way that applying the 'intact' yield would underestimate the overall flux, applying the mean 'disturbed' yield would most likely overestimate the overall flux since some of the remaining land could be an intermediate land-cover class, such as secondary PSF. However, applying the mean 'disturbed' TOC yield to the remaining land area is most probably more accurate (as most peatland is subject to some form of disturbance) and when this is carried out, a 'pre' and 'post' disturbance TOC flux of 22.6 and 26.6 Tg yr^{-1} is estimated, respectively. As the same TOC yield value has been applied to the remaining land area, the same increase in

TOC flux is observed (4.0 Tg), but because it is now part of a larger total flux, the percentage increase drops to 18%. Applying the 'intact' yield to the remaining 50% of Southeast Asia peatland area results in a 'pre' and 'post' TOC flux of 15.5 and 26.6 Tg, respectively. Here, a smaller 'pre' disturbance TOC flux and the same 'post' disturbance TOC flux, results in a larger percentage increase of 72%.

Having applied TOC yields that are most likely under and overestimates, a TOC yield of 90.5 g C m^{-2} yr^{-1} (the mean of intact and disturbed land-cover class yields) was applied to the same land areas and 'pre' and 'post' disturbance TOC fluxes of 19.0 and 21.1 Tg yr^{-1} were achieved. Using this mean TOC yield (90.5 g C m^{-2} yr^{-1}) is the most appropriate scenario because 'degraded PSF', 'secondary PSF' and 'low shrub/fern' land-cover classes account for the highest percentages of land area in Miettinnen and Liew's (2010) most recent assessment of peatlands in Southeast Asia. It would be reasonable to expect these types of land-cover classes to produce a TOC yield value of somewhere between intact and disturbed land-cover classes as they are all intermediate classes. The total Indonesian peatland area (206,950 km^2) annual TOC loss estimated from the Sebangau River basin study was 18.2 Tg (Chapter Four). When this value for total Indonesian peatland area is extrapolated to the total Southeast Asian peatland area (248,000 km^2), it increases from 18.2 to 21.8 Tg yr^{-1}. These two values (21.1 and 21.8 Tg), calculated using methods achieved through two different techniques discussed in this study, closely approximate one another and further strengthen the reliability of the findings on both small and large spatial scales.

6.5.3 Caveats

As with all extrapolation exercises, several caveats are noted. The first and most obvious is that TOC yield data from several sub-catchments in Central Kalimantan were used as indicative yields for the entire peatland area of Southeast Asia. Peatlands in different regions are subject to different disturbance types and will inevitably respond to these

disturbances in different ways. This limitation can only be resolved by collecting annual flux data from several different regions which would increase the extrapolation reliability. It should however be noted that the sub-catchments investigated in this study are highly representative of the majority of intact and disturbed peatlands found across most of Southeast Asia as they incorporate a number of different disturbance types; drainage, deforestation and fire. As well as the type, the severity and incidence of any disturbance should also be taken into account. DPSF2, the most intensely drained site investigated might be considered as an extreme because it encompasses the Kalampangan Canal (up to eight meters deep) which was one of the main MRP drainage channels (as discussed in Chapter 2.2.4). However, the 12 km Kalampangan Canal is representative of over 4,500 km of similarly dug drainage channels throughout the MRP and it can therefore be argued that despite its severe drainage depth, it is representative of large areas within the MRP. This is partly the reason why two catchments subject to different levels of disturbance were investigated and the mean of the two estimated TOC yields used for extrapolation exercises.

6.5.4 Oil Palm plantations

One of the largest remaining uncertainties is the TOC flux value from industrial plantations including oil palm and pulp-wood. Indonesia and Malaysia are the world's largest producers of palm oil, accounting for 87% of the global production between them (Basiron, 2007; USDA-FAS, 2010) and oil palm plantations account for a large percentage of the total land area in Southeast Asia. Oil palm plantations account for ~83,000 km^2 in Borneo, Sumatra and Peninsular Malaysia, of which, according to Koh *et al.* (2011) only one-tenth (8,800 km^2) are established on peatlands. However, this estimate only accounted for mature plantations. By including younger plantations (less than 8 years old), Hooijer *et al.*, (2011) estimate the total area of oil palm plantations established on peatlands to be more than double this area (21,500 km^2). Using either estimate implies that, from a regional perspective, the oil palm industry is not the main perpetrator of

peatland deforestation. At the sub-regional level, however, substantial proportions of PSF in North Sumatra (38%), Southwest Sumatra (35%), and Peninsular Malaysia (27%) have been lost to oil palm plantations (Koh *et al.*, 2011). Without any flux data from plantations, it is only possible to hypothesise as to the most likely range of TOC yields they may produce.

In Chapter Three it was established that discharge is the most important variable in controlling the size of TOC fluxes. High concentrations of organic carbon (as would be expected from any peatland catchment) combined with high levels of rainfall and large discharge rates (as would be expected from anywhere in the wet tropical region), will result in a large TOC flux. The reason for higher levels of discharge in DPSF1 and 2 compared to IPSF was the difference in water balance caused by the overlying vegetation and the peatland drainage channels. Oil palm plantations have a dense network of drainage channels, much like those present in DPSF1 and 2. However, these plantations also have more overlying vegetation than is present in DPSF1 and 2 and therefore there are both similarities and differences between oil palm plantations and the disturbed sites investigated in this study. On the one hand, the dense network of drainage channels should enhance discharge by draining the surrounding peatland. On the other hand, the overlying vegetation should increase rates of evapotranspiration and interception, and in doing so reduce the amount of runoff/discharge from oil palm plantations. Therefore it can be deduced that the most likely TOC yield from oil palm plantations is somewhere in between those observed for intact (62.5 g C m^{-2} yr^{-1}) and disturbed (105-131 g C m^{-2} yr^{-1}) land-cover classes. Without estimating a TOC yield value for oil palm plantations, it would be reasonable to assume that the value will exceed the TOC yield for intact PSF and therefore will increase the additional human-induced TOC flux from the region affected. With primary forests being the source of nearly 60% of new plantations established in Southeast Asia between 1980 and 2000 (Koh *et al.*, 2011) and the Indonesian government recently announcing that it aims to double its palm oil production by the year

2020, the carbon implications from land use change of this type and scale are made all the more concerning.

6.6 The fate of fluvial organic carbon

Having quantified the amount of fluvial organic carbon being discharged from tropical peatlands of varying land-cover classes into riverine and marine systems, it is important to understand the processes which may be affecting the organic carbon while it is in transit and which determine where this fluvial carbon is most likely to go next in the carbon cycle. There are three possibilities (pathways): (i) fluvial organic carbon is transported from the water column to sediments via flocculation, incorporation into biological material and sedimentation of POM; (ii) fluvial organic carbon is degraded by a combination of photochemical and microbial processes, leading to its mineralisation and emission of organic carbon as CO_2, CH_4 and CO; and (iii) fluvial organic carbon flows down the river, unprocessed into marine systems.

6.6.1 Global carbon balance of aquatic systems

The schematic in figure 6.5 illustrates the most recent understanding of the quantities of carbon that enter inland waters from land and exit the inland fluvial system as sediments, to the atmosphere and the ocean. It is based on the 'active pipe' hypothesis first devised by Cole *et al.* (2007) which was advanced with the addition of stream emissions by Battin *et al.* (2008) and increased sediment burial by Tranvik *et al.* (2009). With 900 Tg, or 0.9 Pg of fluvial carbon being transported to the oceans annually, 1.4 Pg carbon emitted via outgassing from inland waters to the atmosphere and 0.6 Pg being buried in sediments, the total amount of organic carbon imported to inland waters from the terrestrial environment approximates 2.9 Pg yr^{-1} (Tranvik *et al.*, 2009; figure 6.5). To put these estimates in context, the annual loss to the atmosphere and sediments of 2.0 Pg is similar

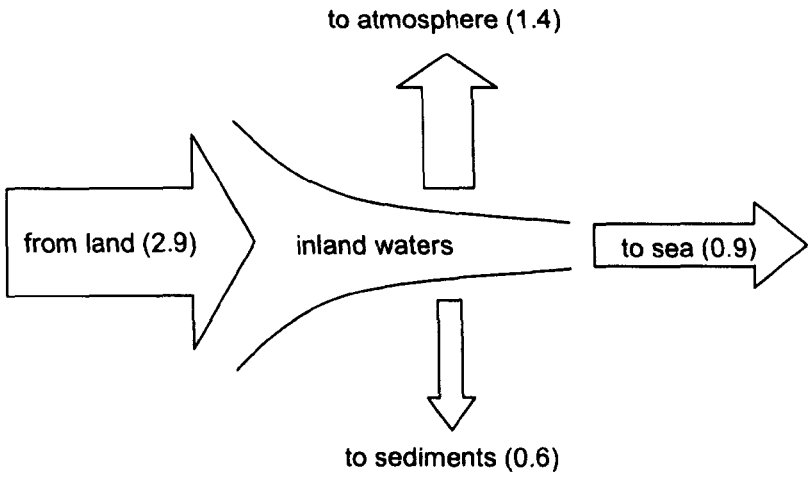


Figure 6.5: Simplified, schematic view of the role of inland aquatic systems in the global carbon balance. Revision by Tranvik *et al.* (2009) of the 'active pipe' hypothesis advanced by Cole *et al.* (2007). Revised values include increased emissions to the atmosphere and increased burial in sediments. Values are in petagrams (Pg).

in size to total global net ecosystem production (Randerson *et al.*, 2002). Further, the annual emissions of carbon from inland waters of 1.4 Pg (which was not previously considered in global carbon budgets), is of the same order of magnitude as annual fossil fuel combustion, carbon emissions caused by deforestation and carbon uptake by the oceans (6.4, 1.6 and 2.6 Pg, respectively; Burgermeister, 2007). It should also be noted that global inland water surface area estimates (used to calculate global carbon emissions to the atmosphere) only consider larger streams and rivers, because it is difficult to estimate accurately the surface area of smaller streams (Battin, 2008). Smaller streams and rivers are therefore excluded, despite being the most reactive in the fluvial network in terms of microbial activity and therefore, most likely the largest emitters of gaseous carbon to the atmosphere (Battin, 2008).

If the estimated values and the ratios between them presented in the global inland water carbon budget are applied to the findings from the Sebangau River basin study (Chapter Four), then it is estimated that 0.72 Tg carbon is emitted to the atmosphere and a further 0.31 Tg carbon buried in sediments. The model therefore implies that more than twice the amount of carbon lost from the mouth of the River Sebangau (0.46 Tg) is either processed

and emitted in gaseous form or buried in sediments while in transit to the ocean (1.03 Tg). This result has significant implications for the total loss of carbon from the Sebangau River basin. For the sub-catchments, it is possible that some of the fluvial organic carbon has been processed within the drainage channels before the water is sampled at the discharge points into the rivers. The River Sebangau is over 150 km in length and water residence time is expected to range from several days to several weeks, depending on flow rates (Haraguchi, 2007). Due to a lack of carbon gas emission data from the River Sebangau, it is not possible to corroborate the estimated outgassing value of 0.72 Tg carbon. However, previous studies have demonstrated that DOC is metabolised continuously throughout fluvial networks in temperate (Raymond & Bauer, 2001; McCallister *et al.*, 2004; McCallister *et al.*, 2006) and tropical (Richey *et al.*, 2002; Mayorga *et al.*, 2005) systems.

Given the warm tropical climate and high levels of solar radiation, the River Sebangau is likely to be subject to considerable amounts of photomineralisation. This process produces CO_2, and where oxidation is not complete, photolysis either enhances or reduces the biodegradability of the remaining DOC (Tranvik & Bertilsson., 2001). Photochemical oxidation in natural sunlight requires days to weeks and with no canopy overhead, and, given the estimated water residence time, there should be sufficient time to process DOC that is in transit in the River Sebangau in this manner.

Nearly all fresh waters contain CO_2 in concentrations that are supersaturated with respect to that of the atmosphere (Aufdenkampe *et al.*, 2011). The partial pressure of dissolved CO_2 (pCO_2) in water in equilibrium with the atmosphere is equivalent to the concentration of CO_2 in the atmosphere, which is currently ~390 parts per million (ppm) (Aufdenkampe *et al.*, 2011). Measured pCO_2 values typically range from 1,000 to more than 12,000 ppm in rivers (Cole & Caraco, 2001; Richey *et al.*, 2002; Johnson *et al.*, 2008; Humborg *et al.*, 2010) and similar values have been recorded in lakes and reservoirs (Sobek *et al.*, 2005; Marotta *et al.*, 2009). Typically, tropical waters exhibit higher concentrations of CO_2 than

temperate waters, with rivers and wetlands containing the highest concentrations of CO_2 (Aufdenkampe *et al.*, 2011). Measured pCO_2 concentrations of 12,000 ppm were recorded in tributaries of the River Kapuas in West Kalimantan which drains a peatland dominated catchment (W. Oechel, 2011, pers comm., 26th March). This implies that the River Sebangau, a peatland fed, tropical river would also have potentially very large water-to-atmosphere CO_2 fluxes.

6.6.2 Metabolic processing of fluvial organic carbon

Metabolic processing of fluvial organic carbon is highest in the headwaters where high densities of diverse microbial communities result in the processing of a broad range of organic molecules (Battin *et al.*, 2008). The outgassing of CO_2 in the headwaters of the Amazon is primarily accounted for by young organic carbon from plant sources (Mayorga *et al.*, 2005). Assuming this is also the case in the Sebangau, the radiocarbon ages would suggest that the processing of young organic carbon from the intact land-cover class is favoured over the older peat-derived organic carbon from the disturbed land-cover classes in this part of the river. Riverine respiration generally declines with increasing distance from the source which is thought to be a consequence of increased DOC recalcitrance following upstream fluvial processing (Battin *et al.*, 2008). However, $SUVA_{254}$ data from the River Sebangau showed no such increase in DOC recalcitrance with distance from source and therefore it is likely that respiration is occurring in the downstream regions of the River Sebangau as well. Isotopic and biomarker analyses have shown that aged terrestrial DOC also makes a significant contribution to the net heterotrophy in rivers and estuaries (Raymond & Bauer, 2001; McCallister *et al.*, 2004; McCallister *et al.*, 2006). This implies that although the majority of DOC lost from the disturbed land-cover classes was from an older peat-derived source, it will most likely be processed at some point within the river as well.

DOC is the most important component of TOC with reference to bioavailability because only low molecular-weight DOC compounds are transported through the microbial cell membrane and subsequently subject to metabolism (Battin *et al.*, 2008). Larger molecular-weight POC compounds must first be hydrolysed by microbial extracellular enzymes, and the resulting DOC molecules can then be subject to microbial metabolism (Battin *et al.*, 2008). With DOC accounting for more than 90% of TOC export from the peatland sub-catchments investigated, as well as the entire Sebangau River basin, the vast majority of fluvial organic carbon is readily available for microbial processing and it therefore follows that large quantities of organic carbon are processed and emitted as gaseous metabolic products from the River Sebangau. In contrast, POC has traditionally been considered old and of low metabolic availability. However, recent research is redressing this perception and now shows that a fraction of this material is more important to net ecosystem metabolism than first thought (Battin *et al.*, 2008). Fresh POC (that is most likely to come from the intact as opposed to disturbed land-cover class) is thought to be consumed quickly and locally without significant transportation downstream. The Sebangau is a low gradient river with low flow rates throughout the year which results in a highly depositional environment. Consequently, transport of POC downstream is probably quite limited with the bulk of it either quickly being consumed or contributing to the organic carbon that is deposited as benthic sediments.

Although no measurements of carbon emission to the atmosphere or burial in sediments are available for the River Sebangau, the environmental conditions present are particularly favourable ones for the processing of large quantities of DOC within the water body. It is feasible that a larger quantity of carbon is processed and emitted to the atmosphere in gaseous form than is estimated as being lost as fluvial carbon at the mouth of the River Sebangau, as is hypothesised in the global scale 'active pipe' model, discussed earlier (Cole *et al.*, 2007; Battin *et al.*, 2008; Tranvik *et al.*, 2009). If this were the case, and emissions of gaseous carbon as well as carbon buried in sediments were

taken into account, the total carbon yield for the Sebangau River basin would increase quite substantially, without changing the observed fluvial organic carbon flux to the ocean.

6.7 Summary and conclusions

- TOC concentrations were highest in the intact land-cover class and lowest in the most severely disturbed land-cover class and showed very little seasonal variation across all sites. DOC accounted for more than 90% of TOC concentration and TOC flux in all sites with the greatest concentration and flux of POC present in both disturbed land-cover classes.

- Annual TOC yields increased with increasing drainage severity, from 62.5 g C m^{-2} yr^{-1} in IPSF to 105 and 131 g C m^{-2} yr^{-1} in DPSF1 and 2, respectively. This represents a 108% increase in TOC export from the intact to the most severely disturbed land-cover class. Higher TOC yields in the disturbed land-cover classes were driven by higher discharge rates which were not counterbalanced by lower TOC concentrations, and occurred despite similar rainfall among the sites. There was no relationship between weekly TOC concentration and TOC flux.

- When including the fluvial TOC loss estimate from DPSF2 (131 g C m^{-2} yr^{-1}), the NEE of the site increases from 433 to 564 g C m^{-2} yr^{-1}. This equates to 30% more carbon lost than previously assumed through gaseous exchange measurements alone and illustrates the importance of including fluvial carbon losses if an accurate assessment on the impact anthropogenic disturbance has on tropical peatland carbon balances is to be achieved.

- Radiocarbon analysis showed that DOC in water draining the intact land-cover class was primarily young, plant derived carbon. In contrast, the DOC in water draining the two disturbed land-cover classes was significantly older and derived from previously stable carbon stored within the peat column. This implies that

DOC does not represent a major loss pathway for long-term stored carbon in intact sites, whereas increased fluxes of DOC being lost from drained sites is depleting a previously long-term store of peat carbon.

- The TOC flux from the River Sebangau to the Java Sea is estimated to be 0.46 Tg yr^{-1}. This equates to a TOC yield over the entire Sebangau River basin of 88 g C m^{-2} yr^{-1}, a figure which exceeds most temperate and other tropical river basins in the world.

- On extrapolating the Sebangau River basin TOC flux to the total peat covered area of Indonesia, a DOC loss of 18.2 Tg yr^{-1} is estimated, which is equivalent to roughly 10% of the global annual riverine DOC discharge into the ocean, a percentage that closely approximates previous published estimates.

- Using the sub-catchment yields observed during the study, it is estimated that since 1990, the conversion of intact PSF into disturbed peatland has resulted in around a 70% increase in the fluvial TOC flux in Borneo, Sumatra and Peninsular Malaysia, and a 53% increase across the whole of Southeast Asia. This increase, alone, approximates the entire annual European peatland fluvial organic carbon flux.

- Qualitative analyses showed no significant differences in the DOC lost between sites. However, it was established that DOC leaching from disturbed peatlands was degraded to a higher oxidative state than DOC leaching intact peatlands. Therefore it can be concluded that the DOC being lost from disturbed peatlands had a higher bioavailability and is more likely to mineralise into CO_2 and H_2O than the more recalcitrant DOC that was lost from the intact site.

- By applying the observed TOC flux from the River Sebangau to the most highly recognized global inland water carbon budget, it is estimated that during transit from terrestrial to marine environments, the River Sebangau emits 0.72 Tg carbon to the atmosphere and buries a further 0.31 Tg carbon in benthic sediments.

These losses combined, more than double the amount of fluvial carbon discharged from the river's mouth into the ocean.

- The findings of this thesis highlight, in the United Nations International Year of Forests, that it is essential to incorporate fluvial organic carbon losses within guidelines for the measurement, reporting and verification of carbon emissions under the United Nations Collaborative Programme on Reducing Emissions from Deforestation and Forest Degradation in Developing Countries (REDD) programme which, on current understanding, may undervalue the benefits to Southeast Asian nations of maintaining and restoring the peatland carbon sink function.

6.8 Recommendations for future work

- Increased sampling resolution via the installation of automated loggers would help to refine TOC fluxes. Given the relative importance of discharge over carbon concentration (which was shown to remain relatively constant throughout the year in this study) in determining TOC fluxes, increasing discharge data resolution should take priority.

- The year during which the investigation was carried out was an 'average' year with respect to rainfall and therefore the results are indicative of 'average' TOC fluxes. However, an extended temporal study over two to three years may reveal cyclic trends over longer timescales and encompass an 'extraordinary' event with respect to rainfall such as El Niño or La Niña. This would allow investigation into the effects of decreased and increased rainfall, respectively, with potential for observing the effects of drought and flooding.

- A diurnal investigation where water samples were collected consistently over 24 hours may reveal greater variation in fluvial carbon concentration and $SUVA_{254}$ values as a result of photochemical oxidation.

- Both disturbed land-cover classes investigated in this study were deforested approximately 15 years ago and drainage is an ongoing disturbance. An investigation into catchments that vary in the number of years since they were last subject to disturbance may expose interesting differences. For example, a study looking at how fluvial carbon dynamics in tropical PSF are affected by large-scale fire events was carried out following the El Niño fires in 2009 (after my PhD field seasons). Data from the six months of monitoring that followed the first rains of the wet season after the 2009 fires demonstrated a large and sustained pulse of fluvial carbon that exceeded values from the preceding year (pre-fire; V. Gauci, 2010, pers comm., May 1st). Once fully analysed, data from this six month fire study may demonstrate that estimates of the impact of anthropogenic disturbance on fluvial carbon loss made during this study are conservative and may be an underestimate when taking into account the immediate short-term impacts following ecosystem disturbance such as a fire event.

- Installation of data loggers at the mouth of the River Sebangau or at least increased sampling resolution from biannual to monthly would help to refine TOC flux estimates from the Sebangau River basin. Currently only three blackwater rivers in Indonesia have been studied. More blackwater rivers in the region should be investigated in order to determine how representative the River Sebangau is and further confine the globally significant export of fluvial organic carbon from Indonesian rivers.

- To address the question of how much fluvial carbon is converted to gaseous carbon a more detailed investigation using the TMAH GC-MS technique should be initiated, looking at qualitative change in DOC from the source to the mouth of the river. Another investigation could involve direct measurements taken from floating

gas chambers. This data could be used to quantify the efflux of CO_2, CH_4 and CO whilst in riverine transit from terrestrial to marine environments in more detail. Pilot studies using these methods on the River Kapuas in West Kalimantan have yielded some interesting initial results that show significant pCO_2 concentrations (12,000 ppm) in the river surface water (W. Oechel, 2011, pers comm., 26th March).

- A more detailed investigation into the fate of the fluvial organic carbon that is not processed on its way through fluvial networks and ends up being discharged into the oceans. This might include use of reprocessed bands of coloured dissolved organic matter (CDOM) from satellite imagery to trace the movement of organic carbon once it enters the marine system (Oney *et al.*, 2011).

- A similar, long-term study that quantifies the fluvial organic carbon fluxes from plantations (in particular oil palm and pulp-wood) would help answer an important knowledge gap, as there is currently no such data available. The study should include monitoring of young as well as mature plantations as differences in quantities of aboveground vegetation may result in different TOC fluxes. Oil palm plantations are of particular interest as the findings from this study suggest that TOC yields could potentially be very high. Given the large proportion of land that is already accounted for by plantations and proposed plans by the Indonesian government for considerable expansion, the consequences of this land use change could have a significant impact on regional, if not global fluvial carbon budgets.

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