WATER QUALITY DYNAMICS IN A LOWLAND TROPICAL CATCHMENT: THE KINABATANGAN RIVER, SABAH, MALAYSIA

By

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A thesis submitted to

The University of Birmingham

for the degree of

DOCTOR OF PHILOSOPHY

School of Geography, Earth and Environmental Sciences

College of Life and Environmental Sciences

The University of Birmingham

February 2013

ABSTRACT

Spatial and temporal trends of dissolved organic matter (DOM) were investigated in the Lower Kinabatangan River, Sabah, Malaysia over the period 2008-2012. The objectives were to: i. quantify DOM in areas of the catchment dominated by oil palm plantations; ii. characterise DOM quantity and quality in waters draining three contrasting land use types (oil palm plantations, secondary forests and coastal swamps); iii. characterise and interpret DOM quantity and quality in the main stem of the Kinabatangan river according to depth; and iv. infer differences in water movement through the catchment. Optical parameters, including fluorescence excitation-emission matrices (EEMs) and ultraviolet absorbance spectroscopy (UV-vis); and Parallel Factor Analysis were used throughout the investigation. The research comprised a preliminary catchment-wide study (225 samples) and concentrated fieldwork campaigns (510 samples). The results indicated the dominance of peaks C and M in waters from the oil palm plantations and coastal swamps respectively. The relative loss of terrestrial derived peaks could indicate progressive DOM degradation from the upper reaches towards the estuary. Results also showed DOM was transported back to the main river, as dominated by fluorescence index peak A/peak C, particularly in the coastal swamps. DOM characterisation with depth in the river, showed the dominance of peaks C and M (relative to terrestrial and microbial and/or photo-degradation processes) in waters near the riverbed.

Untuk Mak dan Abah,

Aishah Pandak Ismail & Harun Saad

To my parents,

Aishah Pandak Ismail & Harun Saad

ACKNOWLEDGEMENTS

Bagaimana sahaya ta'ikat,
Kait-kait dĕngan duri-nya.
Bagaimana sahaya ta'ingat,
Orang baik dĕngan budi-nya.

Could I ever fail to bind,
Lawyer-vine's full of thorny wood?
Could I fail to call to mind,
Persons who are kind and good.[1]

First and foremost, my gratitude goes to my supervisors **Dr. Chris Bradley**, **Prof. Andy Baker** and **Prof. Gilles Pinay**; for their endless support, enthusiasm for the project and kindness that had kept me going.

My appreciation also goes to staff at the School of Geography, Earth and Environmental Sciences (GEES), the Director and colleagues at the Institute for Tropical Biology and Conservation (ITBC), UMS and the organising committees of Chemometrics for Environmental Course II (especially Dr. Colin Stedmon and Dr. Nikoline Juul Nielsen), University of Copenhagen, Denmark for their guidance and help.

Thanks to Mr. Zainal Abidin Jaafar, who had helped me throughout a series of fieldwork. I am grateful to Ms. Asnih Etin and Mr. Baharudin Resake too!

I would like to thank my amazing friends who had supported me all the way: Liz, Zahran, Shahad, Kina, Hana, Eti, Sarah, Renee, Kalsum, Ina, Newati and Sureena. To Diha, Almeezan and Masyhad, I am filled with gratitude for your optimism, support and wonderful friendship for all these years.

I am forever indebted to my family, parents and siblings (Kak Ti, Yang, Amam and Haziq), for their boundless support and always being there for me.

[1] Pantun (pantoum) is a Malay traditional poem equivalent to Japanese Haiku, widely recognised in the Malay Archipelago as one of the classical ways to express feelings courteously. It is characterised by quatrains, often with pleasing assonance; using simple language, nevertheless with deep meaning. The aforementioned pantun was translated by: Hamilton, A. W. 1941. *Malay Pantuns: Pantun Mĕlayu.* Australasian Publishing Co. Pty. Ltd.

I am also thankful to the following institutions and agencies for providing funds and data support: Ministry of Higher Education Malaysia (MoHE), Universiti Malaysia Sabah (UMS), Borneo Marine Research Institute (BMRI), Department of Environment Malaysia (DoE), Sabah Forestry Department (SFD), Sabah Wildlife Department (SWD) and Sabah Biodiversity Centre (SBC).

And finally, to those who had helped me directly or indirectly in this journey:

Tĕrima kaseh. **Thank you.**

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δ^2H	hydrogen isotope
$\delta^{18}O$	oxygen-18 isotope
AB	Abai
AB1 / ABA	Balat Damit
AB2 / ABB	Sg. Merah
BIX	Ratio β/α
BOD	biochemical oxygen demand
BP	Batu Putih
BP1 / BPB	Sg. Pin
BP2 / BPA	Sg. Koyah
BP3	BS Mill
BP4	PS Plantation
BP5	Danau Girang Field Centre
BP6-8	Canal 1-3
BPC	Danau Kaboi
BT	Bilit
BT1	Sg. Tenagang Besar
BT2	Sg. Tenagang Kecil
CDOM	chromophoric/coloured dissolved organic matter
C	carbon
CO	carbon monoxide
CO_2	carbon dioxide

CPOM	coarse particulate organic matter
CS	coastal swamps
DA	discriminant analysis
DGFC	Danau Girang Field Centre
DIC	dissolved inorganic carbon
DNA	deoxyribonucleic acid
DOC	dissolved organic carbon (mg/l)
DoE	Department of Environment Malaysia
DOM	dissolved organic matter
EEM	fluorescence excitation-emission matrix
EPR	electron paramagnetic resonance
FI	fluorescence indices
FPC	Flood Pulse Concept
FPOM	fine particulate organic matter
FELDA	Malaysia’s Federal Land Development Authority
FTIR	Fourier-transform infrared
GF/C and GF/F	grades of glass microfiber filter
GMWL	global meteoric water line
HCl	hydrochloric acid
HDPE	high-density polyethlene
HMW	high molecular weight
HIX	humification index
HPI	hydrophilic organic matter
HPO	hydrophobic organic matter

IBRM	Institute of Borneo Marine Research
IFE	inner-filter effects
INWQS	Malaysian Interim National Water Quality Standard
ITBC	Institute for Tropical Biology and Conservation
IUCN	International Union for Conservation of Nature
LMW	low molecular weight
LUCs	land-use changes
MoHE	Ministry of Higher Education Malaysia
MW	molecular weight
NMR	nuclear magnetic resonance
OM	organic matter
OP	oil palm plantations
PARAFAC	parallel factor analysis
PCA	principal component analysis
peak A	humic-like fluorescence (with absorption in UV range)
peak C	humic-like fluorescence (with absorption in visible range)
peak M	microbial-like fluorescence
peak T	tryptophan-like fluorescence
POC	particulate organic carbon
POM	particulate organic matter
POME	palm oil mill effluent
PP	poly-propylene
PSU	poly-sulfone
PTFE	poly-tetra-fluoro-ethylene

PVDF	poly-vinyl-idine-difluoride
RCC	River Continuum Concept
RPM	Riverine Productivity Model
RMWL	regional meteoric water line
$S_{275-295}$	spectral slope coefficient for interval of 275-295 nm
S	south
SE	southeast
SF	secondary forests
SFD	Sabah Forestry Department
SK	Sukau
SK1 / SKB	Sg. Resang
SK2	Sg. Resik
SK3	Kuala Sukau
SK4 / SKA	Malbumi Plantation
SK5 / SKD	Sg. Menanggol
SK6	Gomantong Caves
SKC	Danau Kalinanap
SRNOM	Suwannee River natural organic matter
SUVA	specific ultraviolet absorbance
SWD	Sabah Wildlife Department
TOC	total organic carbon
TSS	total suspended solids
UMS	Universiti Malaysia Sabah
UV	ultraviolet

UVA	ultraviolet of relatively long wavelengths (320 to 400 nm)
UVB	ultraviolet of relatively short wavelengths (280 to 320 nm)
UVC	ultraviolet of relatively short wavelengths (200 to 280 nm)
UV-vis	ultraviolet visible absorbance spectroscopy
V-SMOW	Vienna standard mean ocean water

1. INTRODUCTION

1.1 BACKGROUND

Dissolved organic matter (DOM) exists almost in all aquatic ecosystems, and represents an important source of carbon and other nutrients for aquatic microorganisms (Docherty et al., 2006). DOM can be derived from a diverse mixture of terrestrial inputs; it can be the product of leaching from terrestrially derived particulate organic matter (POM) or produced *in situ* by the instream biota (Bernhardt and McDowell, 2008). Organic matter (OM) is an analogue to organic carbon and is characterised as total, dissolved or particulate organic carbon – TOC, DOC or POC. It also refers to the entire organic molecule and other elements such as oxygen and hydrogen (Thurman, 1985). DOC is defined as organic matter that is smaller than 0.45 µm in size, while POC is larger than 0.45 µm (Fiedler et al., 2008).

Many studies have examined the sources, transport and transformation of DOM, given its significance for aquatic biochemical processes, in controlling the availability of nutrients for living organisms and its importance within the carbon cycle (Alvarez-Cobelas et al, 2010; Klavins et al., 2012; Schelker et al., 2012; Westhorpe et al., 2012; Yang et al., 2012). These studies have found that wetlands act as an important source of DOM to aquatic ecosystems. Some wetlands have the highest concentration of organic carbon observed, and may potentially represent both a carbon sink and/or a carbon source (Junk, 2002; Paola et al., 2011; Yamashita et al., 2010b). However, the environmental

dynamics of DOM within wetlands, particularly in tropical regions, are still poorly understood and have yet to be fully documented.

Wetlands have been defined by the Ramsar Convention as “areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt including areas of marine water the depth of which at low tide does not exceed six metres” (Hollis and Thompson, 1998). Large wetlands represent a complex of permanent aquatic, palustrine, and terrestrial habitats, and in the case of river floodplains and the tidal zone, of large aquatic/terrestrial transition zones that periodically dry out (Junk et al., 2006). Approximately 7 to 10 million km^2, or ~5–8% of the global land surface, is covered by wetlands (Acreman et al., 2007; Esteves, 1998; Mitsch et al., 2010) and of this total, about 30% of the world’s wetlands are found in the tropics (Mitsch et al., 2010; Mitsch et al., 2011). For example, Brazilian wetlands are estimated to cover ~680,000 km^2, and those of Argentina 60,000 km^2 (Junk, 2002). In 1989, the total wetland area in some countries in Southeast Asia were estimated: Indonesia has the largest wetland area (~258,000 km^2); Malaysia (~49,000 km^2); Philippines (~13,800 km^2); Brunei (~1,400 km^2); Vietnam (~58,100 km^2) (Beazley, 1993); Thailand (~25,120 km^2); Myanmar (~58,680 km^2); Singapore (2.2 km^2); Laos (537 km^2) and Cambodia (54,300 km^2) (Scott, 1989). At present the total area of Ramsar wetlands for these countries are: Indonesia (~9647 km^2); Malaysia (~1342 km^2); Philippines (~1320 km^2); Vietnam (~431 km^2); Thailand (~3728 km^2); Myanmar (~3 km^2); Laos (~148 km^2) and Cambodia (~546 km^2) (Ramsar, 2012).

Wetlands in the tropics are characterised by higher rates of primary production and decomposition, given high temperatures and solar insulation, in common with tropical rain forests (Bartlett and Harriss, 1993; Mitsch et al., 2011). Extensive seasonal wetlands are found along the floodplains of large rivers (Junk et al., 2006) including the Amazon and Orinoco (Bartlett and Harriss, 1993). Currently, tropical wetlands are seriously threatened by environmental deterioration which is particularly evident in S and SE Asia where many catchments have experienced rapid land conversion recently: i.e. primary forests and peat swamp forests have been converted to agriculture and especially to oil palm plantations (Atapattu and Kodituwakku, 2008; Junk, 2002; Sidle et. al., 2006) with a considerable reduction in wetland extent. These land use changes have been found to contribute to changes in DOM character by varying rates of microbial carbon uptake, retention and outgassing (Wilson and Xenopoulous, 2008).

Optical parameters have been used extensively to characterise and determine DOM dynamics, and provide additional insight into the biogeochemical dynamics of DOM in tropical rivers. This builds upon the wide use of fluorescence spectroscopy generally over the past 50 years in water research (Fellman et al., 2010; Hudson et al., 2007; Stedmon et al., 2011). It has been used in studies of the composition, concentration, distribution and the dynamics of organic matter derived from different sources. Recent advances in optical technology permit rapid and automated assessment of fluorescence intensity data across vast ranges of excitation and emission wavelengths (Naden et al., 2010).

This thesis presents a comparison of DOM characterisation at the Lower Kinabatangan River catchment, Sabah, Malaysia both spatially and seasonally, with a re-interpretation of theories including the River Continuum Concept (RCC), nutrient spiralling or the flood pulse concept (FPC) (Chapter 2). It is hypothesised that DOM quality will vary spatially, from the catchment headwaters towards the coast. It is also expected that DOM quality will vary according to the different types of land use, where deforestation has caused secondary forests to regenerate, while agricultural activities especially oil palm plantations are permanently cultivated. Sunlight is abundant in the study area throughout the year and therefore it is hypothesised that DOM quality will also vary by season (wet and dry), as affected by factors such as photolysis/photochemical and microbial degradation.

1.2 SIGNIFICANCE OF STUDY

In general, carbon in the biosphere is unequally dispersed across three major reservoirs: terrestrial, ocean and atmosphere (Cole et al., 2007). The conventional carbon cycle illustrates that carbon enters the biological part of the system via photosynthetic assimilation of atmospheric CO_2 (750 Gt C $year^{-1}$), following fluxes from terrestrial ecosystem respiration (Grace, 2004) together with abiotic oxidation to CO_2 in fire and photo-oxidation, as well as outgassing from the inland waters (Cole et al., 2007; Battin et al., 2009). Carbon sequestration in the ocean is mainly controlled by abiotic drivers including organisms, climate, parent material, time and topography (Townsend et al., 2011), compared to biotic pathways (Cole et al., 2007). Since the industrial era, anthropogenic activities

have altered the global carbon cycle significantly (Amon and Benner, 1996; Falkowski et al., 2000; Stanley et al., 2012; Yool et al., 2013). Deforestation has been identified as causing substantial carbon (1.6 Gt C $year^{-1}$) export from the terrestrial sources to the atmosphere (Grace, 2004). Deforestation in the SE Asia from 1990 to 1997 marked a total annual loss of 2.5 million ha (0.8%) (Grace, 2004) and deforestation rate of 1.0% per year between 2000 and 2010 (Miettinen et al., 2011). A detailed study in Borneo by Langner et al. (2007) found deforestation rates of 1.7% per year from 2000 to 2005. However recently, a reduction in rates of deforestation in the tropics as well as forest regrowth have been identified contributed to a decline in CO_2 emissions from deforestation and other land-use changes (LUCs) (Friedlingstein et al., 2010).

The conventional global carbon cycle has led to the recognition of major knowledge gaps, for example apparent imbalances in the global budget (Cole et al., 2007). A characteristic of this generation of models is that the role of inland aquatic environments is seldom explicitly integrated. Inland waters particularly streams and rivers were considered as **conduits**, rather than **sources** of DOC (Moody et al., 2013). This gap is more prominent in the tropical regions, where the carbon cycle is characterised by abundant sunlight (Luizao et al., 2004; Stevens, 2012), greater precipitations (Kumagai and Kume, 2012), high rates of CO_2 uptake and loss as well as small variations in temperature and precipitations (Townsend et al., 2011). In regions with high erosion rates, whole watershed carbon sequestration rates may be underestimated, as research has focused more on carbon accumulation rates in soils and terrestrial biomass (Battin et al., 2009).

Apparent imbalance in the global carbon budget (Cole et al., 2007), poor understanding of DOM dynamics and the uncertainty of biogeochemical fluxes (Grace, 2004), particularly the carbon cycle within wetland ecosystems (Cawley et al., 2012) have led to the introduction of the concept of the 'boundless carbon cycle' (Fig. 1.1) (Battin et al., 2009). This assigns the most recent vertical and lateral carbon fluxes specifically to and from inland aquatic systems (Regnier et al., 2013). Inland waters have been recognised to significantly transport carbon from land to the ocean (Regnier et al., 2013), mainly in dissolved organic carbon (DOC), particulate organic matter and dissolved carbonates (Hope et al., 1994; Mayorga et al., 2005; Schlesinger and Bernhardt, 2013). The role of rivers in the global carbon cycle is typically expressed as the fluvial export of total organic and dissolved inorganic carbon from land to the ocean, while continental sedimentation may sequester large amounts of carbon in wetlands (Richey, 2010). Both natural and anthropogenic activities were linked to carbon export into the inland waters, while the latter has been associated with increased riverine carbon (Hossler and Bauer, 2013). Consequently, urban land use, agricultural activities, building and road construction (Baker et al., 2008) were also found to correlate positively with greater carbon export into the aquatic ecosystems. Hydrological factors such as discharge and runoff have been identified as one of the main drivers of riverine carbon and organic matter fluxes, with increasing exports of POC, DOC and DIC under significantly high hydrologic flow (Alvarez-Cobelas et al., 2010). Other studies have reported different relationships between riverine carbon flux dynamics and discharge: positive (Hossler and Bauer, 2013),

inverse (Wilson and Xenopoulos, 2008) as well as insignificant (Raymond and Hopkinson, 2003).

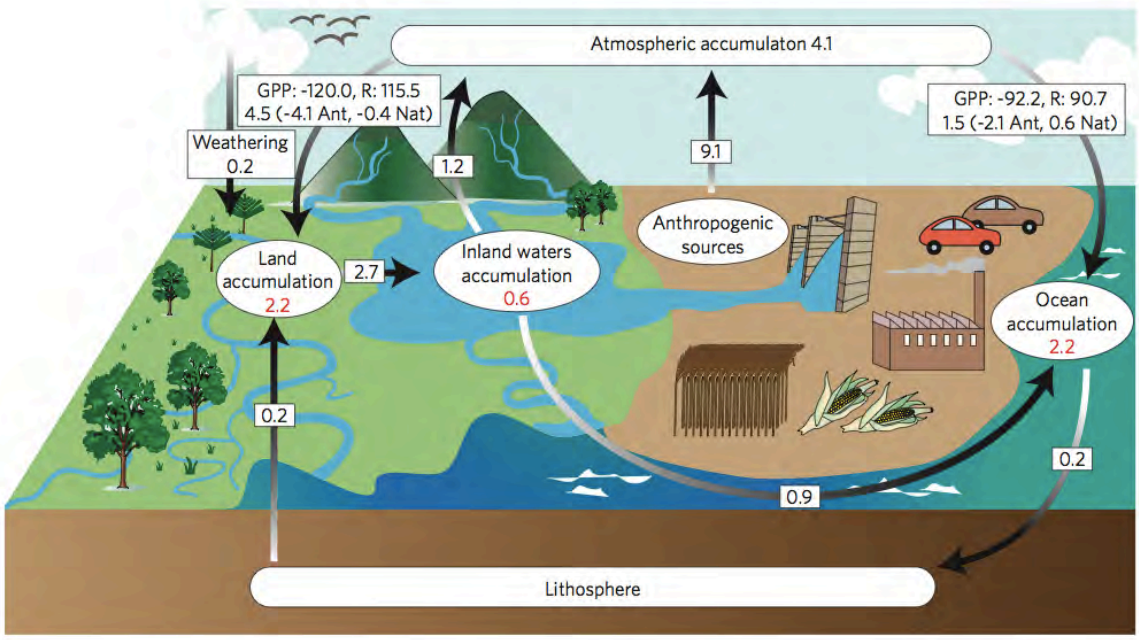


Fig. 1.1 Boundless carbon cycle. Values are net fluxes between reservoirs (black) or rates of change within reservoirs (red); units are Pg C yr^{-1}; negative signs indicate a sink from the atmosphere. Gross fluxes from the atmosphere to land and oceans, and the natural (Nat) and anthropogenic (Ant) components of net primary production are shown for land and oceans (Battin et al., 2009).

Within streams, a variety of processes can alter the export, decomposition or removal of DOC (Stanley et al., 2011). These processes such as photo-degradation and microbial activities are often cited in the literature as research ramifications, although poorly quantified (Moody et al., 2013). The River

Continuum Concept (RCC), nutrient spiralling, Flood Pulse Concept (FPC) and Riverine Productivity Model (RPM) focus on the processes and fate of the nutrients within a river system, however they fail to tackle the fate of individual components of the total carbon fluxes (Moody et al., 2013). In addition, the applicability of the RCC in the tropical forested rivers is uncertain (Greathouse and Pringle, 2006). In the context of this study, which is characterised by high amount of sunlight, precipitation and seasonal variations, the wetland carbon cycle is highly influential in determining the global carbon budgets (Lu et al., 2013). Studies in the Amazon have indicated that surface water and wetlands play important roles in carbon balance (Zhou et al., 2013). Present-day situation of threatened tropical wetlands, affected by rapid land conversion, has aggravated this matter, and recent studies have shown that LUCs affect the amount of, the quality, sources and residence time of DOC in streams and rivers (Lu et al., 2013). Thus, further understanding of environmental controls on riverine carbon fluxes in the tropics such as climate, microbial activities, photo-degradation processes is crucial as anthropogenic impacts substantially affect the total export flux, allochthonous carbon composition and aged carbon composition of riverine POC, DOC and DIC (Hossler and Bauer, 2013).

1.3 SCOPE OF STUDY

This study has been carried out in the catchment of the Lower Kinabatangan River, Sabah, Malaysia. The river has a total catchment of 16,800 km^2 and is 560 km in length. The Kinabatangan is the largest river in Malaysia and covers ~23%

of Sabah. Commercial logging at the Lower Kinabatangan floodplain commenced in the 1960s with development of permanent cultivation, particularly oil palm plantations, from the 1980s to the present. The Lower Kinabatangan floodplain also provides habitat for a unique and endangered flora and fauna. For example, the Proboscis monkey (*Nasalis larvatus*) and Bornean orangutan (*Pongo pygmaeus*) have been listed in the IUCN Red List of Threatened Species (Ancrenaz et al., 2013).

These species have been surveyed periodically and especially during the Lower Kinabatangan Scientific Expedition 2002 (Harun and Mohamed, 2008). A number of studies have been undertaken in the catchment: Harun and Mohamed (2008) identified three categories of research investigation: i. flora; ii. fauna; iii. socio-economic and human dimension and iv. physical science. They include studies of mosses and vascular plants (Suleiman et al., 2003; Gisil et al., 2003) butterflies (Jalil et al., 2003), fireflies (Dawood et al., 2003), primates (Ancrenaz et al., 2003; Boonratana, 2000; Jalil et al., 2003; Matsuda et al., 2009) and pygmy elephants (Alfred et al., 2012). Physical science investigations include studies of water quality (Harun, 2006; Jawan, 2008), land use change (Josephine et al., 2004; Mansourian et al., 2003; Morel et al., 2011) and a geological survey (Tongkul, 1991). The latter study reported that this area has undergone the third episode of rock deformation (from five episodes of the whole area of Sabah), which was associated with the imbrication of the Eocene-Lower Miocene sediments and underlying sediments during the Late Oligocene-Middle Miocene age (Tongkul, 1991).

This area has been chosen for the current investigation due to the significance of the Kinabatangan catchment as one of the most significant habitats for many unique and threatened species that are still found despite the extent of environmental deterioration experienced in the region. In 2008, the Lower Kinabatangan-Segama Wetlands were gazetted as a Ramsar site (Fig. 1.1). This site covers ~78,800 ha of wetlands and intertidal forests: Trusan Kinabatangan Mangrove Forest Reserve, Kulamba Wildlife Forest Reserve and Kuala Maruap and Kuala Segama Mangrove Forest Reserve (Sabah Biodiversity Centre, 2011). Sabah Biodiversity Centre (2011) has identified a number of problems that could potentially affect its integrity as one of the Ramsar sites: logging, soil erosion and loss of wildlife (at the upper area); agricultural impacts include water quality deterioration, habitat loss, soil erosion, oil palm plantations and oil palm mills (in the lower part of the catchment). Here mangrove areas and peatlands are known to be very important due to their ability to retain high quantities of carbon in their soils (Alkhatib et al., 2007). The Kulamba River Basin also potentially plays a significant role in supplying subsurface water storage to preserve the wetland ecosystems (Sabah Biodiversity Centre, 2011).

Fig. 1.2 Satellite image of Lower Kinabatangan-Segama Wetlands (Google Earth, 2012).

The general aims of the study presented in this thesis are:

i) to develop an understanding of fluorescence spectroscopy and isotopic data in order to characterise the DOM of a degraded tropical river and its spatial and seasonal variation;

ii) to develop techniques for the use of fluorescence spectroscopy as a tool to determine the main factors affecting DOM quality in tropical regions;

iii) to evaluate data mining techniques for fluorescence data analysis and information extraction;

iv) to compare the use of fluorescence spectroscopy with the standard DOM characterisation tools (e.g. DOC and UV-vis).

Specifically, this study intends to achieve following objectives:

Objective 1: To quantify DOM in areas of land where the land use is predominately oil palm plantations using optical parameters as a tool.

Objective 2: To characterise and interpret the DOM quantity and quality in waters draining three different land use types (oil palm plantations, secondary forests and coastal swamps) and examine the effects of seasonal variability (wet and dry seasons).

Objective 3: To characterise and interpret both DOM quantity and quality of the Kinabatangan main river according to depth and seasonal variability (wet and dry season).

Objective 4: To infer differences in the pattern of water movement through the catchment using fluorescence as a tool, from three different types of land use (oil palm plantations, secondary forests and coastal swamps) and two types of seasonal variability (wet and dry).

1.4 THESIS STRUCTURE

The thesis comprises eight chapters. Following this introductory chapter (Chapter 1), a literature review is presented in Chapter 2, which summarises a selection of the literature on the processes associated with DOM source and uptake specifically within tropical river systems. The following topics are elaborated from the literature findings: the sources, uptake and loss of DOM within stream systems (section 2.2), DOM in aquatic ecosystems (section 2.3), spatial and temporal trends: DOM quality (section 2.4), DOM biogeochemistry in large tropical rivers (section 2.5), and finally the effect of land use changes on DOM in tropical regions (section 2.6).

Chapter 3 presents a detailed background to the study area (section 3.1), the application of fluorescence spectroscopy (section 3.2) and analytical procedures in the laboratory (section 3.3). Pre-processing of fluorescence data is described in section 3.4 and section 3.5 presents post-processing data by applying Parallel Factor Analysis (PARAFAC) and discriminant analysis (DA) in this study.

Results from the study are covered in three chapters. Chapter 4 presents the results from a preliminary survey that was conducted from August to September 2008. Chapter 5 gives the results from a more detailed sampling

programme, which was undertaken from October 2009 to May 2010. It also presents the DOM composition in terms of spatial and temporal variations. Chapter 6 examines DOM spatial and temporal variations in the main stem of the Kinabatangan River with depth. Chapter 7 summarises the main findings of this research, before the concluding chapter (8). Appendix A presents the comparison between the PARAFAC analysis with excitation wavelength at 250-nm and 290-nm as clarified in section 3.5, while some of the isotopic data in Chapter 4 was presented in Appendix B.

2. ORGANIC MATTER IN TROPICAL FRESHWATER ECOSYSTEMS

2.1 INTRODUCTION

Organic matter (OM) is a dynamic and heterogeneous mixture of chemical compounds that is widely present in terrestrial and aquatic environments: in soil-water, groundwater, lakes, wetlands, estuarine and marine systems, and has an important role in biogeochemical processes (Richey, 2005). Aquatic OM is generally classified according to size fractions (Mayorga and Aufdenkampe, 2002): coarse particulate organic matter (CPOM) (63 μm to ~2 mm), fine particulate organic matter (FPOM) (~0.5 to 63 μm), and dissolved organic matter (DOM) (<0.5 μm) (Richey, 2005). CPOM is commonly derived from riparian vegetation in headwater streams (Johnson et al., 2006; McDonald et al., 2004; MacDonald and Coe, 2007) and can alter the sources of food available within streams (Mendoza-Lera et al., 2012), while FPOM and/or other sources is produced from invertebrate grazing in aquatic ecosystems. DOM is the dissolved fraction of organic matter (McDonald et al., 2004), and makes an important contribution to aquatic food webs, mediating the availability of metals as well as dissolved nutrients (Cawley et al., 2012), and altering light attenuation through water bodies (Findlay and Sinsabaugh, 1999; Pisani et al., 2011). DOM also represents the major type of OM in nearly all aquatic ecosytems (Cawley et al., 2012; Findlay and Sinsabaugh, 1999; Jorgensen et al., 2011). It results from the breakdown of bacterial, algal and higher plant organic material (Cory and McKnight, 2005), while DOM bioavailability depends upon its chemical

composition as reflected by molecular weight and the fraction of protein-like substances (Yang et al., 2012).

Riverine DOM and particulate organic matter (POM) play important roles as heterotrophic substrates (Vannote et al., 1980). In natural water bodies, DOM alters surface water acidity and affects metal speciation as well as ion-exchange between water and sediment phases (Hope et al., 1994; Hudson et al., 2007). DOM also represents a major source of reduced carbon to oceans globally (Richey, 2005). The transfer of OM from terrestrial to marine environments has been identified as the most important pathway responsible for retaining terrigenous production, and hence a main component in the global carbon cycle (Richey, 2005). As OM is transferred from terrestrial to marine environments, it is affected by nutrient spiraling within water bodies particularly in rivers and streams. Here streams can be visualised as the interface between aquatic systems and terrestrial as well as the channel that exports OM and associated constituents to the ocean (Findlay and Sinsabaugh, 1999).

The critical importance of DOM in environmental processes of many regions has been widely discussed in the literature, although studies in the tropics are scarce (Al-Shami et al., 2011; Yule et al., 2010). DOM represents a significant source of energy particularly in stream ecosystems (Hood et al., 2003; Hope et al., 1994), affecting organic pollutant transport, chemistry of surface and colloid particles, and hence nutrient availability and the photochemistry of natural waters in freshwater aquatic systems (Fellman et al., 2008; Hope et al., 1994). DOC has also been found to provide an important link in the microbial loop; it

limits ultraviolet (UV) light penetration and thus affects oxygen concentration (Gondar et al., 2008; Thomas, 1997). This is particularly important in the tropical regions where high amount of sunlight are received throughout the year, thus increasing microbial activities in water bodies (elaborated further in section 2.4). The significance of DOM in this area is highlighted by its role as a carbon sink especially in tropical wetlands. However, degradation of environmental quality in tropical freshwater ecosystems is becoming crucial having been aggravated in recent years by the conversion of tropical forest to areas of cultivation. For example, in Asia, successful economic growth and industrialisation, as well as catchment degradation, has led to environmental problems including land, air and river pollution (Al-Shami et al., 2011; Yule et al., 2010).

Fluvial channel and networks have been recognised as optimising their state to transport water and sediments most efficiently (Battin et al., 2009; Spencer et al., 2012). Richey (2010) suggested that fluvial systems incorporate both hydrological and biogeochemical cycles at different scales from small streams, to regional, and to major basins in the world. Fluxes mobilisation from land to ocean have been interpreted using a number of theoretical concepts from different perspectives. These provide a context for improving our understanding of carbon transportation as described below:

The River Continuum Concept (RCC) provides a framework for understanding these processes. The RCC was introduced by Vannote et al. (1980) and hypothesises that a continuous gradient in physical conditions exists from the catchment headwaters to mouth. The RCC views the river network as

the product of a constantly incorporated series of physical modifications and resource gradients to which the biota and ecosystem processes adjust. Importantly, however, a hypothetical river system in a temperate forest basin was used to illustrate the RCC (Sedell et al., 1989), and the applicability of the RCC to tropical forested rivers is at present uncertain (Greathouse and Pringle, 2006; Winterbourn et al., 1981). For example, Greathouse and Pringle (2006) studied a tropical stream in Puerto Rico and found that the source of allochthonous DOM from macroinvertebrate grazing followed a trend opposite to that predicted by the RCC, although basal resources suggest that its patterns is compatible with the RCC.

Another theory, related to nutrient spiralling and outlined by Newbold et al. (1981), has been used as a tool for investigating solute biogeochemistry in streams (Lutz et al., 2012) especially during the most biologically active periods (Fisher et al., 2004). The nutrient spiralling concept develops the RCC concept by describing the cycling of nutrients as they are removed from water, rapidly integrated and then released back to water bodies by mineralisation, and the resulting material cycle takes the shape of a spiral, oriented parallel to stream flow. The length of the spiral correlates to the average distance an atom travels downstream in one cycle and depends on cycling rapidity, as well as the retentiveness of the ecosystem (Battin et al., 2008; Fisher et al., 2004). Bernhardt and McDowell (2008) are among a number of studies that have applied spiralling theory in their work in comparing DOM uptake during litter leachates releases in Hubbard Brook Valley streams in New Hampshire in 1979 and 2000.

The Flood Pulse Concept (FPC), was presented subsequently in 1994 (McDonald et al., 2004; Junk et al., 1989), and focuses on the flood pulse that links the river channel to the floodplain, which has been recognised as the main driving force for river-floodplain ecosystems. Flood pulses may differ in length, depth, frequency and formation (Junk, 2012). The FPC predicts that the OM derived either directly or indirectly, from floodplain production, and not from upstream sources, can also be described by the nutrient spiralling concept (Battin et al., 2008). Junk (2012) suggests that most tropical South American wetlands are mainly flood-pulsing systems, which fluctuate between a terrestrial and an aquatic phase. FPC modifies primary and secondary production, and affects decomposition and nutrient cycles in water as well as soils. It helps the organisms to make an adjustment in the switch between the aquatic and terrestrial phases, enhancing their ability to effectively make use of periodically available resources. In terms of an estuarine delta, this concept showed that sediment deposits in Mississippi Delta, which have been transited at the leeves ranged from older wood-peat deposits to younger riverine fluvial deposits (Day et al., 2007; Twilley and Rivera-Monroy, 2009). Coarser sediments accumulate at the river mouth and as the delta advances, sand is shifted horizontally to create beach ridges (Day et al., 2007), suggesting riverine deposits were controlled by the tidal effect, exporting sediments back to the river.

Recently, both the RCC and FPC have been challenged by the Riverine Productivity Model (RPM), which was introduced by Thorp and Delong (1994). The RPM proposes that large amount of autochthonous sources, particularly phytoplankton which is produced in the upper river reaches, is recalcitrant, and

that consequently represent less significant sources of energy, compared with allochthonous inputs and labile material that are produced in-stream (Tank et al., 2010; Thorp and Delong, 1994). Even though this model was originally proposed to fit highly regulated river systems that are completely sequestered from their floodplains (Bunn et al., 2003; Tank et al., 2010), Thorp and Delong (2002) later suggested that RPM could also be applied to floodplain and unregulated rivers.

2.2 SOURCE, UPTAKE AND LOSS OF DOM WITHIN STREAM SYSTEMS

Streams in general integrate between terrestrial and aquatic systems and a channel that in time transports organic matter as well as associated elements to the ocean (Findlay and Sinsabaugh, 1999). Terrestrial substances in river systems are mainly derived from small streams, due to the integration of land-water. At this spatial scale, processes can change quickly, which contribute to dynamic chemical conditions in the stream (Ward et al., 2012). Inputs from soils and terrestrial leaf litter are normally the primary source of stream DOM to the streams (Findlay and Sinsabaugh, 1999). Terrestrial leaf litter includes a combination of varied DOM that reflects plant composition and microbes as well as animal products in assorted stages of decomposition (Wetzel, 2001).

DOM is derived from a variety of sources: both allochthonous and autochthonous (Cawley et al., 2012; Lutz et al., 2012) as well as from anthropogenic activities (Hudson et al., 2007). Allochthonous sources of DOM include plant decomposition, dead POM and soil leaching (Cawley et al., 2012; Findlay and Sinsabaugh, 1999; Thurman, 1985), while DOM can also be

generated in situ i.e. autochthonous DOM by living aquatic organisms (bacteria, phytoplankton, microalgae). DOM in soils is mainly derived from organic-rich mineral horizons and litter layers and the upper (Kalbitz and Kaiser, 2007); whereby organic-rich horizons are normally dominated by extractable humic acids and decrease with depth soil profile (Fellman et al., 2009). Anthropogenic DOM sources include wastewater effluents, agricultural runoff (Hudson et al., 2007; Johnson et al., 1995) and industrial discharges (Baker et al., 2008).

Autochthonous DOM inputs, including algal productivity and macrophyte shredding and grazing by invertebrates (Pollard and Ducklow, 2011; Tank et al., 2010) are important contributors to the total pool of OM in the majority of aquatic ecosystems (Bertilsson and Jones, 2003) (Fig. 2.1). Autochthonous DOM in general consists of amino acids, with different amount of carbohydrates, carboxylic acids, alcohols, sterols, hydrocarbons, ketones, pigments, and ethers. These, in conjunction with anthropogenic organic pollutants, form the remaining DOM pool (Thurman, 1985). Carbon loss is an inevitable result of carbon fixation in the course of primary production, and hence diurnal fluctuations in DOM concentration are common (Findlay and Sinsabaugh, 1999; Johnson et al., 1995). Autochthonous pathways to the freshwater ecosystems are affected by light intensity and nutrient deficiency when under nutrient limitation and sufficient light, phytoplankton will release high amount of DOM (Parker, 2005; Solomon et al., 2008).

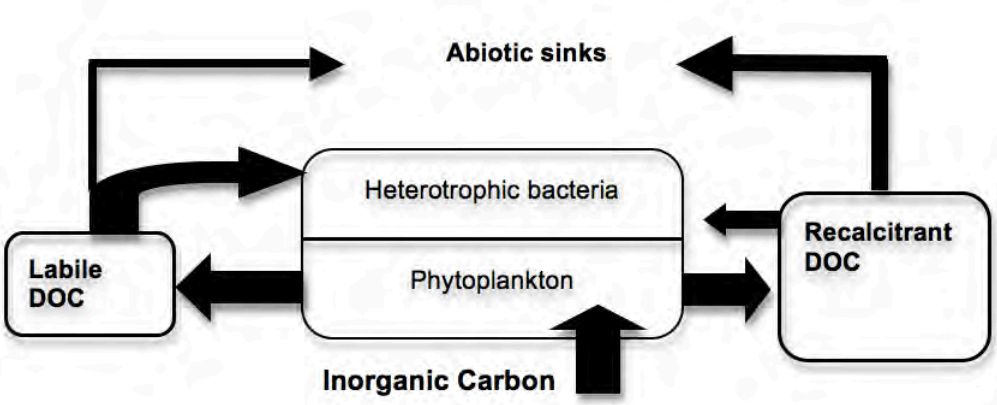


Fig. 2.1 Relationship between biological availability of autochthonously produced DOM (labile/recalcitrant) and: (i) concentration *in situ;* (ii) uptake by heterotrophic microorganisms. Box sizes indicate concentrations volume, whereas arrow thickness show transformation rates (Bertilsson and Jones, 2003).

Allochthonous inputs of DOM to stream systems have a significant impact on aquatic chemistry and biology (Aitkenhead-Peterson et al., 2009). For example, many studies have considered terrestrial leaves to be the main allochthonous source of DOM (Wetzel, 2001). Leaf litter supplies an important energy source, which is colonised by bacteria, and fungi as well as invertebrates (McDowell, 1985; Findlay and Sinsabaugh, 1999). Other sources of allochthonous DOM include soil leaching, seepage from wetlands (Bradley et al., 2007), microbial reworking of adsorbed organic carbon and degradation of terrestrial vegetation (Tank et al., 2010). Allochthonous sources have been recognised as one of the largest contributors to riverine OM (Riggsbee et al., 2008). The quality and quantity of allochthonous DOM can be broadly related to landscape, vegetation, hydrology, and climate (Bradley et al., 2007; Evans et al., 2005). In most cases, allochthonous DOM inputs are associated with advective water transport through the catchment (Aitkenhead-Peterson et al., 2003). Input

from these sources thus makes allochthonous DOM refractory and humified, with a high molecular weight and aromatic fraction (McKnight et al., 2001). The increased presence of lignin from terrestrial OM can be related to 'fresh' OM which has high hydrophobicity (Klavins et al., 2012). Although allochthonous inputs in forested areas (litter inputs) have received less attention in tropical regions (Findlay and Sinsabaugh, 1999; McDowell, 1998), DOC biogeochemistry in tropical forested ecosystems has been found to be similar in many respects to that observed in temperate forests (Greathouse and Pringle, 2006; Johnson et al., 2006; Wantzen et al., 2008).

Terrigenous DOM, which is one DOM anthropogenic input, is constantly discharged by rivers to marine environments (Gueguen et al., 2005; Opsahl and Benner, 1997). In terms of terrigenous DOM transportation, globally rivers transport an estimated 0.25 Pg C (1 Pg = 10^{15} g = 1 gigaton) DOC to the ocean annually (Baker and Spencer, 2004; Bianchi et al., 2004; Stubbins et al., 2010). However, it has been suggested that little of this carbon subsequently accumulates in the ocean (Cole and Caraco, 2001; Opsahl and Benner, 1997). It has been speculated that some of the carbon is decomposed in the river itself (Cole and Caraco, 2001). From a catchment perspective, up-stream sites that receive inputs of more terrestrially derived DOM generally have higher DOC concentrations (Dalzell et al., 2009; De La Cruz, 1986; Mayorga et al., 2005). DOM transport through the catchment is mainly controlled by factors including water pathways and flux (Klavins et al., 2012; Schelker et al., 2012; Stanley et al., 2011), salinity (Hansell et al., 2004; Huguet et al., 2010), temperature, (Tremblay et al., 2005; Xu and Saiers, 2010), phytoplankton biomass, light penetration and

depth of mixing (Findlay et al., 1991; Romera-Castillo et al., 2010; Westhorpe et al., 2012). DOM in downstream sites will frequently be hydrologically controlled by rapid transport especially in large rivers (Findlay and Sinsabaugh, 1999). These factors, however, are complicated by the complex nature of riverine systems, varying with climate, geology, hydrology and anthropogenic impacts, including dams and changes in land-use (Warnken and Santcshi, 2004). Riverine transport of DOM from land to sea modifies the biosphere and represent a key link in the global cycles of bioactive elements (Pérez et al., 2011).

Increased DOC concentration has been correlated positively with increased water fluxes (Schelker et al., 2012). For example, in the UK DOM has been found to increase for varying hydrological pathways (Worrall and Burt, 2004). It has been demonstrated that increased flow can intensify DOC concentration and flux by modifying water flowpath, with increasing runoff throughout shallow and organic-rich soil horizons (Wiegner et al. 2009), corresponding to extensive mineral horizons in relation to high DOC adsorption (Cronan and Aiken, 1985; McDowell and Likens, 1988). Worrall and Burt (2004), however, concluded that DOC trends could not readily be explained by trends in various factors such as pH, alkalinity, turbidity, conductivity as well as water flow.

Temperature and salinity are known to affect the solubility of hydrophobic compounds in water and to alter OM structure (Tremblay et al., 2005). Dai et al. (2012) found that a trend of increasing riverine DOC is likely to be caused by an increase in temperature. Thus, the observed trend of DOC in the UK suggests that DOC might increase as a result of rising temperatures as well as a decrease

in acid deposition (Evans et al., 2005). However, an inverse correlation between DOC and salinity has been observed by several studies. For example, Moore et al. (2011) reported that DOC concentrations in Kalimantan, Indonesia are correlated negatively with salinity. A similar type of DOC-salinity relationship has been reported by Baum et al. (2007) for Sumatra. Significant negative correlations between DOC concentration and salinity were reported by Guo et al. (2004) suggesting that water mixing is significant in controlling the total DOC transport in the water column, even though biological processes also important in DOC production and decomposition.

Phytoplankton biomass, light penetration and depth of mixing have been found to correlate closely in aquatic ecosystems (Westhorpe et al., 2010). Phytoplankton is one of the main sources of DOM and is released to the water column by cell break down (Romera-Castillo et al., 2010). Light penetration is greatly decreased in situations of high turbidity, which may be potentially derived from an increase in humic acids and too much light penetration may reduce phytoplankton biomass, as well as DOM (Romera-Castillo et al., 2010; Westhorpe et al., 2012). An increase in bacterial growth has also been identified as positively correlated with a decrease in phytoplankton productivity. This suggests that a variation in DOM supply can lead to compositional shifts in plankton communities within relatively short periods (Westhorpe et al., 2010; Westhorpe et al., 2012). Degradation of phytoplankton has been shown to cause an increase in terrestrial DOM, suggesting this type of DOM could be resistant to biodegradation (Ishii and Boyer, 2012). In terms of depth, phytoplankton production tends to decline with increasing depth. However, accumulation of

phytoplankton also may increase as a result of reduced water turbulence (Solomon et al., 2008). Fig. 2.2 summarises the composition, processes and the interactions that affect the DOM transport.

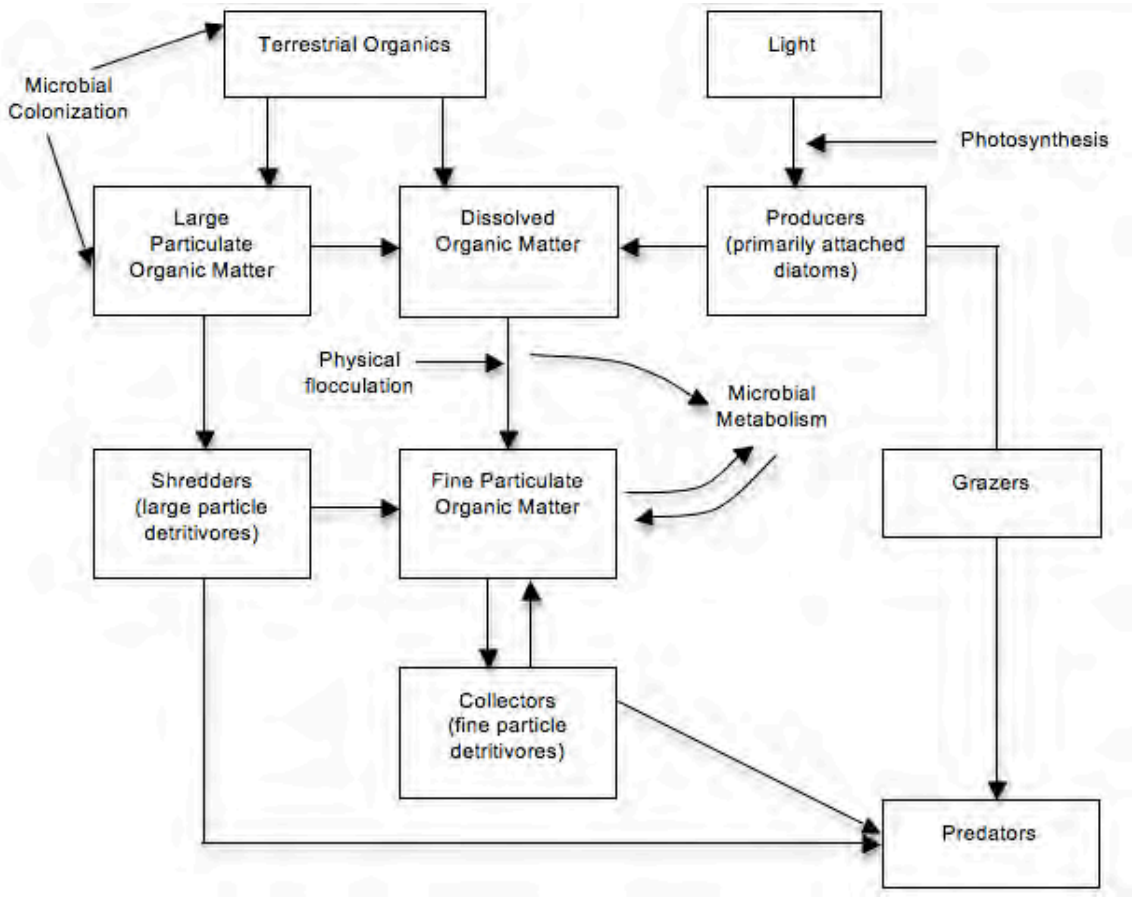


Fig. 2.2 Conceptual diagram highlighting the stream ecosystem structure and function emphasising the supply, composition, metabolism, and transport of DOM (after Cummins et al., 1972).

2.3 DOM IN AQUATIC ECOSYSTEMS

Humic substances has been identified as the main fraction of DOM in aquatic ecosystems and generally constitute between 40 to 75% of total dissolved organic carbon (DOC) (Findlay and Sinsabaugh, 1999; McKnight et al., 2001; Moore et al., 2011; Rocker et al., 2012). Humic acids are non-volatile, and range in molecular weight from 500-5000 Da with elemental composition of ~50% carbon, 4-5% hydrogen, 35-40% oxygen, 1-2% nitrogen and <1% sulfur plus phosphorus (Thurman, 1985). Colloidal organic matter is the other main fraction (0.45 to 0.1 nm) comprising approximately 20% of the bulk DOM pool (Chow et al., 2005; Moore et al., 2011). This DOM is composed of particles that are not significantly affected by gravity (Dodds, 2002). Colloids in general consist of organic and inorganic materials, and biological cells (Lead et al., 2005) with relatively high molecular weight (>1000 Da) (Guo and Santschi, 1997). The colloidal organic matter pool as a whole is still poorly understood and their characteristics largely remain unknown (Guo and Santschi, 1997; Lead et al., 2005).

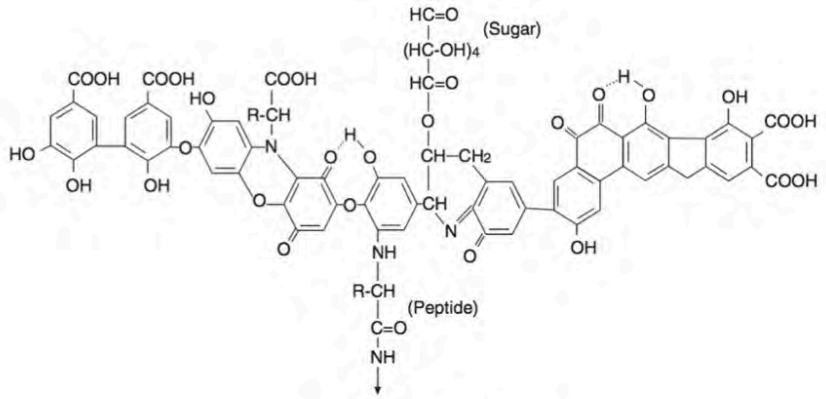
Humic acids are responsible for the dark colour of tropical blackwater rivers (Moore et al., 2011), and humic substances have been found to serve as electron acceptors, and thus influence DOM degradation (Sinsabaugh and Findlay, 2003). Humic substances are mainly formed as a result of microbial activity on plant material (Wetzel, 2001) in the process termed humification (McDonald et al., 2004). Although a large proportion of the reactions responsible for the formation of humic substances remain unknown (van Geluwe et al., 2011),

it has been suggested that they form directly either from i). lignin tissues of plant material (can also occurs in plants without lignin); or ii). the polymerization of noncomplex low molecular weight (LMW) products composed in the degradation of macromolecules degradation processes (McDonald et al., 2004). It has been proposed that the degradation of lignin tissues in plants occurs via two mechanisms: i) lignin is incompletely degraded into smaller compounds such as phenols, methoxyl groups and carboxyl groups (Garcia-Perez et al., 2010); ii) lignin is degraded to generate polyphenols which then undertake enzymatic oxidation to quinones, and polymerise to form humic substances (Li et al., 2012). Polymerization of monomers may occur from degradation of macromolecules that are more resistant to microbial degradation. For example, one of the main components of monomers, polyphenols, are synthesised by microbes and released in lignin degradation. Polymerization is increased in situations of high availability of clays, metal oxides and transition metals in the aqueous solution (McDonald et al., 2004).

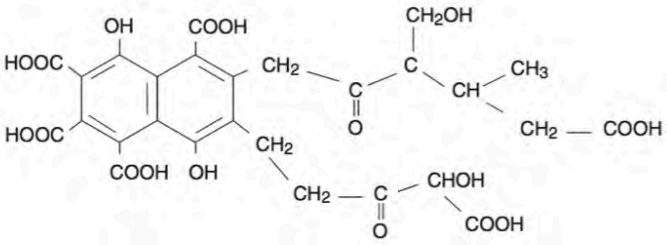
Humic substances can be further subdivided into three categories, according to their solubility at different pHs: humic acids are insoluble at pH <2, nevertheless soluble at higher pH; fulvic acids are soluble at all pH conditions; whilst humins are insoluble at any pH (Hope et al., 1994; Hudson et al., 2007; Mobed et al., 1996). Fulvic acids are typically the major fraction, accounting for approximately 45-65% of DOC (McKnight et al., 2001, Roe et al., 2008) and including a greater extent of aromatic groups, such as methoxyls and phenolics (Aitkenhead-Peterson et al., 2003). Fulvic acids can be subdivided into hydrophobic (HPO) and hydrophilic (HPI) acids (Aitkenhead-Peterson et al.,

2003; Roe et al., 2008). It has been found that humic acids are more hydrophobic acids than fulvic acids, which is related to their higher molecular weights (2000-5000 Da), which contain the majority of the carboxyl groups and sequentially have longer chain fatty acid products (Mobed et al., 1996; Thurman, 1985).

The different structures of individual humic substances are a result of the interactions between a range of small organic compounds released in the course of the metabolism of natural macromolecules (Dolgonosov and Gubernatorova, 2010). Humic substances are characterised by structures, which may exist either in microorganisms and plants or in their decay products (McDonald et al., 2004). The main chemical components of plant litter are phenolic compounds (e.g. lignins and tannins) (Klotzbucher et al., 2011), water-soluble compounds (e.g. ether-, amino and aliphatic acids, sugars) (Badri et al., 2009), alcohol-soluble compounds (e.g. proteins, oils, fats, waxes, pigments and resins) (McDonald et al., 2004), hemicellulose (non-cellulosic polysaccharides) and cellulose (Papa et al., 2008). Other chemical classes of plant litter that were initially thought to be recalcitrant and hence, could potential form part of humic substances include: suberins, carbon black, cutans, algaenans, and sporopollenins which have been found in the outer walls (cuticles) of plants (Shechter et al., 2010) and a number of microalgae (McDonald et al., 2004). Consequently, microbial processes may produce compounds such as carbohydrates, lipids, melanins, other polyketides and proteins (Burdige, 2007; McDonald et al., 2004). A summary of the chemical structure of humic and fulvic acids, which includes the relative amounts of aromatic and saturated moieties, is provided in Fig. 2.3.



(a) Theoretical humic acid



(b) Theoretical fulvic acid

Fig. 2.3 Theoretical structures of humic and fulvic acids (after Hudson et al., 2007).

Due to the complex nature of humic substances, their chemical structure is difficult to determine (McDonald et al., 2004). Chemical structure of humic substances are generally characterised according to chemical properties in terms of macromolecular size and weight (Abbt-Braun et al., 2004; Thurman, 1985), spectroscopic techniques (Chen et al., 2003), hydrophobic characteristics and acidic functionality: hydrophobic acids, bases and neutrals; hydrophilic acids, bases and neutrals; and transphilic OM (Leenheer and Croue, 2003; McKnight et al., 2003; Ravichandran, 2004). However, the characterisation of humic substances in terms of their average structure and functionality is important and

thus, the importance of functional groups present in the humics must not be overlooked (McDonald et al., 2004). Humic substances from different environments may also exhibit many similar characteristics although the relative abundance of functional groups may vary. Table 2.1 lists the important functional groups of DOC with their structure and the environment where they are most likely to be found.

Table 2.1 Important functional groups of DOC. R is aliphatic backbone and Ar is aromatic ring (after McDonald et al., 2004, Sperling et al., 2007 and Thurman, 1985).

Functional group	Structure	Environment	Remarks
Acidic groups			
Carboxylic acid	(Ar–)R–CO_2H	90% of all DOC	Responsible for the majority of the DOC ionic character.
Phenolic OH	Ar–OH	Aquatic humic substances, phenols	Major functional group on humic substances.
Enolic hydrogen	(Ar–)R–CH=CH–OH	Aquatic humic substances	Found in both soil and aquatic humic substances.
Quinone	Ar=O	Aquatic humic substances, quinones	Present at trace levels.
Basic groups			
Amine	(Ar–)R–CH_2–NH_2	Amino acids	Make up about 2-3% of the DOM. An approximate of 20 amino acids is important in the natural waters and combined in proteinaceous matter. Common in the colloidal fraction.
Amide	(Ar–)R–C=O(–NH–R)	Peptides	
Imines	CH_2=NH	(Unstable, forming polymeric derivatives) humic substances	Non-peptidic nitrogen.
Neutral groups			
Alcoholic OH	(Ar–)R–CH_2–OH	Aquatic humic substances, sugars	Also occurs on carbohydrates, simple alcohols and hydrophilic acids. Greatly enhances the aqueous solubility of OM.
Ether	(Ar–)R–CH_2–O–CH_2–R	Aquatic humic substances	Can occur on aromatic or aliphatic molecules.
Ketone	(Ar–)R–C=O(–R)	Aquatic humic substances, volatiles, keto-acids	Adds aqueous solubility and available in hydrophilic and humic substances.
Aldehyde	(Ar–)R–C=O(–H)	Sugars	Interacts with hydroxyl group to form ring structure (common form of monosaccharides in natural waters).
Ester, lactone	(Ar–)R–C=O(–OR)	Aquatic humic substances, hydroxy acids, tannins	A labile functional group that will hydrolyse to a carboxyl group. Present at low levels (~1Meq/mg).
Cyclic imides	(R–)O=C–NH–C=O(–R)	Aquatic humic substances	Polymers with this structure are possibly resistance to hydrolysis.

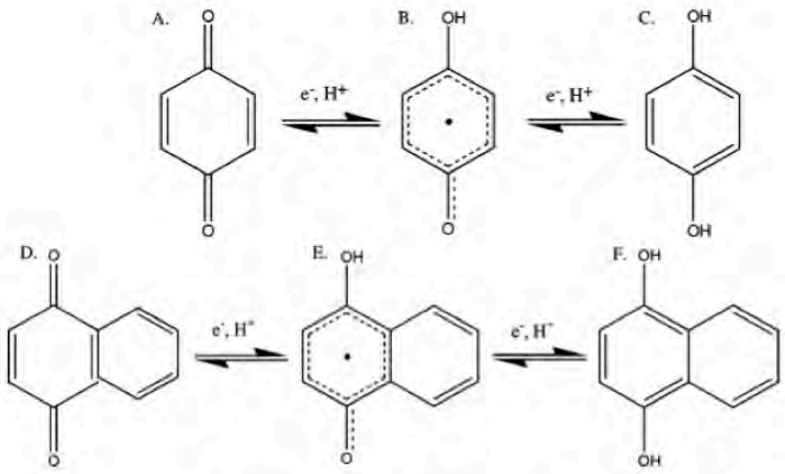
A number of techniques have been developed to study the separation of biomolecules such as amino acids, peptides, proteins, nucleic acids and DNA and hence allow the characterisation of humic substances (Sulzberger and Durisch-Kaiser, 2009). For example, chromatographic analysis by using XAD-8 resin has been widely accepted to isolate humic substances into humic and fulvic acids (Findlay and Sinsabaugh, 1999). Freshwater DOM is commonly sampled by adsorption onto XAD resins (fulvic and humic substances) and is isotopically light ($\delta^{13}C \approx -27$ per mil), with high C/N (40 to 50) and abundant in aliphatic, aromatic, and carboxyl carbon (Hedges et al., 1992). At a molecular level, spectroscopic applications such as nuclear magnetic resonance (NMR), Fourier-transform infrared (FTIR), electron paramagnetic resonance (EPR), ultraviolet-visible (UV-vis) and fluorescence measurements have been found to be invaluable for both quantitative and qualitative DOM characterisation (Chen et al., 2002; Leenheer and Croue, 2003). However, it has been estimated that more than 75% of the DOM pool remains chemically uncharacterised at the molecular level (Seitzinger et al., 2005).

Fluorescence spectroscopy has been used to trace and characterise DOM dynamics given that a fraction of DOM fluoresces (Stedmon et al., 2003). Fluorescence techniques have demonstrated that humic substances always display spectra characteristics that have been ascribed to the presence of aromatic fluorophores with electron-donating functional groups (Chen et al., 2003). It has been found that condensed aromatic molecules and a few highly unsaturated aliphatics chains are the only organic molecules that fluoresce with reasonable efficiency (McDonald et al., 2004; Senesi, 1990). Aromatic organic

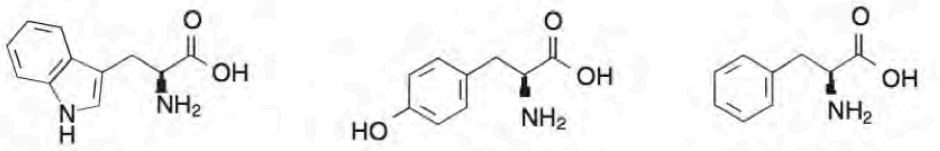
compounds are good subjects for fluorescence studies due to their characteristics: the unpaired electron structure of the carbon ring, and energy sharing. When studying OM fluorescence, compounds that absorb light are called chromophores, and those that absorb and re-emit light energy is called fluorophores (Mobed et al., 1996). The technical details of the application of fluorescence spectroscopy are elaborated in section 3.2.

An example of fluorescence technique in OM characterisation is to detect the quinones redox state and presence. Quinones are flexible biomolecules found in detrital organic matter, extracellular material as well as living cells, they are also a product of lignin oxidation (Cory and McKnight, 2005). Quinones exhibit shifts in fluorescence spectra by reduction reaction, and are converted into fluorescent hydroquinones (Ahmed et al., 2006). The reduction is often accompanied by increased intensity of the energy transitions from ground state to the higher level, and exhibited by darker colour of reduced quinones (Cory and McKnight, 2005). Another example is the fluorescence of the three fluorescent amino acids (tryptophan, tyrosine and phenylalanine), which indicate peptides and protein (Hudson et al., 2007). The protonated state of these amino acids is due to the presence of an indole group (an aromatic heterocyclic compound with a bicyclic structure: a benzene ring and a heterocyclic aromatic ring with a nitrogen atom being part of a ring). It is also could be due to the existence of aromatic ring structure whereby the electrons are “shared”, rather than being a loosely held opposite spin pairs, and available to excite to the higher energy state (Hudson, 2010). Fig. 2.4 (a) and (b) illustrates the redox states of quinones and

chemical structures of the amino acids (tryptophan, tyrosine and phenylalanine) respectively.



(a) Quinones redox state.



trp w Tryptophan **tyr** y Tyrosin **phe** f Phenylalanin

(b) Structures of some of the amino acids

Fig. 2.4 Chemical structures of the: (a) redox state of quinones: one-electron reduction of oxidized quinone to the semiquinone radicals, and then reduced to the hydroquinone. A-C: reduction of benzoquinone, D-F: reduction of naphthoquinone (after Cory and McKnight, 2005); (b) amino acids (tryptophan, tyrosine and phenylalanine) (after Hudson et al., 2007).

2.4 SPATIAL AND TEMPORAL TRENDS: DOM QUALITY

DOM dynamics have been found to be characterised by significant spatial and temporal changes (Findlay and Sinsabaugh, 1999; Ishii and Boyer, 2012; Jaffe et al., 2008). According to Findlay and Sinsabaugh (1999), the main inputs of DOM in stream headwaters are episodic in nature, reflecting soil 'hot spots' and transport is event-dependent resulting in infrequent but sharp rises in DOM concentration. Headwater streams are likely to receive significant freshwater DOM inputs as whilst quantities of water exchange are low, water residence time is high (Maie et al., 2012). Although relatively few studies have been completed, DOM transport from catchment headwaters has been found to control downstream DOM quality (Jaffe et al., 2008; Maie et al., 2012). Due to quick reactions between rivers and precipitation events, rapid and large modifications in loadings from the drainage basins could occur frequently, which results in physical and chemical conditions (Wetzel, 2001).

Findlay and Sinsabaugh (1999) consider that DOM derived from litter and soil is amenable to physical adsorption and is bioavailable to some degree, however, these processes are probably insufficient to counterbalance rapid downstream transport (Fig. 2.5). Relatively low amounts of DOM will be lost from a water mass as it is transported downstream unless it is introduced to new inputs of DOM or affected by dilution. Further downstream, it may be characterised by the more open canopy, litter inputs will decrease and it will receive more sunlight, thus, increasing the irradiation of the bed sediments and stream water. Greater light intensities will result in higher DOM with

autochthonous origins in relative importance (Wetzel, 2001). High water volumes could indicate that localised ‘hot spots’ of DOM generation will slightly influence the DOM concentrations. The river downstream is most complex to generalise, as significant anthropogenic alteration has taken place (Findlay and Sinsabaugh, 1999). Thus Massicotte and Frenette (2011) showed that terrestrial DOM in St. Lawrence River, North America is produced very rapidly and is recalcitrant, while protein-like DOM is produced at slower rate but has a rapid turnover. This river constantly receives DOM from inflowing tributaries, which results in DOC accumulation on the longitudinal axis. Hydrological differences between years will also lead to variations in DOM concentrations in the long term (Salisbury et al., 2011). The temporal pattern will reflect seasonal increases in DOM, but there are also likely be interannual variations in DOM concentration, driven by floodplain inundation (Massicote and Frenette, 2011).

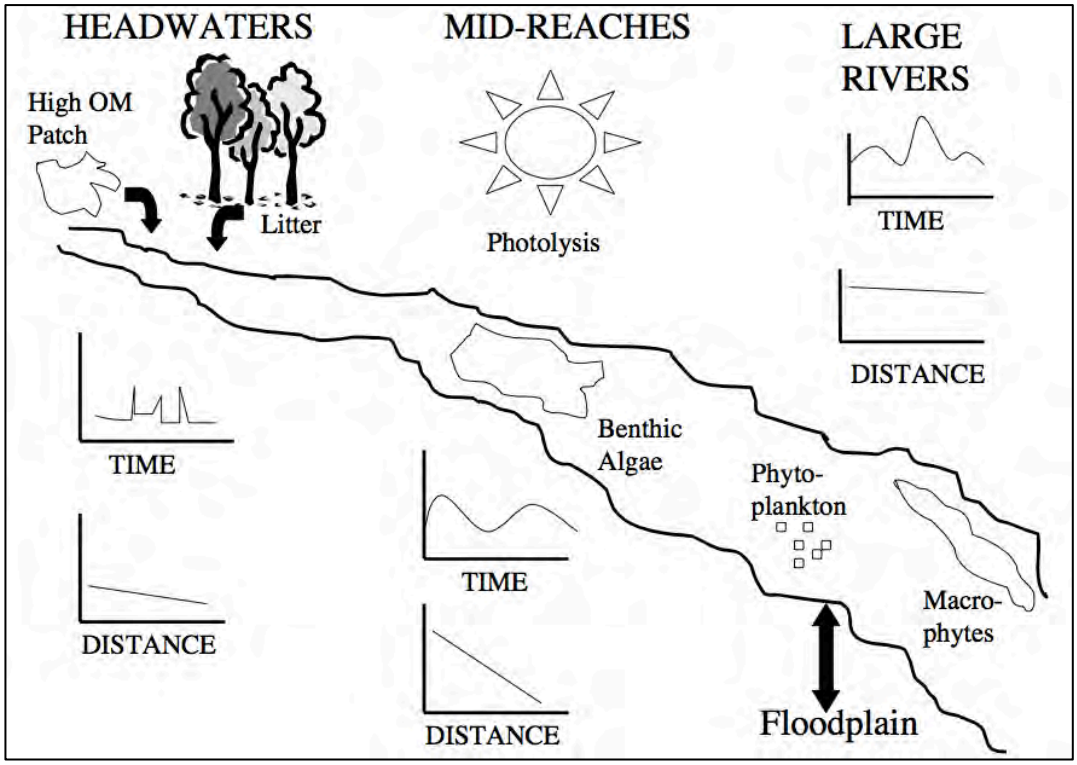


Fig. 2.5 Conceptual model of DOM inputs from headwaters to the estuary (Findlay and Sinsabaugh, 1999).

Seasonal variations in DOM concentration may be considerable. Wantzen et al., (2008) found significant differences in leaf decomposition rates between phases when the floodplain is inundated (back-flooded) and when the flood-waters are rising (flashy-discharge) in the Arenosa stream in Columbia. In seasonal tropical streams, the wet season flushes out much of the litter that has accumulated during the dry season. Frequent flood events may also 'reset' the system and leaves before degradation can occur (Wantzen et al., 2008). In a large pristine tropical river, the Congo, Spencer et al. (2010) showed that the highest concentrations of DOC and lignin carbon-normalised occurred in the inundated period, due to leaching from organic rich horizons and high surface runoff, while the lowest values occurred during the dry season. Similarly a study

in Florida Bay showed that the fluorescence index (FI) (section 3.2) varied seasonally, ranging from terrestrially influenced DOM (at low values) to strongly microbial influenced DOM (at high values), and found that there is less intense microbial influence during the dry season (Jaffe et al., 2008). Maie et al. (2012) reported that spatial patterns of DOC in the early and late wet season were similar, but higher in the dry season (July). However, the fluorescence peaks A and M clearly differed seasonally, suggesting that the distribution is driven hydrologically, by which the largest discharge from the freshwater and terrigenous DOM input happens during the subsequent phase of wet season (September-December).

While DOM quality varies seasonally, it has been reported that DOM quality can also change hourly (Hood et al., 2006). This is supported by Pollard and Ducklow (2011), who found that the water column in a subtropical river (Bremer River, Australia) turned over every two days. This is due to DOC consumption by bacteria with bacterial specific growth rates that were ~20 times higher than that previously observed in marine ecosystem. OM biodegradation has been found to significantly increase in tandem with high river discharge in temperate and high-latitude regions, indicating that storm events are important in the transportation of potentially labile terrestrial carbon (Ward et al., 2012). Ward et al. (2012) showed that dissolved and particulate organic matter and carbon concentrations as well as river discharge were correlated significantly during autumn and winter storms in the Pacific Northwest. During these storm events, a distinctive phenolic composition for dissolved lignin was found, which was rapidly transported from surface soils in proportion to the dissolved lignin base flow. This

result showed the degradation rate of rapidly transported dissolved lignin is higher than the dissolved lignin base flow. Looking from a spectrometric perspective, the specific UV absorbance (SUVA, at 254 nm) of DOC has been found to increase by 9 to 36% during storm events, suggesting that aromaticity of DOC transferred from catchment soils is higher during storms than during baseflow (Hood et al., 2006).

2.5 DOM BIOGEOCHEMISTRY IN LARGE TROPICAL RIVERS

The carbon cycle concept is normally viewed as a system with components such as terrestrial (soil and vegetation), atmospheric and oceanic pools of carbon (Dawson and Smith, 2007). Carbon and nutrient fluxes in large floodplain rivers are a reflection of both catchment and floodplain, and an extension of the properties of smaller tributary rivers. Carbon sources may potentially be thousands of kilometres away in upland regions, and are supplemented by carbon introduced continuously from the adjacent floodplain (Aufdenkampe et al., 2011; Richey et al., 1990). Fluvial biogeochemical dynamics demonstrate the interaction of biological, terrestrial and geochemical weathering reactions, which as a result produce dissolved and particulate inorganic and organic compounds (Aufdenkampe et al., 2011; Richey, 2005). Thus it reflects the natural variability in compositions, process rates and concentrations, as well as their main environmental controls and sources (Mounier et al., 2002). Generally, transported riverine carbon is a mixture of materials ranging from those introduced

continuously from the adjacent floodplain to those originating in catchment headwaters.

Organic carbon is commonly flushed into rivers, and then transported to oceans in dissolved (DOC) and particulate (POC) forms (Moore et al., 2011; Stanley et al., 2011). The amount of organic carbon in water (both dissolved and particulate) depends on the time of year and the amount of decaying organic matter available. Allochthonous OM input from fresh leaf litter is an important source of DOC in forested catchments (Hongve, 1999) but the role is diminished in non-forested areas (Stanley et al., 2011). Once terrestrial DOC is transported to water bodies, its quantity and quality can be altered (Stanley et al., 2011). Anthropogenic activities (i.e. nutrient enrichment from agricultural runoff, sewage effluent, atmospheric deposition) have been found to enhance the decomposition rate (Benstead et al., 2009; Gessner and Chauvet, 2002; Stanley et al., 2011). The alteration of OM within rivers and streams is mainly affected by factors such as microbial activities (Cory et al., 2007), high sediment loads (Thurman, 1985), water discharges, photochemical reactions (Stanley et al., 2011; Zepp et al., 1998), water residence time and salinity (Aminot et al., 1990). It has been suggested earlier (in section 2.2) that humic acids especially those that are terrestrial-derived are mainly refractory (Wetzel, 2001), however recent studies (Benner and Kaieser, 2011; Hur et al., 2011; Rocker et al., 2012; Traversa et al., 2011) have found that biologically and chemically refractory DOM especially UV-absorbing compounds such as humic substances, are readily susceptible to photo- (Kohler et al., 2003) and bacterial degradation (Findlay and Sinsabaugh, 1999; Winter et al., 2007). As bacteria are largely responsible for the OM

transformation (Cole et al., 1988), bacterial production is significant as a key process in DOM flux (Lee and Bong, 2006).

Photoreactions and microbial activities are both responsible for the efficient removal of terrigenous DOM from the oceans and sequential microbial and photochemical degradation by which photoproducts (i.e. dissolved inorganic carbon) stimulate bacterial growth (Pisani et al., 2011; Scully et al., 2003; Spencer et al., 2009). DOM can be converted into photoproducts such as inorganic forms, low molecular weight organic compounds, trace gases, phosphorous-and nitrogen-rich compounds, as well as bacterial substrates to increase turnover rates of DOM especially in surface waters (Cory et al., 2007; Kowalczuk et al., 2009; Moran et al., 2000; Winter et al., 2007). Another potential source of bacterial substrates from photoreactions is modified DOM, which comprises of higher molecular weight compounds and uncharacterised fractions of DOM (Miller and Moran, 1997).

DOM degrades to smaller photoproducts from exposure to sunlight via two mechanisms: i. direct volatilization of carbon gases; and ii. rapid microbial consumption (Miller and Moran, 1997). Volatile photoproducts are normally dominated by carbon monoxide (CO) and dissolved inorganic carbon (DIC), while compounds that are readily assimilated by bacteria are generally termed biologically labile photoproducts (Zepp, 2005). Interestingly, most of the labile photoproducts were found only in freshwater environments (Moran and Covert, 2003). At least nineteen different compounds have been identified as being readily incorporated by bacterioplankton and nine have been reported from

freshwater systems: butyrate, acetate, citrate, levulinate, formate, succinate, oxalate, dissolved carbohydrates and malonate (Moran and Covert, 2003). These compounds enter the microbial food web, which consist of microbial communities such as heterotrophic bacteria, viruses, flagellates and ciliates (Moran and Covert, 2003). Heterotrophic bacteria convert autochthonous and allochthonous DOM into POC which is subsequently grazed by small ciliates and heterotrophic flagellates (Basu and Pick, 1997). Microbes especially have a larger role in OM decomposition in large rivers or lotic systems, which are unable to support a vast community of shredding macroinvertebrates (Tank et al., 2010). Given that DOM decomposition rates tend to increase with temperature, decomposition also parallels microbial metabolism (Wantzen et al., 2008).

DOM is the key sunlight absorbing element of natural waters (Brinkmann et al., 2003), and terrestrial DOM is normally subject to intensified UV exposure (Kohler et al., 2003). Both DOM and POM have been recognised for their ability to absorb light at similar wavelengths to allow large molecules to break down (Pisani et al., 2011). Photolysis and photochemical processes, that induce changes in natural DOM, can influence many aspects of carbon cycling. Photochemical degradation of DOM has been found to result in a decrease in aromaticity (Cory et al., 2007). Winter et al. (2007) suggested that this decrease is due to the binding of metals to the more aromatic groups especially in the darker organic matter. However, photochemical processes are not expected to be as dominant as temperature-dependant processes that occur in surface waters (Cory et al., 2007). It has been found that photochemically mediated transfer of carbon into microbial food web is more pronounced for deep-water marine DOM

than for the surface (Moran and Covert, 2003). Consequently, comparison between surface and deep water samples showed that biological lability of deep-water DOM was consistently high even after exposure to sunlight, while the surface-water DOM was greatly depleted due to irradiation (Benner and Biddanda, 1998).

Tropical regions experience high levels of incident solar radiation (Graneli et al., 1998; Hader et al., 1998; Latrubesse et al., 2005; Saigusa et al., 2008) and it has been shown that microbes in the tropics are also more important in terms of OM processes, than in temperate areas (Wantzen et al., 2008). There is a relationship between sunlight availability and bacterial growth, although, the availability of UV-B has been found to affect bacterial growth and abundance (Alonso-Saez et al., 2006; Bertilsson and Tranvik, 2000; Hader et al., 1998; Wantzen et al., 2008; Zepp et al., 1998), especially in highly polluted areas (Lee and Bong, 2006). For example, a bacterial growth rate study on the carbon flux in Port Klang, Selangor, Malaysia showed that bacterial growth rates in both a highly eutrophic and deteriorating site and in an estuarine mangrove ecosystem in Matang, Perak, Malaysia were high and fell within the same range (Lee and Bong, 2006). This suggests that photolysis and microbial activities are likely to have more effect on processes affecting both labile and recalcitrant DOM in tropical regions, compared to temperate environments.

Wantzen et al. (2008) compared ecological and biogeochemical processes between the tropics and temperate zones and concluded that rates of faunal and biogeochemical recovery in these regions appear to be similar and rather swift

respectively. A further study, by Pollard and Ducklow (2011), found that bacterial specific growth rates were about 20 times higher than that previously observed in marine ecosystems. Rapid removal of terrigenous DOC in the Arctic shelf sea indicated a high correlation with microbial-loop activities (Letscher et al., 2011) and Jiao et al. (2010) found identical observations in the Antarctic. Table 2.2 summarises the differences of biogeochemical processes in these regions.

Table 2.2 Summary of biogeochemical processes reported by some recent literatures in different regions.

Zone	Recent literature source	Remarks
Antarctic	Dai et al. (2012)	DOC tends to increase with rising temperature and atmospheric CO_2.
	Jiao et al. (2010)	Marine primary production has been highly associated with microbial-loop activities, which varies over time.
Arctic and subarctic	Letscher et al. (2011)	Terrigenous DOC from rivers in Arctic Ocean were removed very rapidly (about 2.5-4 times higher than previously observed, and correlated with microbial-loop activities).
	Olefeldt et al. (2012)	DOC composition in a subarctic river in northern Sweden is associated with absorption with mineral soils, microbial degradation, and photodegradation.
Temperate	Ward et al. (2012)	A shallow nutrient-rich pool of POM and DOM were accumulated in watersheds during summer period and has been mobilised by autumn and winter storms.
	Xu and Saiers (2010)	DOM mobilisation in response to storms correlated positively with temperature and negatively with rainfall intensity and frequency.
Tropical and subtropical	Spencer et al. (2010)	Temporally, DOM quality in Epulu River, Congo is associated with the increased residence time during wet period, thus, greater microbial mineralisation.
	Yamashita et al. (2010b)	DOM concentrations mainly associated by microbial activities and light penetration. Spatial variations were probably associated to vegetation cover.

2.6 EFFECTS OF LAND USE CHANGE ON DOM IN TROPICAL REGIONS

Anthropogenic modifications to headwater streams and catchments influence stream metabolism in a number of ways. Land use changes may modify proximal factors controlling stream metabolism by altering flow regimes. This may include changes in the intensity or timing of flow; and increased nutrient, sediment, and pollutant runoff from agricultural and urban sources, such as from the use of fertilisers (Bernot et al., 2010). DOM concentrations and properties may also be affected by land use changes in wetlands (Glatzel et al., 2003). However, deforestation and forest degradation are primarily responsible for changes in tropical land cover that affect DOM concentrations (Miettinen et al., 2011).

Deforestation has been generally defined as 'the conversion of forested areas to non-forest land through cutting, clearing and removal of rainforest or related ecosystems into less biodiverse ecosystems such as pasture, cropland, plantation, urban use, logged area or wasteland' (Sehgal, 2010). Deforestation of tropical rainforests has been approximated to contribute ~6 to 17% of total anthropogenic CO_2 emissions to the atmosphere (Baccini et al., 2012; Saner et al, 2012). Importantly, Southeast Asia currently has the highest rate of deforestation in the world (Dudgeon, 2003; Miettinen et al., 2011), and Malaysia has been identified as one of 14 countries where annual rates of deforestation exceed 250,000 ha (McMorrow and Talip, 2001). In Malaysia, deforestation has led to a ~20% reduction in forest land (Wicke et al., 2011), to the point at which in 2010, ~42% of the forest cover has been lost across the country (Miettinen et al., 2011).

Deforestation for agricultural activities such as the establishment of permanent crops, shifting cultivation and cattle farming, is generally associated with increased soil erosion and land degradation (Atapattu and Kodituwakku, 2009). Globally, agricultural activities and cattle farming are thought to account for at least 50% of rainforest deforestation (Cansier, 2011). Deforestation normally leads to a lower biomass even after a period of recovery (Henson, 1999). For example, forests in Peninsular Malaysia were extensively evaluated in 1970-72 and at that time were estimated to contain between 212-533 tonnes dry matter per hectare (100-260 tonnes carbon per ha.) and this has declined substantially then, due to deforestation (Henson, 1999). In Borneo, the current aboveground biomass is approximately 60% (457 Mg C/ha) (Saner et al., 2011). Large-scale deforestation for mechanised agriculture e.g. oil palm and rubber plantations typically results in an ecological imbalance that affects the hydrological cycle, nutrient recycling, microclimatic, and biotic environments (Lal, 1981). There is a clear contrast, for example, between forested and deforested areas in mesoscale atmospheric circulation that is responsible for the diurnal rainfall cycle especially during the dry season, consequently influencing the rainfall spatial distribution (Silva et al., 2012). Riparian vegetation removal along streams has also been found to lead to an increase in water temperatures, light levels and nutrient concentrations (Doyle and Shields, 2012; Kiffney et al., 2003; MacKenzie, 2008). This increases filamentous algal and microbial production, thus altering the food webs of stream fauna as well as community structures (MacKenzie, 2008).

As a result of deforestation, rapid growth of ‘secondary’ or ‘regenerating’ forests are increasing, thus, becoming a common land cover type in the tropics (Chokkalingam and Jong, 2001; Fortini et al., 2010; Jong et al., 2001; Schedlbauer and Kavanagh, 2008), however, there have been few studies on secondary forests (Fonseca et al., 2011). Brown and Lugo (1990) defined secondary forests as those ‘resulting from abandonment of cleared forest lands generally from agriculture. It also results from continuous human uses of forests, such as grazing, fuelwood collection and burning’. Chokkalingam and Jong (2001) and Jong et al. (2001) provide a more concise definition: i.e. ‘forests that are regenerating largely through natural processes after significant human and/or natural disturbance of the original forest vegetation at a single point in time or over an extended period, and displaying a major difference in forest structure and/or canopy species composition with respect to nearby primary forests on similar sites’.

Secondary forests may vary in age, and it is generally agreed that forests beyond age 60-80 years old are categorised as undisturbed or primary forest (Brown and Lugo, 1990). They have became a major concern, particularly in situations when secondary forests act as host to non-native species, due to anthropogenic activities. Non-native species are considered ecological villains as some have competitive advantages as well as the lack of natural rivals (predators, pests, competitors) and/or the ability to fix nutrients such as nitrogen, therefore booming in the new environment and outnumbering certain native species (Hashim et al., 2010).

It has been estimated that secondary forests account for 35-40% of tropical forests globally (Hughes et al., 1999; Fonseca et al., 2011; Fortini et al., 2010), and ~63% in Southeast Asia (Kenzo et al., 2010). Secondary forests, however, have the potential to absorb and store a reasonably large amount of the carbon and nutrients lost throughout land use changes and deforestation (Hughes et al., 1999; Schedlbauer and Kavanagh, 2008; van Breugel et al., 2011). Secondary forests act as nutrient sinks and thus accumulate nutrients rapidly with time (Brown and Lugo, 1990; Silva et al., 2011). Proportional to its role as a carbon sink, secondary forest vegetation intensified its nutrient sink function during the early stages of forest growth, as young trees incline to store more nutrients compared to mature vegetation. In terms of organic matter production, secondary forests store less nutrients in their litter, however, they return high amounts in litter fall (Brown and Lugo, 1990; Silva et al., 2011). This results in high nutrient cycling rates in litter, especially on nutrient recycling or, alternatively, nutrient loss (Brown and Lugo, 1990).

Various studies have been conducted to determine the quantity of carbon lost to the atmosphere from deforestation. Secondary succession has been found to release carbon in the atmosphere more rapidly than in any other biome (Wright, 2010). Two tropical countries (Brazil and Indonesia) have been estimated to account for ~60% of total carbon emissions (Houghton, 2010). Moreover, Baccini et al. (2012) estimated that the total carbon emissions from land use and tropical deforestation to be 1.0 Pg C/year. In Brazil, it has been estimated that the losses of carbon from deforestation from 2006 and 2050 would be 0.2 to 0.4 Pg CO_2 (Galford et al., 2010). Deforestation generally leads to a

loss of terrestrial carbon but it can also encourage new forest development (Dawson and Smith, 2007), while in the wider catchment it leads to sedimentation and degradation of lakes and rivers (Dudgeon, 2003). Deforestation has also been associated with immediate changes in seasonal and annual stream flow (Mustafa et al., 2005) as well as in organic sources of riverine heterotrophic energy (Mayorga et al., 2005). However, it has been argued this is consistent with monitored interval times in vast organic composition (Mayorga et al., 2005). It has also increased rates of soil erosion, which has caused increased sedimentation of coastal ecosystems (Jakobsen et al., 2007).

Agricultural activities are one of the main processes responsible for the reduction in extent of tropical rainforest, which is 70% in Africa, 50% in Asia and 35% in Latin America (Kobayashi, 1994). In South Asia, about 94% of the land area suitable for agriculture has been cultivated, providing few opportunities for agriculture to expand (Atapattu and Kodituwakku, 2009). In Malaysia large-scale agriculture has long been dominated by cultivation of perennial tree crops such as rubber, oil palm, coconuts and cocoa. Such crops are considered to partially emulate the rainforest as they provide a continuous canopy cover, which should favour long-term soil stability (Henson, 1999). However, agricultural and related industrial developments such as oil palm plantations and oil palm mills and saw-mills, have been found to contribute to pollution in coastal environments through inputs from fertilisers, pesticides, organic matter and bacteria, as they are transferred through the catchment (Jakobsen et al., 2007). The conversion of floodplains and riparian zones conversion to agriculture is harmful to the biota of riverine wetlands (Dudgeon, 2003). Agricultural land use increases the nutrients

export, for example phosphorus and nitrogen to fluvial ecosystems, and significantly influenced DOM characteristics in both streams and rivers (Wilson and Xenopoulous, 2008).

Oil palm (*Elaies guineensis)* plantations are increasing in extent throughout the tropics, most notably in SE Asia (Wilcove and Koh, 2010). The first stage of oil palm plantations in Malaysia and Indonesia (the largest producers countries of palm oil globally) (Koh and Wilcove, 2008) was in 1900-1950s (Abdullah and Hezri, 2008). In 2008, Malaysia's Federal Land Development Authority (FELDA) envisaged the establishment of oil-palm plantations in Kalimantan (20,000 ha), Aceh (45,000 ha), Brazil (100,000 ha) and Papua New Guinea (105,000 ha), while in June 2009, oil palm developers in Malaysia announced plans to establish a 100,000 ha oil palm plantation including an extraction facility in Mindanao, Philippines (Wilcove and Koh, 2010). The annual carbon storage for oil palm plantations is potentially high: before harvest its capability is 1340 g C m^{-2} yr^{-1} (i.e. 13.4 tC ha^{-1}) in optimal ecological conditions, which is significantly greater than forest ecosystems (150 g C m^{-2} yr^{-1} on average) (Lamade and Bouillet, 2005). In terms of biomass, oil palm can potentially store four times more carbon per hectare compared to a forest ecosystem, however, rates of litter production and decomposition are low: 130-180 g C m^{-2} yr^{-1} in Sumatra compared to 390-500 g C m^{-2} yr^{-1} for natural forests (Lamade and Bouillet, 2005). Lamade et al. (1996) studied on carbon allocation of oil palm from soil respiration to the roots and showed that the total amount of CO_2 released throug a year was around 1610 g C m^{-2} yr^{-1}.

Estuarine areas in tropical and subtropical regions, which are dominated by wetland ecosystems comprising peat swamp, mangrove forest and mudflats (Jakobsen et al., 2007; Polidoro et al., 2010) are known to be one of the largest terrestrial carbon stores (Alkhatib et al., 2007). Peatlands are normally characterised by black-water rivers with low pH, low concentrations of dissolved inorganic nutrients and suspended sediments and high concentrations of DOC (Alkhatib et al., 2007). Mangrove forests are important for their socio-economic values and provide habitat for a wide range of flora and fauna (Ashton and Macintosh, 2002). Despite their importance, land development such as conversion to agricultural activities, coastal industralisation and urbanisation currently are putting mangroves, particularly along the coastline of SE Asia, in danger (Ashton and Macintosh, 2002; Polidoro et al., 2010). Various vegetation types e.g. Avicienna, Nypa, and Rhizophora are common in mangrove forests (Ashton and Macintosh, 2002) and provide rich polyphenols and tannins, although their concentrations may vary seasonally (Kathiresan and Bingham, 2001). Decomposition of mangrove litter commences as leaves fall from mangroves and are exposed to microbial degradation as well as leaching processes (Sahoo and Dhal, 2009), where leaching alone is able to produce high levels of DOM (Benner et al., 1990; Kristensen et al., 2008). Potassium and carbohydrate has been found to leach very quickly during early vegetation growth, compared to tannins (Kathiresan and Bingham, 2001). High tannin concentrations, however, are likely to be associated with decreasing bacterial counts (Sahoo and Dhal, 2009).

The ability of land use changes to modify the water quality of aquatic ecosystems is generally known. In terms of global DOM dynamics, Wilson and Xenopoulos (2008) found that DOM quality in Ontario, Canada could be affected by agricultural land use. Schelker et al. (2012) showed that riverine carbon fluxes in four boreal headwater streams in northern Sweden increased significantly after forest clear-cutting. In addition, Chari et al. (2012) found differences in DOM concentrations between estuary and the ocean. However, slight differences can be seen in the tropical regions. While DOM in oil palm plantations seems to have a significant signature (Alkhatib et al., 2007; Limpens et al., 2008), Yamashita et al. (2010b) indicated that DOC concentrations in subtropical Everglades, USA appeared to be distributed conservatively. Nevertheless, DOM dynamics still could be characterised throughout the wetlands. Guo et al. (2011) showed that autochthonous DOM from headwater and mangrove wetlands in subtropical Jiulong Estuary decreased rapidly in coastal regions, suggesting the riverine DOM experienced significant modifications in estuarine environments.

2.7 CONCLUSION

DOM represents the major type of organic matter in almost all water bodies and is the product of the breakdown of bacterial, algal, phytoplankton and higher plant organic material, and includes material that may be of allochthonous or autochthonous origin. Riverine export from land to the ocean is mainly determined by factors including hydrological pathways and flux, salinity, light penetration, temperature, phytoplankton biomass, light penetration and depth of mixing. Specifically in tropical regions, DOM biogeochemistry is driven more by

photoreaction and microbial activities, whereby photoproducts tend to stimulate bacterial growth.

DOM quality is also typically characterised by spatial and seasonal changes. In terms of temporal changes, the quality of DOM in tropical catchments may vary seasonally between the wet and dry season and in some cases hourly. Land use conversion of tropical forests to agriculture in the tropics has become a topical issue, especially when environmental deterioration, particularly in aquatic ecosystems, is becoming crucial. Land use changes and regeneration of secondary forests have been found to modify the river flow system and DOM export rates, thus, altering DOM dynamics.

Various studies on land use changes and their effects on DOM quality have been documented, although there has been relatively little work on tropical regions. While different types of land use seem to have significant signature on the DOM quality, this is not the case in the tropics. It could be driven by several factors, especially hydrology and primary production. However, since this area receives abundant sunlight throughout the year, it could also be primarily controlled by processes of photoreaction and microbial degradation. Therefore, more research is urgently needed which is directed towards a better understanding of DOM characteristics and dynamics in tropical catchments in particular those that are affected by on-going deforestation and agricultural development.

3. MATERIALS, METHODS AND ANALYTICAL PROCEDURES

3.1 INTRODUCTION

DOM characteristics were determined in waters sampled from selected sites in the Lower Kinabatangan River catchment, Sabah, Malaysia. The Kinabatangan River (560 km in length) has a total catchment area of 16,800 km^2 (23% of Sabah) and is the second longest river in Malaysia (Fig. 3.1). The area has a humid tropical climate: daily temperature ranges between 22°C to 32°C, and mean annual rainfall is between 2,500 and 3,000 mm (Boonratana, 2000; Josephine et al., 2004). There is considerable inter-annual variability in precipitation: heaviest precipitation occurs during the northeast monsoon between October and March, at which time the floodplain and coastal plain are widely flooded. Widespread areas of floodplain were inundated in 1963, 1967, 1986, 1996 and 2000 (Fletcher, 2009). It has been estimated that the flood-prone area in the Kinabatangan catchment is ~17.0 km^2 (Town and Regional Planning Department Sabah, 1998). Transition periods, defined as the inter-monsoonal period, normally occur in April and October. Dambul and Jones (2008) observed the lowest rainfall during this period, but there is the possibility of significant precipitation events (Gazzaz et al., 2012; Suhaila et al., 2010). Over the rainy season, the floodplain and coastal plain are widely inundated but there is considerable inter-annual variability in rainfall (both total and inter-annual distribution).

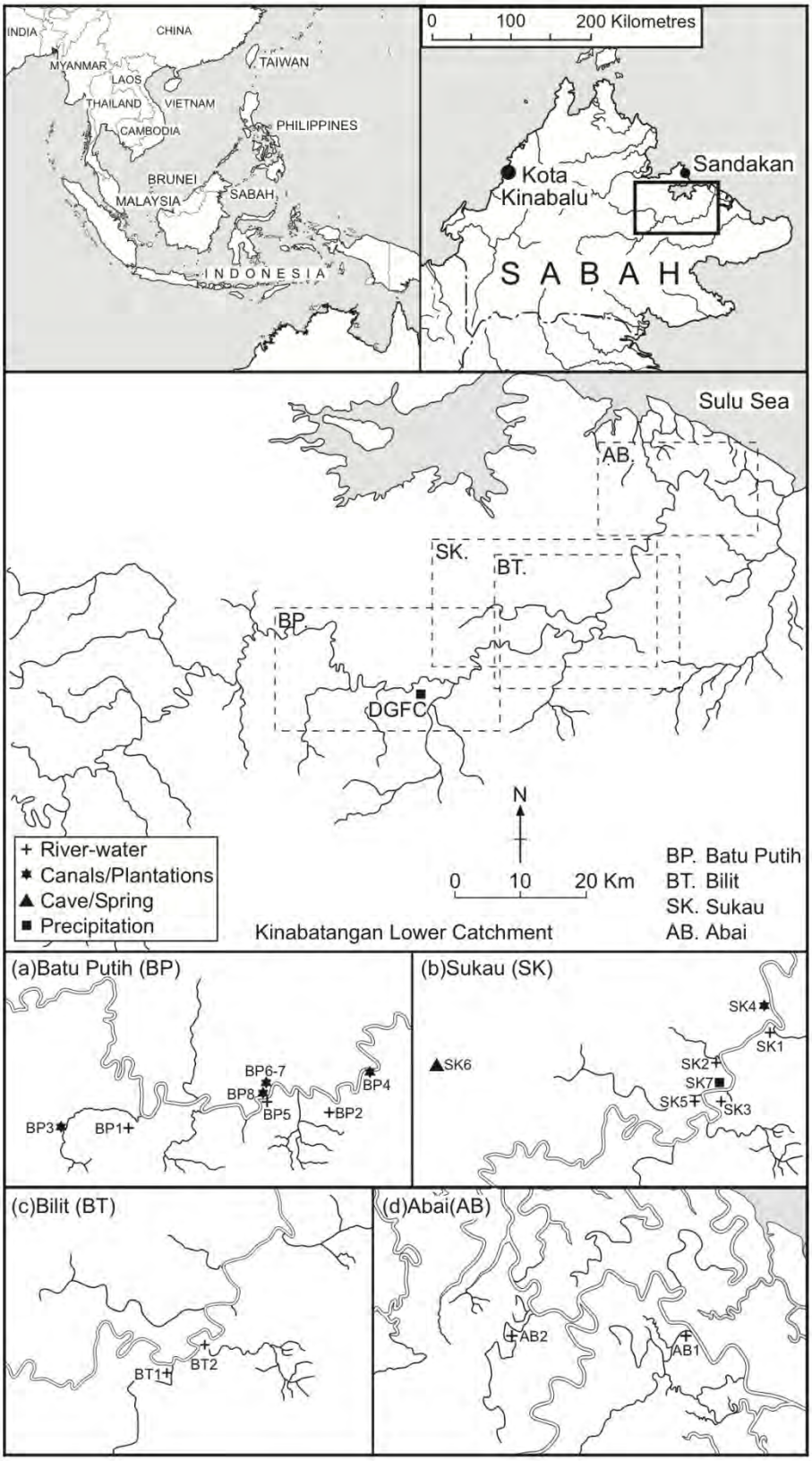


Fig. 3.1 Sampling stations during the preliminary survey in 2008.

The Lower Kinabatangan floodplain extends over >280,000 ha, and comprises the largest wetland in Sabah. There are three primary categories of land cover in the catchment: (i). forest (mangroves and peat swamps); (ii). agriculture (primarily oil palm plantations which covered ~4,100 km^2, 25% of the basin, in 2009); and (iii). other land cover including built-up areas and water bodies (Department of Environment Malaysia, 2009). The natural floodplain vegetation, which is the dominant land cover (about 74% of the basin) is riverine and freshwater swamp forest (at elevations <70 m asl) characterised by open reed swamp, and pristine lowland dipterocarp forest in areas that are inundated infrequently (Boonratana, 2000; Department of Environment Malaysia, 2009). Nipah palm (*Nypa fruticans*) covers extensive areas of low level tidal swamps (Kathiresan and Bingham, 2001) and generally occurs inland from mangrove swamps extending inland as a narrow border along the river margins, can also occur close to the sea suggesting higher tolerance of salinity compared to mangrove (Acres and Folland, 1975).

In terms of physiographic regions, the eastern lowlands are defined as land below 300 m (1,000 ft), and comprise five main areas: Lokan Peneplain, Kinabatangan Lowlands, Sandakan Peninsula, Dent Hills and Eastern Deltas (Acres and Folland, 1975). The Lokan Peneplain is situated to the north of the Kinabatangan; the Kinabatangan Lowlands consist of the major valleys of the Kinabatangan and Segama Rivers and are largely hilly terrain draining to the north-east; the Sandakan Peninsula (largely low hills) is bounded by Sandakan Harbour to the south and by the sea to the north and east. The Dent Hills, located to the north, and the Eastern Deltas comprise swamps, formed by the deposits of

the main stem of the Kinabatangan flowing into the Sulu Sea (Acres and Folland, 1975). In a more recent publication, the physiographic subdistricts of eastern Sabah have been classified as follows: Northern Islands, Kaindangan and Lokan Plains, the Deltas of Kinabatangan, Segama, Sugut and Labuk Rivers, the Bongaya Hills, Sandakan Peninsula, Kinabatangan Lowlands, Segama Valley, Dent Hills, and the Semporna Lowlands (Hutchinson, 2005).

Due to the scarcity of studies in this region, references to the geology and soils are largely drawn from a series of unpublished reports 'The Soils of Sabah' (Acres and Folland, 1975) and 'Sabah Coastal Zone Profile' (Town and Regional Planning Department Sabah, 1998). Geologically eastern Sabah (including the Kinabatangan) is predominantly covered by sandstone and shales, with minor occurrence of cherts and limestones, while the igneous rocks are mainly basalts, serpentinites, gabbros, volcanic breccias and tuffs (Tongkul, 1991). Four broad groups of soil parent material were identified by geological surveys conducted in the early 1950s: undifferentiated alluvium, peat, sandstone and mudstone and limestone (Acres and Folland, 1975; Town and Regional Planning Department Sabah, 1998). Undifferentiated alluvium comprises both terrace and recent alluvium. Recent alluvium, originating mainly from sedimentary rocks, can be found widely on floodplains and in freshwater swamps. The texture is mostly fine and rich in magnesium. Adjoining sandstone hills, on levees and in the upper reaches of valleys, the texture of the surficial deposits are predominantly medium or coarse with low nutrients, while coarse-textured with ~90% silica minerals (mainly quartz) are found on beaches (Acres and Folland, 1975). The dipterocarp forests are situated along the banks of the main stem and tributaries are mainly

found on raised alluvial terraces and plains, which range in width from 10m to >1km. The low-lying swamps have mainly alluvial soils, rich in minerals such as magnesium in contrast to the lowland forests, which have a permanently high water table (Payne, 1989).

Peat soils occur in swamps from Batu Putih towards the estuary. They are derived from the remnants of swamp forests and are composed of woods and sedges with various levels of decomposition; their depth normally exceeds 6 m (Acres and Folland, 1975; Town and Regional Planning Department Sabah, 1998). Mudstone and sandstone in this area are extensive, occurring from the upper part of the Lower Kinabatangan towards Sandakan Harbour across the Kinabatangan valley to the Segama. The mudstone is generally dark grey, while greenish or bluish-grey are less common (Acres and Folland, 1975). Limestone outcrops in the catchment; dominating the Gomantong Formation (Gomantong caves and a number of small outcrops near Sukau), which is of late Miocene age, consists of compressed, debris, grayish-orange limestone, algae and corals, mostly crystalline, composed of foraminifers, as well as rare quartz sand. Thick limestone lenses are also present at the Lower Kinabatangan valleys. The limestones in general are impure and weathered, and as a result, fine-textured deposits are produced on gentle slopes. These deposits normally lack coarse clasts, and are decalcified with limestone fragments (Acres and Folland, 1975).

The Kinabatangan River is the main domestic water source for local communities (Boonratana, 2000). Mean daily river flow recorded by the Department of Irrigation and Drainage Malaysia in the upper catchment (Fig. 3.2)

is within the range 2.5-60 m^3/s (Department of Environment Malaysia, 2009). The highest monthly average of daily mean discharge recorded in 1997 was in February (~667 m^3/s), while the lowest in June (109 m^3/s) (Town and Regional Planning Department Sabah, 1998).

During the course of the research presented here, waters were sampled according to two sampling designs: i. a preliminary survey; and ii. a concentrated field-work programme. Widths and depths of the main stem of the Kinabatangan were recorded throughout the survey and range from 90 to 160 m (width) and from 5 to >20 m in depth. First, a preliminary survey was completed, focusing upon the spatial variability of selected water quality determinants and, secondly, more detailed sampling programmes were undertaken that sought to determine trends in water quality i. seasonally; and ii. related to different land uses. Sampling seasons covered both the dry and wet seasons, while three types of land use comprised of oil palm plantations, secondary forests and coastal swamps.

3.1.1 Preliminary Survey

Water samples were collected during summer baseflow conditions at selected locations in the Kinabatangan catchment between August and September 2008, including sites that were closely associated with oil palm plantations and mills (Fig. 3.1) (Chapter 4). Sample sites were selected on the basis of their accessibility and included: i. the main stem of the Kinabatangan River and

tributary streams; ii irrigation ditches associated with selected oil palm plantations; and iii. groundwater springs. Water samples from tributary streams were collected from points ~2-3km above their confluence with the Kinabatangan. These samples were collected from Batu Putih (BP), Sukau (SK), Bilit (BT) and Abai (AB).

In total, 225 water samples were collected in 2 ml glass vials (in most cases from a boat) at three points across the channel: adjacent to both riverbanks and in the channel mid-point. Small sample sizes were chosen to permit rapid shipment of the water samples (unfrozen) to Birmingham, UK, for laboratory analysis. Other physicochemical parameters including pH and water temperature were measured in-situ using a Hanna multi-parameter water quality meter (Model HI9828). Sample vials were stored in cool, dark conditions before shipment to the UK. In the laboratory, all samples for organic matter fluorescence analysis were filtered through Whatman GF/F syringe filters (nominal pore size 0.7 μm), and stored in the dark at 4ºC until analysis, which occurred within 1 month of sampling. Due to relatively small sample size, 0.7 μm filters were employed to avoid losing too much DOM and hence information related to DOM characteristics. It also enables the inclusion of large DOM size fractions, which are normally found in colloidal and dissolved forms (Fellman et al., 2008). Fellman et al. (2008) found insignificant differences between two sizes of filters (0.2 and 0.7 μm) used in their study in Juneau, Alaska.

In addition, a total of 6 precipitation and 83 surface water samples for stable isotopes analysis were collected in 2 ml glass vials. Rainfall samples were collected manually using a small container to intercept precipitation, which was

immediately transferred to a sample vial. Samples were filtered and stored in an identical manner to the samples collected for DOM determination.

3.1.2 Concentrated Sampling Programme

Subsequently, a total of 510 water samples were collected manually during five field sampling campaigns in 2009-2010, one of which corresponded with inter-monsoonal period (October 2009), three corresponded with the wet season (November, December 2009 and February 2010); and one the dry season (May 2010). Sampling stations were located in the same locations as for the preliminary survey with the exception of Bilit (BT). Thus samples were collected from Batu Putih (BP), Sukau (SK) and Abai (AB). Samples from Bilit, collected in the preliminary survey, were found not to differ significantly from the other sampling areas, and no further samples were collected in this area. Water samples were collected from streams or creeks situated entirely within: i. oil palm (*Elaies guineensis*) plantations: BPA, BPB, SKA and SKB (220 samples); ii. secondary forests: BPC, SKC and SKD (139 samples) and iii. coastal swamps where the nipah palm, *Nypa fruticans,* is widespread: ABA and ABB (151 samples) (Fig. 3.2). At each point, 200 ml water samples were collected from the middle of the river / stream from a boat at three points in the water profile: from the surface, the mid-point and near the base of the water profile using a WaterMark Horizontal Polycarbonate water sampler. This sampler is designed to collect water samples from a specific depth of up to 30 m. The sampler was lowered to the depth required, at which point a mechanism is triggered closing

the chamber, and water samples were then collected via a rubber tube. Fig. 3.3 shows the WaterMark water sampler in use. Samples were stored in high-density polyethylene (HDPE) bottles pre-washed with 10% hydrochloric acid and deionised water. pH and salinity were determined using a Hanna Water Quality Multiparameter (Model HI 9828) immediately before the water samples were filtered using pre-combusted 0.45 μm Whatman glassfiber GF/C filter. Filtered water samples were kept in the dark and stored at 4 ºC until shipment to the UK for laboratory analysis at the University of Birmingham, which occurred within seven days of sampling.

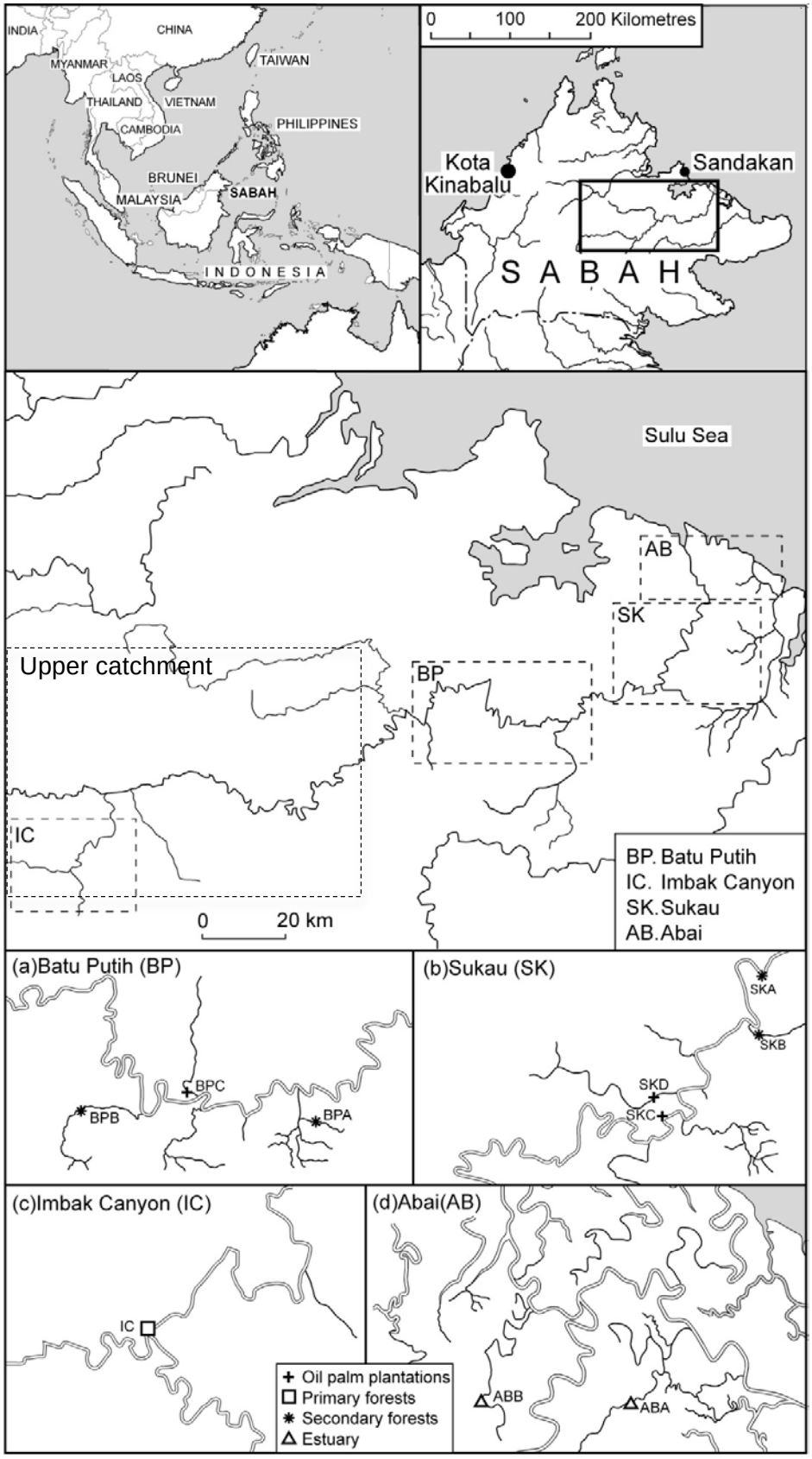


Fig. 3.2 Sampling stations during sampling period from 2009-2010.

Fig. 3.3 Water sample collection at pre-determined depth by using WaterMark Horizontal Polycarbonate water sampler.

With respect to possible fluorescence degradation between the point of sampling and analysis, relatively minimal DOM degradation is possible. By calculating fluorescence intensities of peaks A and C, as indicated during the preliminary study (section 3.1.1), it was found that there was no fluorescence loss between filtered and post-filtered samples, although microbial activities had occurred within the post-collected samples. Furthermore, this is supported by various studies which showed that fluorescence signals for peaks A and C were unchanged after three months of storage at 4℃ in the dark (Hudson, 2010; Ghervase et al., 2012). In order to maintain the natural character of DOM, samples were analysed at their natural pH and were not freezed or thawed, as described by Spencer et al. (2007) and Fellman et al. (2008). Spencer et al. (2007) found that pH is highly sensitive with thawing or freezing procedures, and

consequently will change the spectrophotometric properties of DOM. Furthermore, it has been found that within the typical pH observed in freshwaters, the response of spectrophotometric applications were restricted.

Main Stem Samples

DOM characteristics were determined for waters sampled from nine sampling points along the main stem of the Lower Kinabatangan River, Sabah, Malaysia (Fig. 3.2). A total of 128 water samples were collected manually at nine sampling points during five fieldwork campaigns in 2009-2010, one of which corresponded with the inter-monsoonal period (October 2009), three correspond to the wet season (November 2009, December 2009 and February 2010); and one the dry season (May 2010). Water samples were collected in three areas of the catchment: i. Batu Putih (BPA, BPB and BPC: 42 samples); ii. Sukau (SKA, SKB, SKC and SKD: 59 samples) and iii. Abai (ABA and ABB: 27 samples). At each sample point, waters were sampled from the centre of the river at three points in the water profile: near the water-surface, the mid-point and near the base of the water profile using a WaterMark Horizontal Polycarbonate water sampler (Fig. 3.3). The total depth of the main river was first measured and then divided by two, to obtain the mid-point depth. The mean depth for each sampling point is presented in Table 3.1. The depth of the main river increases from Batu Putih downstream: from an average depth of ~7.9 m at Batu Putih to 14.9 m at Sukau; and 14.3 m at Abai; with widths varying between 100 – 120 m.

Table 3.1 Information on sampling area with number of samples and average depths according to each sampling point.

Sampling area	No. of samples	Average depths (m)
Batu Putih		
Sg. Pin (BPA)	15	7.8
Sg. Koyah (BPB)	12	7.6
Danau Kaboi (BPC)	15	8.4
Sukau		
Malbumi Plantation (SKA)	15	15.2
Sg. Resang (SKB)	14	14.7
Danau Kalinanap (SKC)	15	14.8
Sg. Menanggol (SKD)	15	14.5
Abai		
Balat Damit (ABA)	12	12.3
Sg. Merah (ABB)	15	16.2

3.1.3 Sampling Locations

Initial site selection largely reflected logistical constraints and ease of access. There are approximately 104 villages located in the Kinabatangan District with 13 in the floodplain (Josephine et al., 2004). Of these, the villages of Batu Putih, Bilit, Sukau and Abai are experiencing an increase in tourism, and are readily accessible either by road or main river (Fletcher, 2009). Batu Putih, Bilit and Sukau have road access, while Abai is only accessible by the river. However, certain sampling stations such as the Danau Girang Field Centre (DGFC) in Batu Putih can only be accessed by river. Details of each sampling location are as follows. Both sampling designs are summarised in Table 3.2. Consequently, Fig. 3.4 shows the satellite images for each sampling area, while type of land use is summarised in Table 3.3:

Batu Putih (BP): (a) Batu Putih (BP) area; (b) Sg. Koyah (BPA); (c) Sg. Pin (BPB); (d) Danau Kaboi (BPC). This area situated ~95 km from the nearest major town, Lahad Datu, and has a population of 1200-1400 inhabitants (mainly ethnic Orang Sungai), with a number of small settlements.

Sukau (SK): (e) Sukau (SK) area; (f) Malbumi Plantation (SKA); (g) Sg. Resang (SKB); (h) Danau Kalinanap (SKC); (i) Sg. Menanggol (SKD). Lies on the Kinabatangan River, Sukau is located about 134 km upstream of the city of Sandakan (Payne, 1989). The population is ~2,000 with small settlements scattered along the riverbank. Many villagers are self-sufficient farmers, but there are still areas of riparian forest. In places, untreated sewage from individual settlements discharges to the river. Situated ~26 km from Sukau Village, Gomantong Caves are protected as a swiftlet nesting area, and the immediate surrounding area remains relatively pristine.

Abai (AB): (j) Abai (AB) area; (k) Balat Damit (ABA); (l) Sg. Merah (ABB). Relatively close to the estuary of the Sulu Sea, this area is near the newly designated (2008) Ramsar wetland of Kinabatangan - Lower Segama. Although there are small settlements in this area, the population in 1996 was only 290 (Payne, 1996). Freshwater swamp vegetation, such as *Nypa fruticans*, is widespread along the estuary.

(a) Batu Putih (BP) area

(b) Sg. Koyah (BPA) (Imagery date: 24/06/2013)

(c) Sg. Pin (BPB) (Imagery date: 24/06/2013)

(d) Danau Kaboi (BPC) (Imagery date: 24/06/2013)

(e) Sukau (SK) area

(f) Malbumi Plantation (SKA) (Imagery date: 24/06/2013)

(g) Sg. Resang (SKB) (Imagery date: 24/06/2013)

(h) Danau Kalinanap (SKC) (Imagery date: 21/06/2005)

(i) Sg. Menanggol (SKD) (Imagery date: 24/06/2013)

(j) Abai (AB) area

(k) Balat Damit (ABA) (Imagery date: 24/06/2013)

(l) Sg. Merah (ABB) (Imagery date: 24/06/2013)

Fig. 3.4 (a)–(l) Satellite images for each sampling location with specific imagery dates. (Source: Google Earth software, 2012).

Table 3.2 Summary of sampling sites during the two sampling programmes, together with indications of sample type (main-stem, tributary, oil palm plantation ditch and oxbow lake) and distance from the Sulu Sea. The number of samples collected are indicated by a = October 2009, b = November 2009, c = December 2009, d = February 2010 and e = May 2010. Sample site locations are given in Fig. 3.1 and Fig. 3.2.

Sampling programme	Sampling site	Sample type	Distance from sea (km)	No. of samples
Preliminary survey	Batu Putih (BP)			
	• Sg. Pin (BP1)	Tributary stream	81.8	20
	• Sg. Koyah (BP2)	Tributary stream	66.9	17
	• BS Mill (BP3)	Plantation mill	87.7	3
	• PS Plantation (BP4)	Plantation mill	62.2	13
	• DGFC (BP5)	Ox-bow lake	71.1	1
	• Canal 1 (BP6)	Ditch	70.8	1
	• Canal 2 (BP7)	Ditch	70.9	1
	• Canal 3 (BP8)	Ditch	71.4	1
	Sukau (SK)			
	• Sg. Resang (SK1)	Tributary stream, main stem	34.6	27
	• Sg. Resik (SK2)	Tributary stream, main stem	40.1	11
	• Kuala Sukau (SK3)	Tributary stream, main stem	40.8	18
	• Malbumi Plantation (SK4)	Tributary stream, main stem	34.0	12
	• Sg. Menanggol (SK5)	Tributary stream, main stem	43.0	18
	• Gomantong Caves (SK6)	Groundwater spring	62.6	1
	• Rainfall 1 (27/08/2008)	Precipitation	-	2
	• Rainfall 2 (28/08/2008)	Precipitation	-	1
	• Rainfall 3 (29/08/2008)	Precipitation	-	1
	• Rainfall 4 (30/08/2008)	Precipitation	-	1
	Bilit (BT)			
	• Sg. Tenagang Besar (BT1)	Tributary stream, main stem	47.1	21
	• Sg. Tenagang Kecil (BT2)	Tributary stream, main stem	43.5	12
	Abai (AB)			
	• Balat Damit (AB1)	Tributary stream, main stem	19.8	33
	• Sg. Merah (AB2)	Tributary stream, main stem	29.5	15
Concentrated sampling programme	Batu Putih (BP)			
	• Sg. Pin (BPA)	Tributary stream, main stem	81.8	15^a, 12^b, 12^c, 9^d, 12^e
	• Sg. Koyah (BPB)	Tributary stream, main stem	66.9	21^a, 9^b, 9^c, 9^d, 9^e
	• Danau Kaboi (BPC)	Ox-bow lake	77.0	9^a, 9^b, 9^c, 6^d, 6^e
	Sukau (SK)			
	• Malbumi Plantation (SKA)	Tributary stream, main stem	34.0	6^a, 9^b, 9^c, 6^d, 5^e
	• Sg. Resang (SKB)	Tributary stream, main stem	34.6	12^a, 12^b, 14^c, 15^d, 15^e
	• Danau Kalinanap (SKC)	Ox-bow lake	45.1	8^a, 12^b, 12^c, 6^d, 12^e
	• Sg. Menanggol (SKD)	Tributary stream, main stem	42.7	11^a, 9^b, 9^c, 9^d, 12^e
	Abai (AB)			
	• Balat Damit (ABA)	Tributary stream, main stem	19.8	15^a, 14^b, 15^c, 15^d, 18^e
	• Sg. Merah (ABB)	Tributary stream, main stem	29.5	15^a, 18^b, 6^c, 17^d, 18^e

Table 3.3 Approximate land-use distribution in the Lower Kinabatangan floodplain, Sabah, Malaysia.

Area	Population	Land-Use	Source
Batu Putih (BP)	1200-1400	Oil palm: 96,000 ha (79%); alienated forest[1]: 11,500 ha (10%); Protected forest: 11,130 ha (9%); state land forest: 1,300 ha (1%); water bodies: 1,280 ha (1%)	Department. of Environment Malaysia (2009)
Sukau (SK)	2,000	Oil palm: 71,190 ha (42%); alienated forest: 11,070 ha (7%); protected forest: 57,550 ha (34%); state land forest: 24,600 ha (15%); water bodies: 4,700 ha (28%); built-up area: 440 ha (0.3%)	Department. of Environment Malaysia (2009)
Bilit (BT)	~300	Oil palm: 16,600 ha (56%); alienated forest: 3,200 ha (19%); protected forest: 8,100 (27%); water bodies: 915 ha (3%); built-up area: 130 ha (0.4%)	Department. of Environment Malaysia (2009)
Abai (AB)	~300	Oil palm: 71,189 ha (42%); nypa swamp: 39,400 ha (50%); mangrove swamp: 15,590 ha (20%); peat forest: 17,200 ha (22%); seasonally flooded forest: 3,100 ha (4%); marshes: 2,250 ha (3%)	Department. of Environment Malaysia (2009); Sabah Forestry Department (2009)

3.2 FLUORESCENCE SPECTROSCOPY

Fluorescence is an invaluable technique for studying and monitoring the concentration and nature of aquatic DOM. For example, studies conducted by Spencer et al. (2010) in a pristine tropical river in the Congo and Yamashita et al. (2010) in the subtropical Everglades (Florida) showed that fluorescence is a useful tool to provide information on the chemical composition of DOM. Organic

[1] Alienated forest - forest that alienated under leases and provisional leases, native titles and on field registers, settlement schemes, village reserves and areas proposed for alienation.

matter fluorescence occurs when organic matter (OM) is exposed to an external light source, leading to the absorption of a photon by the molecule (Lakowicz, 2006). This leads to a change in the electron configuration whereby an electron from the ground state is excited to a higher energy level. The absorption spectrum is defined by the position of the maximum (λ_{max}) and the molar extinction coefficient calculated at the maximum (ε). The relation between sample concentration (c), ε and the thickness (concentration) of the absorbing medium (fluorophore) through the cuvette or also known as optical path length (d) can be characterised by the Beer-Lambert Law: $A = \varepsilon cd$ (Lakowicz, 2006; Reynolds, 2002). Absorption and excitation occur when a photon is emitted during the transition of an electron from an excited energy level to the ground state, hence, stimulating fluorescence to occur (Hudson et al., 2007; Lakowicz, 2006). The absorption (excitation) and emission of the wavelengths are characteristic of a specific molecular conformation – the fluorophore (Henderson et al., 2009; Hudson et al., 2007; Lakowicz, 2006).

Inner-filter effects (IFE) normally occur due to high concentrations of absorbing molecules including fluorophores particularly in turbid samples due given the presence of larger aggregates or macromolecules that scatter light (Lakowicz, 2006). As incident light passes through the sample it is partly absorbed, as described by the extinction coefficient. Therefore, the light intensity is quenched and reduced whilst going through the solution (Albani, 2007). Consequently, scattering and quenching within the samples disturbs the trilinearity of the data (Andersen and Bro, 2003). The IFE correction applied in this study is explained further in section 3.3.1.

Energy transfers, which involve processes that occur between absorption and emission of light, can be illustrated by using Jablonski energy diagram (Fig. 3.5). The singlet ground, first and second states are represented by S_0, S_1 and S_2 accordingly. An electron is normally excited to some higher vibrational level of either S_1 or S_2 within 10^{-15} s. However, there are times where molecules in condensed phases relaxing in rapid to S_1, which has the lowest vibrational level. This is called internal conversion and normally occurs within 10^{-14} to 10^{-11} s. Fluorescence occurs within 10^{-9} to 10^{-7} s, when relaxation from internal conversion is accompanied with by emission of a photon (Lakowicz, 2006).

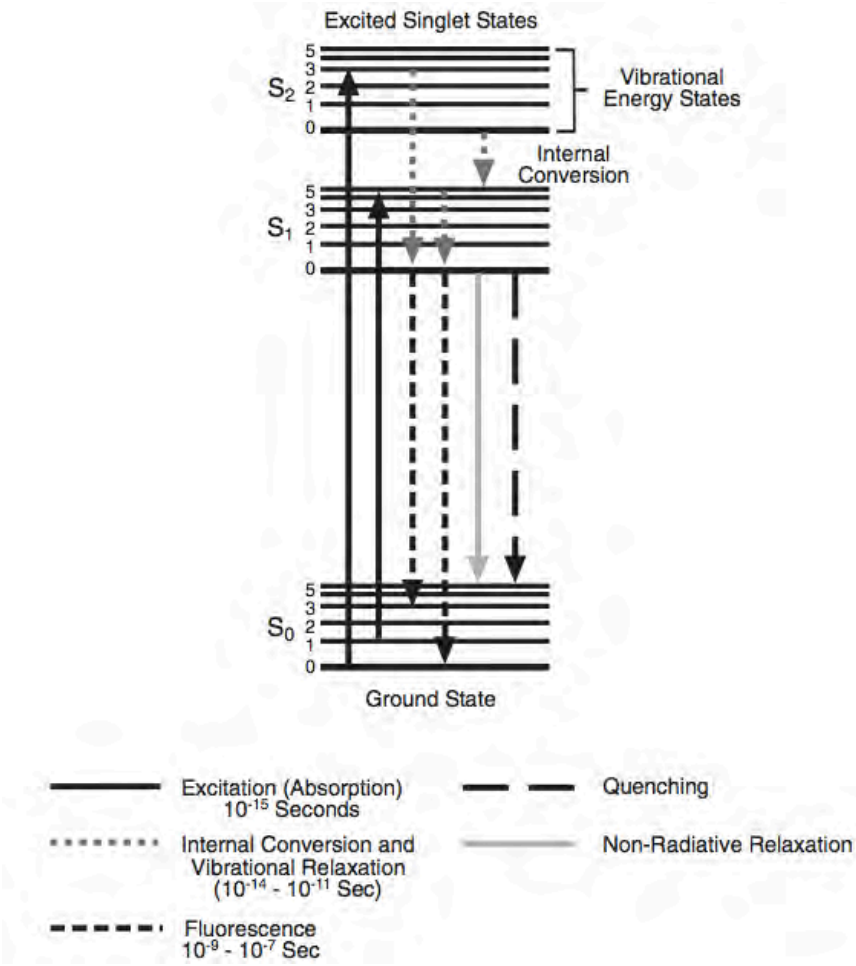


Fig. 3.5 Jablonski diagram illustrates excitation of a molecule by absorption and possible path of energy loss (internal conversion and vibrational relaxation) when returning to the ground state. Collisional quenching occurs when the excited-state molecule is deactivated upon interaction with a second molecule in solution (quencher). Consequently, the fluorescence intensity will be decreased (Hudson et al., 2007; Lakowicz, 2006).

When excitation, emission and fluorescence intensity scanned over a range of wavelengths synchronously and plotted on a single chart, constructing an optical space map, known as excitation-emission matrix (EEM). Fluorescence characteristics of DOM are characterised by two broad peaks. These are

commonly described as peaks A and C, and peaks T and B at shorter emission wavelengths, which are associated with microbially derived organic matter (i.e. tryptophan- and tyrosine-like) (Coble, 1996; Parlanti, 2000). Fig. 3.6 demonstrates fluorescence EEM with common fluorescence features (peak A, C, T and Raleigh-Tyndall effect) and Table 3.4 represents the description for each peak. Advancements in fluorescence spectroscopy have allowed rapid and automated collection of fluorescence intensity data (of shorter wavelengths), thus, enabled more detailed investigation of OM and its water reactivity (Baker 2002b; Hudson et al., 2007; Naden et al., 2010). In addition, fluorescence spectrometry has become increasingly available, with the scanning of a range of emission wavelengths for a fixed excitation. This increases the range of aromatic organic compounds that can be detected (Hudson et al., 2007).

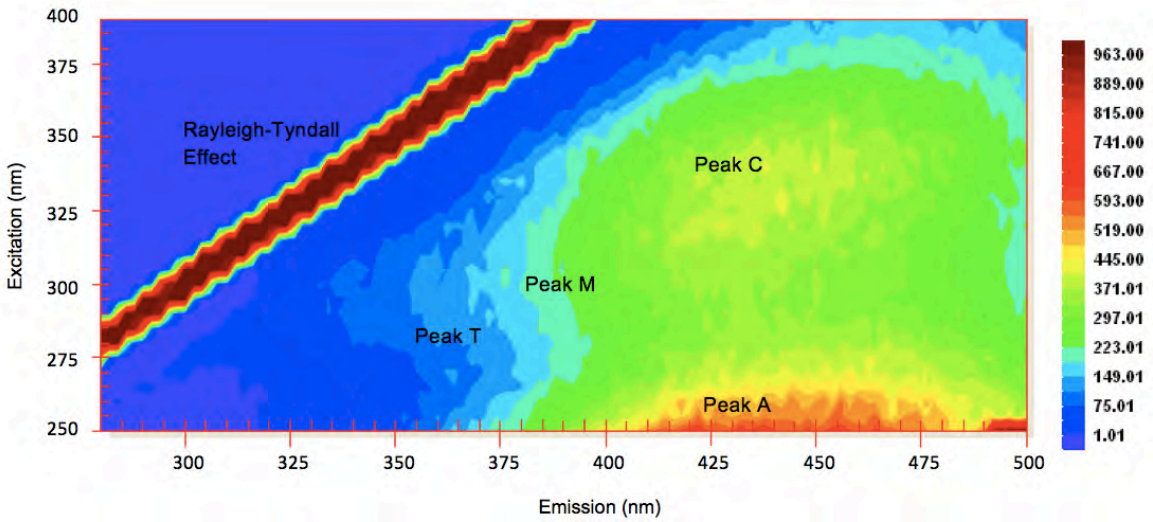


Fig. 3.6 Fluorescence EEM from a stream within an oil palm plantation, with common fluorescence features (peak A, C, M, T and Rayleigh-Tyndall effect) (after Coble, 1996; Parlanti, 2000).

Table 3.4 Description for each common peak in fluorescence EEM as identified by Coble, 1996 and Parlanti, 2000 (in bracket).

Peak	Excitation$_{max}$ / Emission$_{max}$	Description and probable source
A (α')	230-260 / 380-480	Terrestrial humic-like substances.
C (α)	330-360 / 420-480	Terrestrial humic-like substances.
M (β)	310-320 / 380-420	Marine humic-like substances.
T (δ)	270-280 / 320-350	Protein-like; autochthonous; biologically labile.

Various environmental factors have been found to affect DOM fluorescence including pH, temperature, salinity, metal ions and photodegradation. It has been found, for example, that photodegradation is related closely to water level and DOM source (Westhorpe et al., 2012). In natural waters photodegradation impacts DOM structure and character with changes to smaller molecules, and an associated effect on bioavailability. Thus, it is likely to alter fluorescence character as indicated by the presence or absence of peaks or modifications in relative fluorescence intensities on an EEM (Hudson et al., 2007).

A variety of fluorescence indices (FI) are commonly used to synthesise the significant quantities of data that are present in a fluorescence EEM. FIs are defined as the ratio of fluorescence intensity measured at two different points or regions in optical space. Various FIs have been developed since the late 1990s. Indices developed by McKnight et al. (2001), Perrette et al. (2005), Proctor et al. (2000) and Kalbitz et al. (1999) can be correlated with the aromaticity, hydrophobicity and humification of the peak C fluorescence fraction. However, this is only valid for terrestrial waters, which are dominated by natural OM, and many of the correlations used resin extracted samples. A Humification Index

(HIX) developed by Zsolnay et al. (1999) used the ratio of emitted fluorescence 330-345 nm to 435-480 nm with excitation at 245 nm. However, this excitation wavelength (245 nm) is not the maximum excitation wavelength for any fluorescence peak. In this thesis, one of the fluorescence intensity ratios (peak T/peak C) has been used which is considered indicative of the BOD/DOC ratio in terrestrial waters, thus providing a measure of water quality (Hudson et al., 2007; Hudson et al., 2008), as well as enabling comparisons with other studies. The Ratio β/α (BIX) of Parlanti et al. (2000), which captures the peak M and peak T/peak C intensity, is a transferable index of marine and freshwater mixing in marine and estuarine samples. This index appears to be straightforward to interpret and is potentially more transferable in surface waters, with various studies demonstrating a microbial source for peak T fluorescence (Elliott et al., 2006; Hudson et al., 2008).

Filter artefacts in this study have been found to be insignificant when the syringe filters were tested and both poly-vinyl-idine-difluoride (PVDF) and poly-sulfone (PSU) media displayed minor fluorescent peaks, compared to poly-tetra-fluoro-ethylene (PTFE) and poly-propylene (PP) (Urquhart, 2008). A replicate sample survey was completed in October 2009 and a comparison of the effects of filtering in the field vs. filtering post-collection was made between the two data sets. The triplicate samples collected in 2008 had both peak A and C intensities that varied with a coefficient of variance less than 11% (over the range of 130-318 mean intensity units), whilst peak T_{280} intensity had the highest coefficient of variance (41%). Both peak A and C emissions were consistent (coefficient of variance 3% and 2% respectively) and replicate samples had an identical

uncertainty for peaks A and C intensity and peaks A and C emission (coefficient of variance less than 6% over the range 211-349 units, and less than 3% in emission). There was much less variability in peak T_{280} (coefficient of variance less than 17%) indicating that some microbial activity had occurred within the samples post-collection. However, there was no correlation between peak T_{280} intensity and peak C emission for both sampling periods (Fig. 3.7), suggesting the storage and transport prior to filtering did not change the fluorescence characteristics.

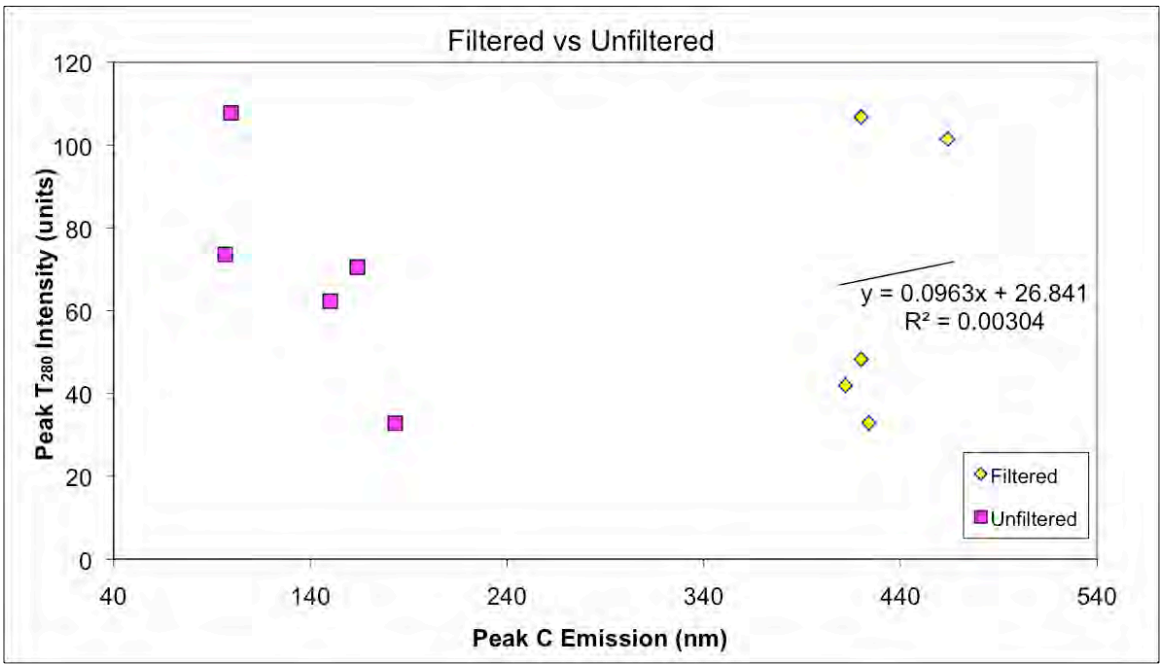


Fig. 3.7 Peak C emission wavelength against peak T_{280} intensity for filtered and unfiltered samples, collected during the preliminary survey and in October 2009.

3.3 LABORATORY METHODS

3.3.1 Excitation-Emission Matrices (EEMs) Spectroscopy

Fluorescence intensities were determined using a Varian Cary Eclipse fluorescence spectrophotometer equipped with a Peltier temperature controller. Emission scans were performed over the wavelengths from 280 to 500 nm, with data collected at 2 nm intervals, and excitation wavelengths from 250 to 400 nm, at 5 nm intervals. Instrument filtration has been applied to remove excitation wavelengths <250 nm. Excitation and emission bandpass were set to 5 nm and photomultiplier tube voltage to 725v. Spectrophotometer output was monitored by regular determination of the Raman calibration of ultra pure water in a sealed 10 x 10 mm cuvette at 348 nm excitation and 5 nm bandpass. This enables a quantitative comparison between different fluorescence measurements. The Raman value during the study period varied within the range 26.0 to 28.2 units with a mean intensity of 27.3 units (st. dev. of 0.7). All fluorescence intensities were corrected and calibrated to a Raman peak intensity of 20 units at 396 (392-400) nm emission wavelength.

EEMs were obtained for each water sample indicating the wavelength at which individual fluorophores emit light. Fluorescence regions can be attributed to both natural fluorescence i.e. humic- and fulvic-like. Normally when analyzing fluorescence EEM data, the position of maximum fluorescence intensity for each peak is recorded, together with its specific spectral location described by the excitation and emission wavelengths. In this study, fluorescence peaks C (excitation 300-340 nm; emission 400-480 nm), peak T (excitation 270-280 nm; emission 340-360 nm) and peak A (the maximum fluorescence at 250 nm

excitation; emission 400-480 nm) were identified. Peak B was not observed in any of the samples.

Absorption coefficients at 254 and 340 nm (a_{254} and a_{340}) and spectral slope for the interval of 275-295 nm ($S_{275-295}$) (Helms et al., 2008) were determined using a Lightwave (WPA) spectrophotometer and 2 ml (10 x 5 mm; 5 mm path length) cuvettes. Absorption coefficients at 254 and 340 nm were calculated as follow (Helms, et al., 2008):

$$a = 2.303A/l \quad (1)$$

where A is the absorbance provided by the spectrophotometer; l is path length of the cuvette (m).

Consequently, $S_{275-295}$ was calculated by linear regression of the log-transformed a spectra. It is derived from DOM absorption spectra by fitting the absorption data to following equation (Helms et al., 2008):

$$a\lambda = a\lambda_{ref}e^{-S(\lambda-\lambda_{ref})} \quad (2)$$

where a is Napierian absorption coefficient (m^{-1}), λ is wavelength (nm) and λ_{ref} is reference wavelength (nm).

Distilled deionised water was used as a reference, and absorbance readings were corrected, where necessary, for long-term baseline drift. In this study, an IFE correction was applied to the entire data set using the following calculations (Ohno, 2002):

$$I = I_0 (10^{-b(Aex+Aem)}) \quad (3)$$

where I is detected fluorescence intensity; I_0 is fluorescence in the absence of self-absorption; b is the path length for both the excitation and emission beam; A_{ex} is absorbance at wavelength ex; and A_{em} is the absorbance at wavelength em.

3.3.2 Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) concentrations were determined using a Shimadzu TOC-V-SCH analyser with auto-sampler TOC-ASI-V. Samples were acidified to pH ~2 with HCl and analysed within one month of sample collection. The acidified samples (pH~2) were sparged for 8 minutes at 75 or 100 ml/min^{-1} with either ultra-pure oxygen to remove all inorganic carbon from samples prior to measurement.

3.3.3 Stable Isotopes

Stable isotope analyses were undertaken at the University of Birmingham using a GV Instruments Isoprime isotope-ratio mass spectrometer connected to a Eurovector elemental analyser. Stable isotope values are expressed using the δ convention, where $\delta^{18}O = (^{18}O/^{16}O_{sample}) / (^{18}O/^{16}O_{standard}) - 1$, and similarly for hydrogen isotopes ($\delta^{2}H$) expressed as ‰ (per mil) where the standard is Vienna standard mean ocean water (V-SMOW). For hydrogen isotope analysis, approximately 0.3 µl of water was injected from sample vials on an autosampler into a column where reduction to hydrogen took place at 1050 ºC over a chromium metal catalyst. At least two successive analyses were made by repeat injections from the same vial. Internal (within-run) precision is 0.4 per mil for δD

and overall (external) precision is greater than 1 per mil.

Oxygen isotope analyses were undertaken using an equilibration technique. 200 µl water samples were left to equilibrate (CO_2) in a sealed container for a period of 7 hours allowing the headspace CO_2 to take on the $\delta^{18}O$ composition of the water. The equilibrated CO_2 was then analysed on the Isoprime mass-spectrometer. The internal precision for $\delta^{18}O$ is typically 0.08 per mil, external precision is better than 0.15 per mil.

3.4 DATA PRE-PROCESSING

Prior to data analysis, areas that were identified as having redundant and noisy signals during processing of the fluorescence data were removed. Fluorescence spectra were normalised to the Raman scatter peak at an excitation wavelength of 348 nm of deionised water by subtracting the Raman signal from the raw data (Stedmon et al., 2003). IFE correction has also been applied as described in section 3.3.1.

3.5 DATA POST-PROCESSING

3.5.1 Parallel Factor Analysis (PARAFAC)

Data generated by fluorescence spectroscopy in general have caused difficulties in analysing given the quantities of data generated. One approach developed to overcome this problem is PARAFAC which was introduced by Stedmon et al. (2003). PARAFAC is a novel statistical modeling approach which decomposes EEMs into their individual fluorescent components. This technique has been

widely used and recently, the combination of EEM-PARAFAC has been found useful to detect small but significant impairs in DOM composition in subtropical wetlands (Yamashita et al., 2010). In this study, PARAFAC modeling was first completed on samples from the preliminary survey and then on data from the entire sampling programme. It was conducted following Bro (1997) and Stedmon et al. (2003). Fluorescence EEMs from each data set were combined into a 3-dimensional data array separately, and the data were decomposed to a set of trilinear model and a residual array (after Kowalczuk et al., 2010; Stedmon et al., 2003):

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk} \qquad i = 1,\ldots,I \qquad j = 1,\ldots,J \qquad k = 1,\ldots,K \qquad (4)$$

where x_{ijk} is the fluorescence intensity for sample *i* at emission wavelength *j* and excitation wavelength *k*; a_{if}, b_{if} and c_{kf} are the loading matrices. *F* is the number of components in the model, and e_{ijk} is the residual noise (variability not explained by the model). In this analysis, scatters in the high turbid EEMs samples (results of suspended sediments presented in Chapter 6), which occurred within 250 to 280 nm excitation and 280 to 290 nm emission wavelengths also have been removed. Filtration and instrument filtration in this study do not allow acceptable signal/noise for excitation <290 nm. Consequently, microbial peak, which located at 280 nm excitation has been removed in the PARAFAC results/components. Nevertheless, the peak picking approach managed to provide the information within this missing region. Appendix A presents PARAFAC components with excitation started at 250 nm and 290 nm.

The model was derived by minimising the sum of squared residuals using a least squares algorithm. Signals from fluorescent DOM can be separated using this technique, without assumptions on the spectral shape or number. The only assumptions in the PARAFAC algorithm are that the spectra from each component differs and that there are no negative concentrations or spectra. A PARAFAC model with a non-negativity constraint on all modes (samples, emission and excitation) was implemented in Matlab (Bro, 1997; Andersson and Bro, 2000; Kowalczuk et al., 2010).

The model also returns relative intensities of derived components (scores) as the specific absorption and quantum yield of fluorescence of individual components is unknown. I_n (intensity of the nth component in a given sample) was calculated as the fluorescence intensity at the peak excitation and emission maximum of the nth component using the following equation (after Kowalczuk et al, 2009):

$$I_n = \text{Score}_n * \text{Ex}_n(\lambda_{max}) * \text{Em}_n(\lambda_{max}) \quad (5)$$

where Score_n is the relative intensity of the nth component, Ex_n (λ_{max}) is the maximum excitation loading of the nth component, Em_n (λ_{max}) is the maximum emission loading of the nth component derived from the model. The total fluorescence intensity of a given sample was calculated as the sum of the components present in the samples:

$$I_{TOT} = \sum_{1}^{n} I_n \quad (6)$$

The percentage contribution of a given component to total fluorescence intensity was calculated as the ratio of the *n*th component intensity to a total fluorescence intensity of a given sample.

The data were then split into two random halves, representing a calibration data array and a validation array. The appropriate number of components (the model rank) was determined by comparing the excitation and emission spectra of the components between the calibration and validation data arrays. Using this technique (split-half analysis), a number of components were validated from the data-set. If the correct number of components has been chosen, then the loadings from both models would be the same, which reflects the uniqueness of the PARAFAC model (Stedmon et al., 2003).

The number of studies that have used PARAFAC to characterise the DOM has steadily increased over the last few years. However, several limitations involving PARAFAC components with respect to the interpretations as well as the uncertainties in the robustness have been addressed by several publications. For example, Murphy et al. (2011) and Fellman et al. (2009) considered the limited chemical interpretation of PARAFAC components, representing the fluorophores. PARAFAC components also tend to overlap as the model relatively relies on the each component concentrations as well as their unique behaviour (Fellman et al., 2009; Stedmon et al., 2003). Fellman et al. (2009) also highlighted that PARAFAC approach potentially has component selection problem.

Two categories of independent data sets from the sampling campaign were successfully validated using the split-half validation procedure to ensure the

correctness of the modeled DOM components. The first category data-set is based on an inter-seasonal comparison between samples collected in the wet and dry season, whilst the second category is based on the type of land use predominant in the area where a sample was collected: oil palm plantations (OP), secondary forests (SF) and coastal swamps (CS).

In order to gain more insight on DOM characterisation, FI were also used. Ratios derived from peak picking were generated: peak C/a_{340}, peak A/peak C intensity; as well as from the PARAFAC components that were equivalent to the peak picking parameters. FI has been applied extensively given its strong correlation with many functional assays (Baker et al., 2008). UV absorbance at 340 nm (a_{340}) and spectral slope for the interval of 275-295 nm ($S_{275-295}$) have been found to approximate DOM molecular weight, and the ratio of (component that equivalent to peak C e.g. IC1 in Chapter 5) to a_{340} has been interpreted as the ratio of DOM concentration to molecular weight (Baker et al., 2008; Helms et al., 2008).

3.5.2 Discriminant Analysis (DA)

Discriminant analysis is a multivariate statistical modeling technique, which can be used as a tool for pattern recognition. Objects can be classified into mutually-exclusive groups according to a set of independent variables (Gazzaz et al., 2012). Discriminant analysis has been applied to both the peak picking and PARAFAC data sets to characterise the DOM in this study. Values of peak C emission, UV absorbance at 340 nm, spectral slope and different type of

fluorescence indices (as explained in sections 3.2 and 3.5.1) have been used to determine the pre-dominance of each parameter in the objectives of this study. For the main stem samples, the predominance of each parameter was determined firstly at different depths, secondly with distance downstream; and thirdly at sampling periods (to identify DOM variation between wet and dry seasons).

3.6 CONCLUSION

The Lower Kinabatangan River catchment, Sabah, Malaysia is very important not just as a water source for local communities but is also associated with a wide and diverse flora and fauna, including many unique and endangered species. Land use changes and progressive environmental deterioration from commercial logging activities and development of the oil palm plantations since the 1980s represent on-going threats to this area. A water quality study conducted in 2005 to 2006 indicated the waters in this area was Class IIB (equals to maximum total suspended sediment concentrations of 50 mg/l).

Water and precipitation samples have been collected according to two sampling designs: i. preliminary survey in August-September 2008 and ii. sampling programme in 2009 to 2010. A total of five data sets have been obtained during the more detailed sampling campaign. It was consisted of two seasons (wet and dry) and three types of land uses (oil palm plantations, secondary forests and coastal swamps). Sampling locations were chosen based on their ease of access and logistical limitations. Samples from Batu Putih, Bilit,

Sukau and Abai have been collected during the preliminary survey, while Bilit has been omitted during the sampling campaign.

Characterisation of DOM has been determined by using fluorescence spectroscopy, dissolved organic carbon (DOC) and stable isotopes. Excitation-emission matrices (EEM) were obtained and mapped when excitation, emission and fluorescence intensity were synchronously scanned over a range of wavelengths. Parallel Factor Analysis (PARAFAC) was used to decompose the EEMs into their individual fluorescent component, which is related to DOM origin material. The results are presented in the following chapters.

4. CHARACTERISATION OF DISSOLVED ORGANIC MATTER IN THE LOWER KINABATANGAN RIVER, SABAH, MALAYSIA

Scope of Chapter

Spatial trends in dissolved organic matter (DOM) were investigated in the Lower Kinabatangan River catchment, Borneo. Water samples were collected during summer baseflow in August and September 2008 (preliminary survey) from areas with oil palm plantations (Batu Putih, Sukau, Bilit and Abai). Sample fluorescence, absorbance and, for a sub-set ^{18}O and ^{2}H isotopic compositions, were determined. The isotopic ratios clarified catchment water dynamics, indicating that surface waters in oil palm areas were characterised by a strong evaporative effect**,** indicating long residence times compared to other surface water samples. DOM is best characterised by variations in fluorescence peak C intensity, UV absorbance and spectral slope, while the presence of a DOM fraction with high peak C fluorescence intensity – UV absorbance ratios in samples from tributary rivers indicate the relatively unprocessed end-member of fresh DOM. Parallel Factor Analysis (PARAFAC) was used to decompose the fluorescence excitation-emission matrices (EEMs). Three PARAFAC components were extracted (C1, C2 and C3), of which the peak M component could be derived from microbial sources and/or photo-degradation processes. Strong positive correlations were found between PARAFAC components and peak C, peak A and peak T_{280} intensities. Both peak picking and PARAFAC were found to follow the same trend in DOM degradation from upstream to downstream. It is

hypothesised that the upstream DOM is rapidly photo- and microbially- degraded to less fluorescent DOM, and is probably stabilised as fine colloidal complexes. In contrast, downstream DOM concentration and character is controlled by hydrological processes: specifically by variable rates of water movement downstream.

4.1 INTRODUCTION

Tropical wetlands perform a number of globally significant ecosystem functions. They are characterised by marked annual cycles in precipitation, high solar radiation (Graneli et al., 1998; Hader et al., 1998; Saigusa et al., 2008) and diverse biological communities (Dudgeon, 2003; Junk, 2002) with rapid rates of nutrient recycling and processing (Hader et al., 1998). Wetlands act as a universal store and possible sink for carbon (Alkhatib et al., 2007; Limpens et al., 2008; Richey et al., 2002) and where closely integrated with fluvial systems, they form an important part of the pathway connecting sources of carbon from continental to marine environments (Stephens and Rose, 2005). Tropical wetlands, for example, have been estimated to contribute ~60% of the total water, sediment and organic carbon input to the ocean globally (Alkhatib et al., 2007).

Dissolved organic matter (DOM) is ubiquitous in aquatic systems (Baker and Spencer, 2004; Evans et al., 2005; Oliveira et al., 2006) but many types of wetland are notable by the high quantities of DOM that are frequently present (Mladenov et al., 2007; Stern et al., 2007). DOM fluxes from wetlands represent an important carbon input to river systems, as they represent the largest and most bioavailable pool (Wilson and Xenopoulos, 2008). The presence of organic matter

affects the transport of organic pollutants, particle surface and colloid chemistry, photochemistry of natural waters and nutrient availability in freshwater aquatic systems (Fellman et al., 2008; Hope et al., 1994), whilst DOM also contributes to chemical processes in natural water bodies by altering the acidity of surface waters, affecting metal speciation and ion-exchange between water and sediment phases. Both dissolved and particulate forms of organic matter are also an important source of energy in stream ecosystems (Hope et al., 1994).

DOM characteristics may change significantly as a result of photochemical degradation in shallow waters as a result of greater penetration of UV-B radiation, mixing within the water body and input of terrestrial material (Findlay and Sinsabaugh, 1999; Spencer et al. 2009). Moreover, DOM may be degraded directly (by alteration of the DOM structure) or indirectly (by reactions with free radicals created by the application of light). From a catchment perspective, up-stream sites are generally dominated by inputs of more terrestrially derived DOM and have higher concentrations of dissolved organic carbon (DOC) (Dalzell et al., 2009), whilst downstream DOM will often be hydrologically controlled by rapid transport especially in large rivers (Findlay and Sinsabaugh, 1999). Light penetration at downstream sites may also be less and mixing depths greater, decreasing the effects of photolysis. The photoproducts from photochemical reactions including low molecular weight organic compounds, trace gases, inorganic carbon, phosphorous- and nitrogen-rich compounds (Cory et al., 2007; Kowalczuk et al., 2009; Winter et al., 2007).

In natural water bodies DOC provides an important primary food source for aquatic food webs (Pace et al., 2004) and ecosystem metabolism (Bradley et al.,

2007). High DOC concentrations are common particularly in organic soil pore-waters, and in surface and sub- surface water flows from wetlands (Evans et al., 2005). However, the magnitude and nature of these carbon fluxes are likely to be affected by catchment management, including wetland drainage, river channelisation and/or regulation. This is particularly evident in South and Southeast Asia where many catchments have experienced rapid conversion of land to agriculture (Atapattu and Kodituwakku, 2009; Mattsson et al., 2000; Sidle et al., 2006) with a considerable reduction in wetland extent. In Indonesia, for example, ~45% of the original peat swamp forest has been lost (Rixen et al., 2008) and a substantial proportion has been converted into rubber (*Hevea brasiliensis*) and oil palm plantations (*Elaeis guineensis*) (Hooijer et al., 2006). In Malaysia land use has changed primarily as a result of government development policies (Abdullah and Nakagoshi, 2006), which in Sabah (Malaysian Borneo) has encouraged the development of oil palm plantations. Land conversion has been extensive and rapid especially in east Sabah (in Sandakan, Lahad Datu and Tawau), however, many of the environmental implications of the developing agro-forestry industry have not been fully quantified.

The ability to determine the impacts of environmental degradation on freshwater systems has been significantly enhanced by a number of new techniques to characterise the nature of DOM, including fluorescence excitation-emission matrices spectroscopy (EEMs) (Coble et al., 1990; Baker et al., 2008; Hudson et al., 2007; Mariot et al., 2007; Parlanti et al., 2000). EEMs provide a summary of the total luminescence spectra which are exhibited as contour maps of the fluorescence landscape with iso-intensity levels portraying various peaks.

Advances in bench top spectrofluorometers enable EEMs that extend into the shortwave UV (>200 nm) to be generated rapidly, permitting DOM to be characterised by individual fluorescence centres using shortwave excitation and emission maxima (Spencer et al., 2007).

The nature of DOM reflects the influence of many factors including landscape, vegetation / land use, hydrology and climate, and it is important to understand the way in which water moves through a catchment when interpreting EEMs. Here, determination of environmental isotopes (^{2}H and ^{18}O) can provide invaluable information on the relative contributions of recent rainfall events and stored waters to river systems from which it may be possible to quantify the mixing between meteoric and groundwater end-members (Darling, 2004; Kendall and Coplen, 2001).

This chapter presents the results from a summer base-flow sampling programme in the Lower Kinabatangan River, Sabah, Malaysia. This work sought to characterise DOM composition, and its relationship to recent meteoric and stored groundwater sources as inferred by stable isotopes, in a tropical catchment which is undergoing rapid agricultural change from logging and development of oil palm plantations. Specifically, the objective is to characterise and interpret spatial patterns and trends in DOM (concentration and quality) across a tropical agricultural catchment using UV-visible absorbance, fluorescence spectroscopy and isotope ratio mass spectrometry and inferring differences in the pattern of water movement through the catchment from environmental isotopes (^{18}O and ^{2}H).

4.2 RESULTS

4.2.1 Stable Isotope Analyses

The results of stable isotope analyses ($\delta^{18}O$ and $\delta^{2}H$) are shown in Table 4.1 and plotted on Fig. 4.1. The isotopic composition of rainfall varies on a global scale and defines the global meteoric water line (GMWL, defined as $\delta^{2}H = 8 \times \delta^{18}O + 10$), local or regional meteoric water lines that have slightly different slopes and intercepts can be determined from annual precipitation records. Araguás-Araguás et al. (1998) established a RMWL for neighbouring Sarawak which provides a useful reference for the present study. Most meteoric water will lie along the RMWL, surface waters that subsequently evaporate from an RMWL source will progress at a lower slope away from that line, as they become isotopically heavier. Since the initial water vapour from oceanic sources does not form completely in equilibrium, there is a slight surplus of $\delta^{2}H$, known as the d-excess of about +10 per mil $\delta^{2}H$ (see GMWL equation above). The deuterium excess is established at the time of vapour formation, usually from an oceanic source, and can be used to identify different water vapour sources. There are few studies on the stable isotopes of surface waters and rainfall in this part of SE Asia but Stephens and Rose (2005) provide some data from a study in neighbouring Sarawak which is included in the table below (Table 4.1).

Table 4.1 Summary isotope data for the Lower Kinabatangan River Catchment (standard deviations in parentheses) and comparison with data from Niah in Sarawak (from Stephens and Rose, 2005).

Sampling Station	No. of samples		Sampling date (dd/mm/yy)	pH		Water temperature (°C)		$\delta^{18}O$ (‰) V-SMOW		$\delta^{2}H$ (‰) V-SMOW		d-Excess (‰)	
	From main river												
Batu Putih (BP)													
Sg. Pin (BP1)	6	**	23/08/08	7.9	(0.3)	30.6	(0.7)	-6.8	(0.1)	-46.6	(0.44)	3.2	(0.5)
Sg. Koyah (BP2)	6	**	23/08/08	6.9	(0.3)	29.6	(2.9)	-7.3	(0.1)	-49.3	(0.25)	4.6	(0.6)
BS Mill (BP3)	1	**	24/08/08	4.9	**	31.2	**	-6.7	**	-43.9	**	5.1	**
PS Plantation (BP4)	5	**	25/08/08	4.9	(0.2)	27.9	(0.9)	-7.2	(0.6)	-47.2	(3.3)	6.1	(1.3)
Rainfall (DGFC)	1	**	25/08/08	**	**	**	**	-4.0	**	-25.4	**	3.9	**
DGFC (BP5)	1	**	27/08/08	5.0	(0.04)	25.9	**	-6.3	**	-43.9	**	2.3	**
Canal 1 (BP6)	1	**	25/08/08	5.7	**	29.2	**	-5.1	**	-39.7	**	-2.5	**
Canal 2 (BP7)	1	**	25/08/08	7.0	**	28.5	**	-6.7	**	-43.8	**	5.2	**
Canal 3 (BP8)	1	**	25/08/08	6.0	**	28.9	**	-7.0	**	-44.4	**	7.0	**
Sukau (SK)													
Rainfall 1	2	**	27/08/08	**	**	**	**	-2.5	(0.1)	-7.9	(0.41)	10.7	(0.7)
Rainfall 2	1	**	28/08/08	**	**	**	**	-2.9	**	-7.8	**	13.2	**
Rainfall 3	1	**	29/08/08	**	**	**	**	-6.5	**	-36.5	**	11.3	**
Rainfall 4	1	**	30/08/08	**	**	**	**	-9.7	**	-60.8	**	10.4	**
Sg. Resang (SK1)	8	1	28/08/08	6.5	(0.5)	29.1	(0.6)	-7.9	(0.1)	-50.0	(0.86)	8.4	(0.6)
Sg. Resik (SK2)	3	1	28/08/08	7.4	(0.1)	30	(0.8)	-7.9	(0.1)	-51.0	(0.16)	7.2	(0.5)
Kuala Sukau (SK3)	5	1	28/08/08	7.5	(0.1)	29.4	(0.6)	-7.9	(0.1)	-50.9	(1.0)	7.5	(1.3)
Malbumi Plantation (SK4)	3	1	02/09/08	6.5	(0.1)	28.7	(0.5)	-7.4	(0.1)	-49.0	(0.66)	5.6	(0.6)
Sg. Menanggol (SK5)	5	1	02/09/08	6.4	(0.04)	27.4	(1.1)	-7.1	(0.2)	-48.0	(1.23)	4.6	(0.6)
Gomantong Caves (SK6)	2	**	03/09/08	7.1	(0.02)	24.7	(0.4)	-6.3	(0.03)	-40.4	(0.24)	6.1	(0.02)

Sampling Station	No. of samples	From main river	Sampling date (dd/mm/yy)	pH		Water temperature (ºC)		$\delta^{18}O$ (‰) V-SMOW		$\delta^{2}H$ (‰) V-SMOW		d-Excess (‰)	
Bilit (BT)													
Sg. Tenagang Besar (BT1)	6	1	02/09/08	6.4	(0.2)	28.4	(0.4)	-6.2	(0.5)	-43.5	(4.59)	2.5	(1.7)
Sg. Tenagang Kecil (BT2)	3	1	02/09/08	6.4	(0.03)	27.8	(0.4)	-6.4	(0.8)	-43.6	(4.58)	3.6	(1.0)
Abai (AB)													
Balat Damit (AB1)	11	1	29/08/08	6.2	(0.5)	28.5	(0.4)	-7.7	(0.4)	-49.7	(2.59)	6.9	(0.8)
Sg. Merah (AB2)	6	1	29/08/08	6.5	(0.2)	29	(0.6)	-7.8	(0.1)	-50.7	(0.3)	6.5	(0.6)
Data from Niah (from Stephens and Rose, 2005)													
S. Niah	15	**	26/04/01	**	**	**	**	-7.9	(0.3)	-49.0	(4.1)	13.5	(2.9)
S. Niah	1	**	27/04/01	**	**	**	**	-8.3	**	-52.4	**	13.0	**
South China Sea	1	**	26/04/01	**	**	**	**	-4.6	**	-29.3	**	7.0	**
K. Niah	3	**	26/04/01	**	**	**	**	-6.9	(3.1)	-33.0	(19.1)	6.8	(5.0)
G. Kira cave interior drip	2	**	23/04/01	**	**	**	**	-6.7	(0)	-38.9	(0.6)	14.2	(0.7)
Rain outside West Mouth	2	**	25/04/01	**	**	**	**	-10.8	(0.1)	-71.0	(0.5)	14.2	(0.8)
G. Kira cave mouth drip	2	**	23/04/01	**	**	**	**	-8.2	(0)	-53.3	(1.1)	11.8	(1.2)
Rain outside Gan Kira	1	**	23/04/01	**	**	**	**	-4.8	**	-26.0	**	11.6	**
Rainforest pool	1	**	27/04/01	**	**	**	**	-7.3	**	-44.6	**	13.3	**
Rainforest stream (S. Subis)	1	**	27/04/01	**	**	**	**	-8.4	**	-54.7	**	12.1	**

** - Data are unavailable

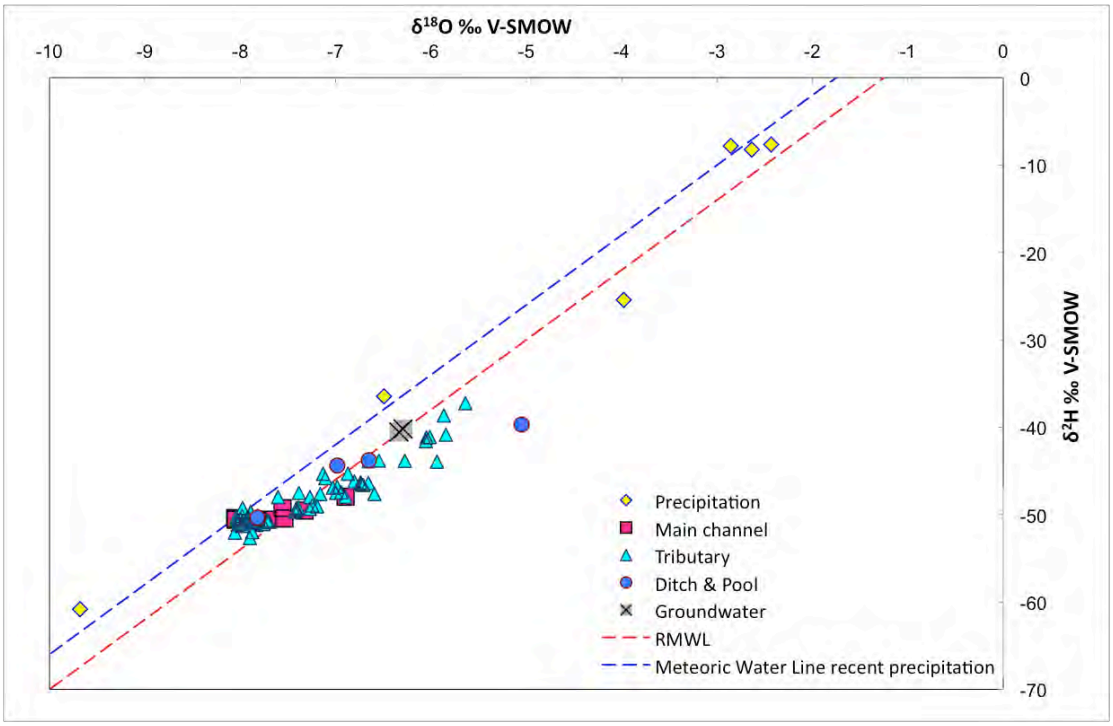


Fig. 4.1 Plot of $\delta^{18}O$ versus $\delta^{2}H$ for sampling sites at the Lower Kinabatangan River Catchment, and comparison with the regional meteoric water line (RMWL) and the meteoric water line for local precipitation.

Opportunistic spot sampling of meteoric events was undertaken in the Kinabatangan catchment in August and September 2008. The $\delta^{18}O$ of meteoric water in Sukau ranged from -9.7‰ to -2.5 ‰ while $\delta^{2}H$ values ranged from -61 ‰ to -7.6 ‰, all lying parallel to, but slightly above, the RMWL. The recent precipitation has a d-excess of +11.9 compared to the RMWL published value of 9.2, indicating a slightly heavier vapour source for these short-term events compared to the longer-term mean. The large absolute range of values observed can be explained by the fact that the rainfall samples were not representative of complete events, but only a small part of them. Deuterium isotope values within single rainfall events can vary by as much as 30‰ in a period of 15 minutes within a single rainfall event at temperate latitudes.

Isotopic variability within single rainfall events in tropical regions will also be strongly controlled by the ‘amount effect’ (Dansgaard, 1964).

The environmental isotopes provide useful background information on the dynamics of water movement through the Lower Kinabatangan catchment. The isotopic composition of precipitation samples varies significantly in $\delta^{18}O$ and $\delta^{2}H$ during the period of sampling, becoming isotopically lighter over time. The groundwater samples from Gomantong Caves are indicative of the mean annual isotopic composition of precipitation in the catchment: approximately -40 ‰ for $\delta^{2}H$ and -8 ‰ for $\delta^{18}O$. The isotopic composition of the main stem of the Kinabatangan River and tributaries are lighter than the annual mean composition of precipitation, intersecting the regional (and recent) meteoric water lines at approximately -50 ‰ ($\delta^{2}H$) and -8 ‰ ($\delta^{18}O$). These waters evolve away from the meteoric water lines at a lower slope as a result of evaporation. Some of the tributaries respond more strongly (i.e. with a reduced slope) indicating greater evaporation across these sub-catchments. This might reflect a slower rate of water movement to the channel and/or higher evaporation from intercepted precipitation. Significantly, samples collected from canals associated with oil palm plantations are amongst the most evolved waters, which suggests a different pattern of water movement through the oil palm plantations sampled. This may be a result of the canals intercepting the regional water-table and thus have a higher groundwater component of total flow.

4.2.2 DOM Characteristics

This chapter reports the results of a single, summer base-flow survey in the form of the mean and standard deviation of fluorescence and UV-visible absorption of multiple samples analysed within each study site across the four study regions. In-situ measurements at the time of sampling indicated that water temperatures (pH) in Batu Putih ranged from 25.6 - 31.7 ºC (4.8 – 8.5); 26.7-30.2 ºC (5.5 – 7.6) at Sukau; 25.0-28.8 ºC (6.4 – 6.6) at Bilit and 27.8-29.9 ºC (5.0-6.6) at Abai.

Table 4.2 and Fig. 4.2 summarise the results of the DOM absorbance and fluorescence analyses across all sampling sites within the Lower Kinabatangan catchment, while three contrasting sample EEMs are given in Fig. 4.3. The DOM peak A and C intensities (Fig. 4.2d & 4.2f) indicate that across all sites, mean peak A intensity ranged from 140 to 1031 units, and mean peak C intensity from 114 units to 886 units. The two peaks are also strongly correlated (r=0.9, n=225), as observed in other DOM studies (e.g. Baker and Spencer, 2004) indicating that both fluorescence peaks are likely to have no significant contribution from other fluorescent molecules such as optical brighteners, which would generate additional fluorescence in the peak C region (Baker, 2002a). Lowest peak A and C fluorescence intensities are observed in the groundwater springs (SK6).

Table 4.2 Summary mean of absorbance, spectral slope, fluorescence emissions and intensities and PARAFAC data for the Lower Kinabatangan River Catchment (standard deviation in parentheses).

Sampling Station	Sample number	From main river	Absorption coefficient a_{254} (/m)		Absorption coefficient a_{340} (/m)		Spectral Slope (/nm)	Fluorescence								PARAFAC Components			
								Peak A				Peak C				Peak T_{280}		I_{tot}	I_{C1}	I_{C2}	I_{C3}
								Emission λ (nm)		Intensity (units)		Emission λ (nm)		Intensity (units)		Intensity (units)					
Batu Putih (BP)																					
Sg. Pin (BP1)	21	**	97.6	(3.5)	33.6	(1.8)	0.013	428	(7)	898	(68)	422	(7)	612	(57)	161	(30)	62.5 (9.1)	20.4 (3.9)	28.1 (5.6)	14 (5)
Sg. Koyah (BP2)	18	**	82.1	(3.4)	28.7	(1.4)	0.013	430	(6)	655	(60)	424	(7)	424	(42)	112	(28)	40.7 (4.8)	13.6 (1.7)	18.7 (2.3)	8.4 (1.8)
BS Mill (BP3)	3	**	89.2	(2.2)	34.2	(2.0)	0.012	421	(6)	635	(18)	423	(5)	401	(13)	120	(10)	41.3 (0.5)	13.6 (0.5)	18.3 (0.3)	9.5 (1.0)
PS Plantation (BP4)	13	**	81.6	(5.2)	30.9	(2.0)	0.013	428	(11)	499	(163)	426	(11)	256	(116)	109	(49)	26.5 (11)	8.7 (4.2)	10.8 (5.2)	7.1 (1.8)
DGFC (BP5)	1	**	62.2	**	20.3	**	0.019	408	**	409	**	430	**	194	**	255	**	27.0 (**)	5.9 (**)	9.1 (**)	12.0 (**)
Canals (BP 6-8)	3	**	142.5	(39.8)	47.9	(15.0)	0.013	436	(3)	822	(295)	441	(14)	671	(274)	105	(33)	57.4 (20.1)	24.4 (11.9)	24.4 (8.4)	8.6 (2.7)
Sukau (SK)																					
Sg. Resang (SK1)	27	3	81.9	(3.8)	34.8	(1.8)	0.011	428	(9)	351	(90)	431	(12)	185	(62)	70	(32)	17.4 (5.4)	6.3 (2.5)	7.1 (2.2)	4.0 (1)
Sg. Resik (SK2)	12	3	90.0	(1.7)	40.1	(1.1)	0.010	424	(4)	297	(16)	430	(7)	154	(7)	58	(11)	14.6 (0.8)	5.1 (0.3)	6.1 (0.5)	3.5 (0.3)
Kuala Sukau (SK3)	18	3	86.8	(2.2)	40.6	(1.2)	0.009	428	(9)	303	(17)	428	(10)	162	(13)	52	(8)	15.1 (0.8)	5.3 (0.5)	6.4 (0.4)	3.4 (0.3)
Malbumi Plantation (SK4)	12	3	123.7	(14.5)	59.8	(9.0)	0.008	431	(9)	325	(87)	429	(15)	209	(63)	59	(15)	17.3 (4.1)	6.3 (1.8)	7.1 (1.8)	4.0 (0.5)
Sg. Menanggol (SK5)	18	3	106.8	(8.4)	47.6	(6.9)	0.010	432	(6)	443	(129)	437	(14)	282	(64)	57	(12)	23.9 (6.6)	9.6 (3.1)	10.1 (2.9)	4.2 (0.7)
Gomantong Caves (SK6)	1	**	24.4	**	10.1	**	0.007	436	**	254	**	430	**	101	**	49	**	**	**	**	**

Sampling Station	Sample number		Absorption coefficient a_{254} (/m)		Absorption coefficient a_{340} (/m)		Spectral Slope (/nm)	Fluorescence								PARAFAC Components			
								Peak A				Peak C				Peak T_{280}		I_{tot}	I_{C1}	I_{C2}	I_{C3}
		From main river						Emission λ (nm)		Intensity (units)		Emission λ (nm)		Intensity (units)		Intensity (units)					
Bilit (BT)																					
Sg. Tenagang Besar (BT1)	21	3	101.0	(5.1)	39.1	(3.9)	0.013	431	(10)	605	(173)	427	(5)	379	(118)	121	(41)	36.7 (11.8)	11.7 (3.7)	17.0 (5.7)	8.0 (3)
Sg. Tenagang Kecil (BT2)	12	3	73.9	(11.0)	30.3	(6.5)	0.011	429	(9)	461	(115)	433	(12)	257	(50)	72	(15)	23.1 (5.3)	8.2 (2)	10.3 (2.7)	4.6 (0.8)
Abai (AB)																					
Balat Damit (AB1)	36	3	92.3	(10.5)	39.5	(3.7)	0.010	436	(14)	435	(168)	441	(11)	251	(121)	61	(26)	21.8 (8.8)	9.0 (4.9)	8.9 (3.7)	3.9 (0.7)
Sg. Merah (AB2)	21	3	82.1	(6.3)	34.0	(2.7)	0.012	422	(12)	317	(26)	429	(7)	150	(5)	64	(20)	14.2 (1.8)	4.9 (0.2)	5.8 (0.7)	3.5 (1.7)

** - Data are unavailable.

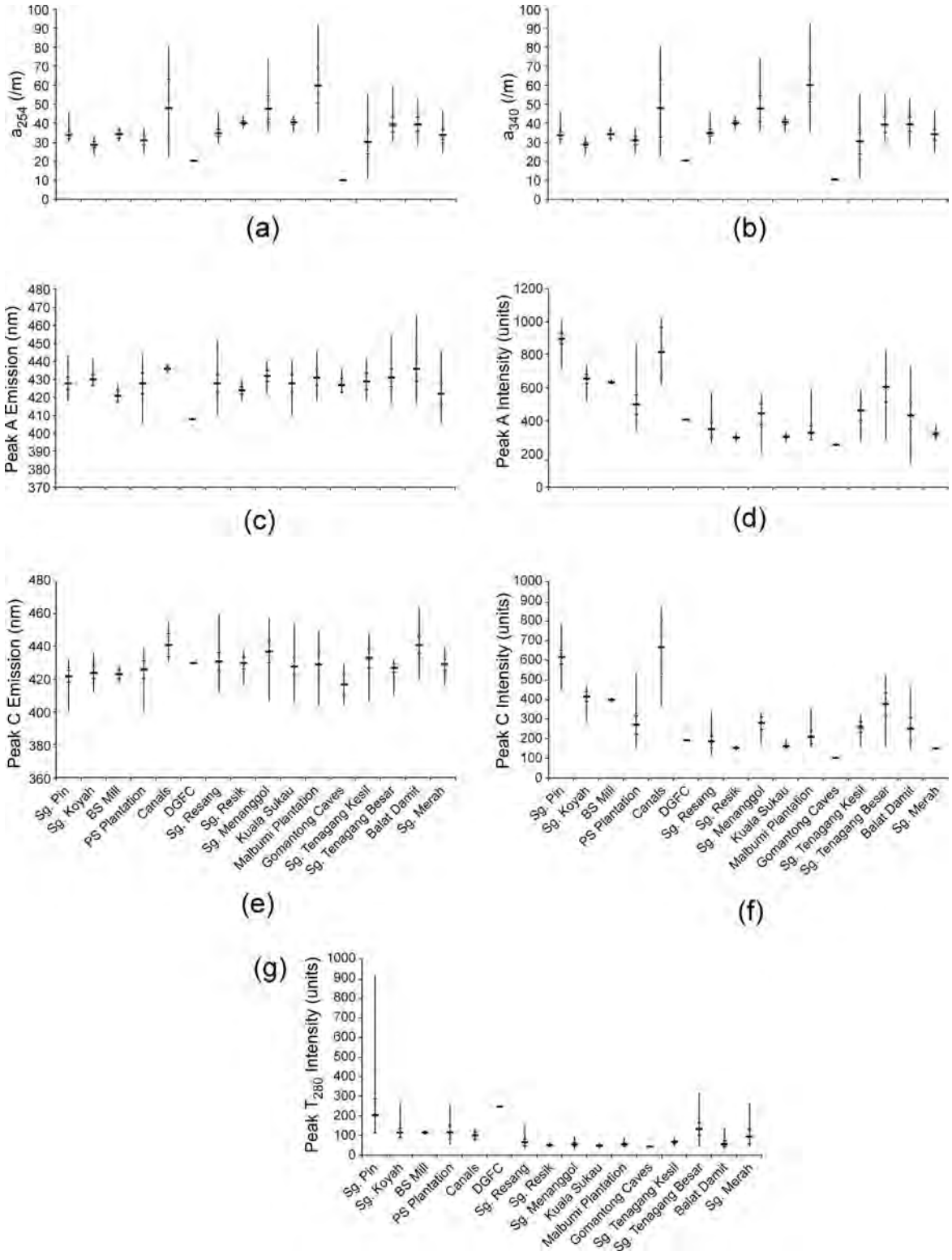


Fig. 4.2 Trends in absorbance and FDOM for each sampling site in the Lower Kinabatangan River: (a) a_{254}; (b) a_{340}; (c) Peak A emission; (d) Peak A intensity; (e) Peak C emission; (f) Peak C intensity; (g) Peak T_{280} intensity.

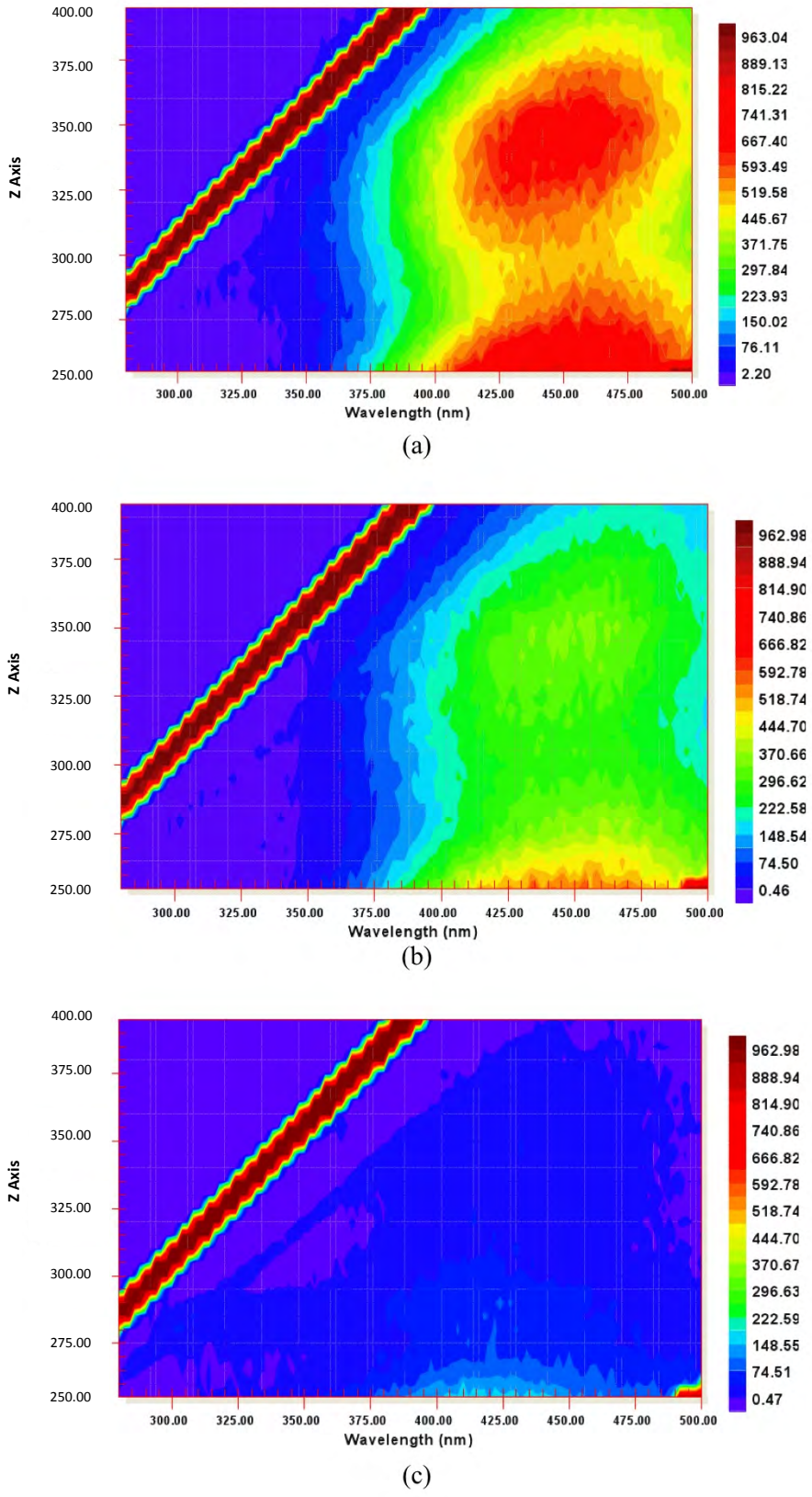


Fig. 4.3 Illustrative fluorescence EEMs for selected sampling sites: (a) Ditch 3 (BP8); (b) Balat Damit 3 (AB1); (c) Gomantong Caves (SK6).

Fluorescence intensities were unusually high at some sites. Particularly high fluorescence peak A and C intensities were found in Batu Putih (Table 4.2) and a greater range in peak A and C intensities was found within this sample area than elsewhere in the catchment (i.e. site mean peak A intensity ranged from 409 to 898 units; site mean peak C from 194 to 671 units). Very high fluorescence intensities were found at the Plantation Ditches (highest peak C intensity: 1031 units) and Sg. Pin (highest peak A intensity: 1013 units). Comparable data (analyzed using the same instrumentation and Raman calibration) from a UK study of a lowland catchment yielded a mean and standard deviation for peak A and peak C of 309±88 and 172±69 units respectively (Cumberland and Baker, 2007) and 192±76 and 93±79 units respectively for a range of SW England rivers (Hudson et al., 2008).

The maximum emission wavelengths of peak A and peak C fluorescence (Table 4.2; Fig 4.2c & 4.2e) are similar across all samples sites except for Sg. Tenagang Besar (BT1). The difference between sites in mean peak C and peak A emission wavelengths were relatively small for peak A: 422-436 nm at Abai; 408-436 nm at Batu Putih; 424-432 nm at Sukau and 429-431 nm at Bilit. Fluorescence peak C emission wavelengths have been correlated with the hydrophobicity of DOM (Baker et al., 2008; Spencer et al., 2009) and conceptually this parameter is related to fluorescence indices associated with peak C intensity (McKnight et al., 2001; Parlanti et al., 2000). Assuming that the fluorescence – hydrophobicity relationship is transferable, then the emission wavelengths of the maximum peak C fluorescence observed (420-440 nm; Table 4.2), indicated a DOM percentage hydrophobicity within the range of ~40-

70%. This highlights the high molecular weight and aromatic nature of the samples collected from the Lower Kinabatangan River.

Peak T_{280} intensities across all sampling sites varied from 32 to 255 units. This fluorescence peak is related to microbial activity and the length of time between sampling and analysis could account for the increased variability in this parameter and the results should therefore be interpreted with caution. Fluorescence peak T_{280} intensities at the upstream Batu Putih sites were high compared to other sampling sites, ranging from 60 to 255 units. Sg. Pin (BP1), Sg. Koyah (BP2), PS Plantations (BP4), Sg. Resang (SK1), Balat Damit (AB1) and Sg. Merah (AB2) had statistically significant for fluorescence peak T_{280} intensities. Particularly high peak T_{280} intensities were found in an oxbow lake (Danau Girang Field Centre; DGFC) in Batu Putih (255 units). Peak T_{280} fluorescence has been shown to be positively correlated with high biological activity and to be strongly related to biochemical oxygen demand (BOD) (Hudson et al., 2008). These high intensities probably reflect, in part, the presence of the Field Centre and a tourist lodge adjacent to the ox-bow lake. This study observed the discharge of untreated sewage directly into the lake, and the peak T_{280} intensity could provide a suitable anthropogenic signal in this area.

UV-visible absorption coefficients at 254 and 340 nm (Table 4.2; Fig 4.2a & 4.2b) exhibited considerable variability between sample sites. UV absorption has been widely observed to correlate with DOC (Baker and Spencer, 2004), and given an absence of direct DOC analyses (as a result of sample size) the results can be interpreted as indicating relative variations in DOC. The

groundwater springs had the lowest absorption coefficients, demonstrating the low DOC in groundwater. The greatest variability in absorption coefficients at 254 (340) nm were found at sites associated with oil palm plantations: BP6-8: 142.5 (47.9) m^{-1} and SK4: 123.7 (59.8) m^{-1}.

Several parameters can be derived from the UV-visible absorbance and fluorescence results, including ratios of fluorescence intensity and the linearised gradient of absorbance or spectral slope. Following Helms et al., (2008) the latter has been calculated at between 275 and 295 nm. Principal components analysis (PCA) of the fluorescence and absorption coefficient data has been conducted to investigate the variability of fluorescence and absorbance properties in the dataset (Baker, 2002b; Spencer et al., 2007). This revealed three parameter clusters: fluorescence intensities of peaks A, C and T_{280} and $S_{275-295}$ comprised one cluster (strongly correlating with PC1; 39% of the variance), absorption coefficients at 254 and 340 nm the second cluster (strongly correlating with PC2; 26% of the variance) and fluorescence emissions of peaks A and C the third cluster (strongly correlating with PC3; 14% of the variance). Fig. 4.4 exhibited the PCA loading components for intensities of peaks A, C and T_{280}; emissions of peaks A and C; and UV absorbance at 254 and 340 nm.

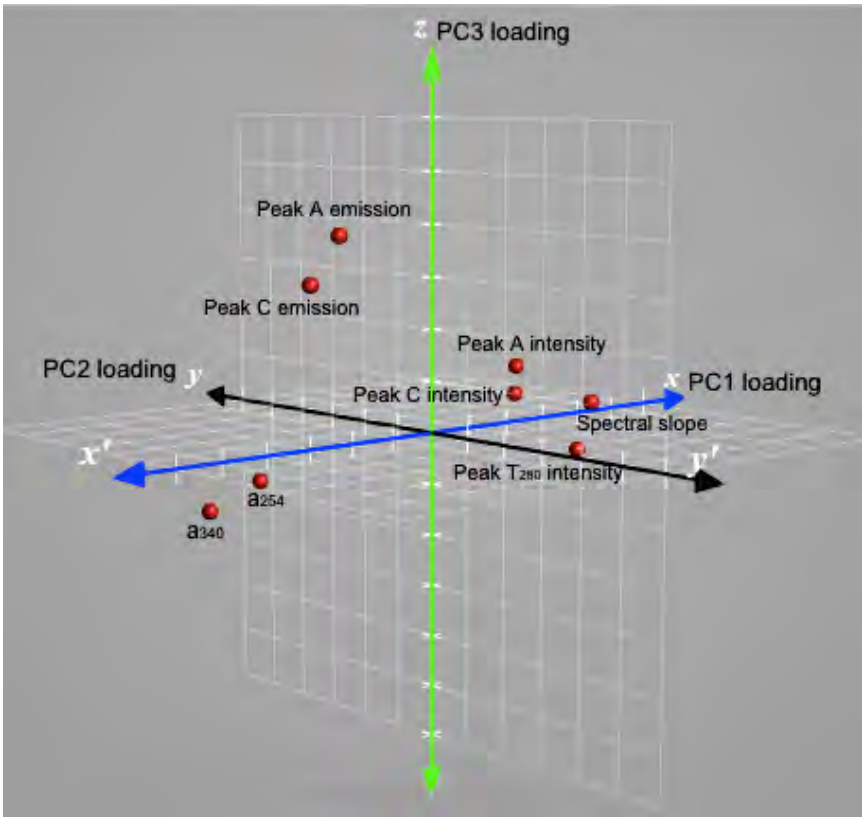


Fig. 4.4 PCA loading components for intensities of peaks A, C and T_{280}; emissions of peaks A and C; and UV absorbance at 254 and 340 nm.

Selected parameters from each cluster group were then plotted against each other. Fluorescence peak C intensity plotted against a_{340} is shown in Fig. 4.5. Fluorescence peak C intensity, when normalized to absorbance at 340 nm, has been found to correlate positively with DOM hydrophilicity and inversely with metal and organic binding capacity (Baker et al., 2008). Particularly high fluorescence per unit absorbance was found in Batu Putih at Sg. Pin site (BP1), the Plantation Ditches (BP6-8), Sg. Koyah (BP2) and BS Mill (BP3) which may reflect the output of fresh DOM derived from the oil palm plantations and mill. Fluorescence intensities per unit absorbance decrease both within individual sample regions, as well as between regions, as the sampling points approach

the coast. Theoretical lines of constant fluorescence per unit absorbance are also shown in Fig. 4.5; water samples would be expected to lie on one of these lines if there were no change in DOM character between sites, and if the intensity of both parameters was determined by dilution. Fig. 4.5 suggests that one subset of samples, those from the main stem of the Kinabatangan and the groundwater sites, fall along a dilution line. This also corresponds to the lowest fluorescence per unit absorbance of all the samples, with a gradient of 49. This is similar to observations by Baker and Spencer (2004) (gradient range 2-6) in the UK. The results suggest that there is a loss of fluorescent DOM (within the peak C region) between the catchment tributaries and the main stem of the river, leading to DOM in the main stem that is relatively less fluorescent per unit absorbance.

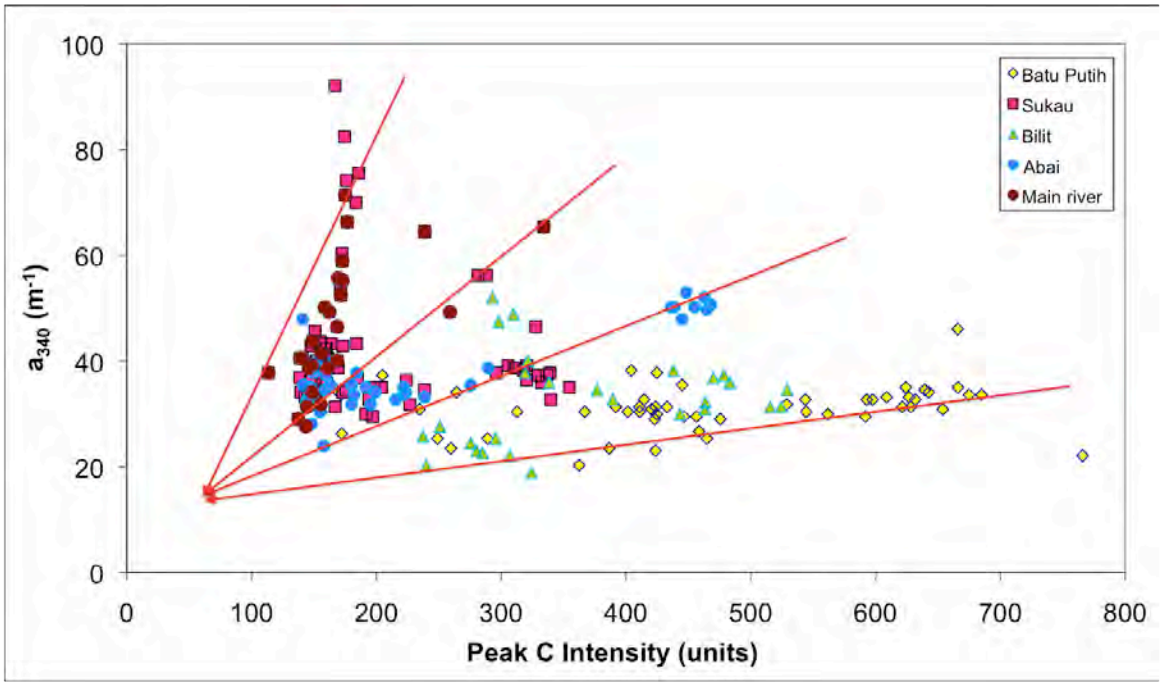


Fig. 4.5 Trends of absorbance against fluorescence peak C intensity for the Lower Kinabatangan River catchment.

Spectral slope also yields useful information about DOM character and has been found to correlate strongly with the molecular weight (MW) of fulvic acid isolates (Helms, et al., 2008). Results for the sites, plotted against a_{340} as an indicator of DOM concentration, are presented in Fig. 4.6. The spectral slope is lowest in Sukau (SK1-6), indicating DOM of a higher molecular weight, whilst samples from Batu Putih have the highest spectral slope (lowest molecular weight). An indicative four times difference in molecular weight can be seen between the results and the spectral slope of Suwannee River natural organic matter (SRNOM) (Helms et al., 2008). Other studies have reported $S_{275-295}$ to be ~13-17 x 10^{-3} nm^{-1} in freshwater samples from Chesapeake Bay, USA (Helms et al., 2008), 12.2-19.9 x 10^{-3} nm^{-1} in Yukon River, Alaska (Spencer et al., 2009) and ~18-19 x 10^{-3} nm^{-1} from eutrophic Lake Taihu, China (Zhang et al., 2009b). Spectral slope was found to increase with irradiation (Helms et al., 2008; Zhang et al., 2009a; Zhang et al., 2009b). However, the main stem river-water samples were characterised by a lower spectral slope (7-19 x 10^{-3} nm^{-1}), especially in the main river compared to tributaries, suggesting that the former are relatively higher molecular weight. This relatively non-fluorescent and high molecular weight DOM might occur due to the formation of relatively stable organic complexes given the high concentration of fine sediment within the fine colloidal (<0.7 μm) size range, rather than as a result of photo-degradation processes.

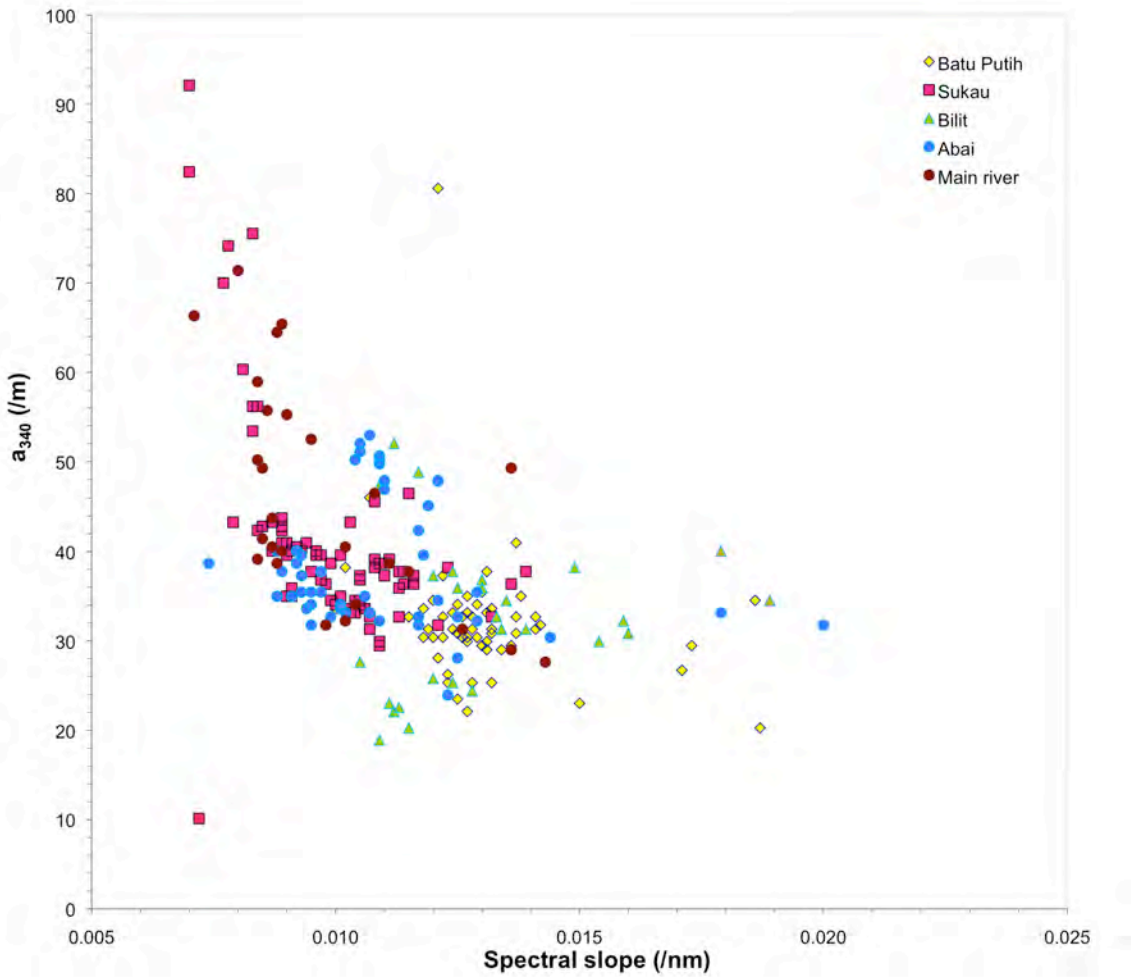


Fig. 4.6 UV absorbance at 340 nm against Spectral Slope ($S_{275-295}$) for each sampling site.

4.2.3 Parallel Factor Analysis (PARAFAC) Modelling

Three fluorescent components were identified by PARAFAC using EEMs of all samples collected from the study area (Fig. 3.1), with the exception of the groundwater samples. The ratio of the PARAFAC component intensity to the total fluorescence intensity for each sampling site is summarised in Table 4.2. The excitation and emission pairs of the main peak positions for each component are presented in Fig. 4.7, while Table 4.3 summarises the results together with details of PARAFAC components identified by selected previous

studies. The PARAFAC model identified three terrestrial (ubiquitous) peaks as characteristic fluorescent components in the Lower Kinabatangan River catchment. The average DOM composition pattern of samples collected is: C1 > C2 > C3.

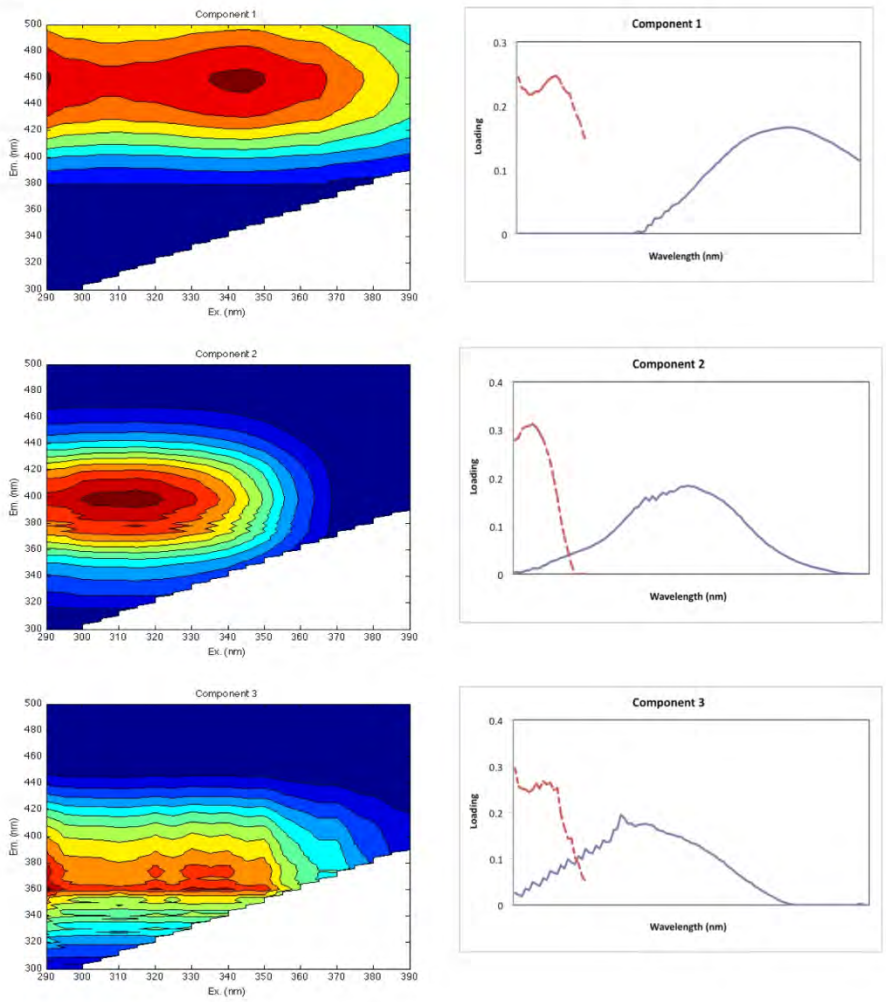


Fig. 4.7 Fluorescence signatures of three identified PARAFAC model components. Contour plots present spectral shapes of excitation and emission of derived components. Line plots adjacent to each contour plot present split-half validation results for each identified component. Excitation (dotted line) and emission (solid line) loadings for each component, obtained from two independent PARAFAC models on random halves of the data array.

Table 4.3 Spectral characteristics of excitation and emission maxima of three components identified by PARAFAC modeling for the whole EEMs data set collected in the Lower Kinabatangan River catchment compared to previously identified sources.

Component no.	Excitation maximum (nm)	Emission maximum (nm)	Coble et al. (1996); Parlanti et al. (1998)	Description and probable source
1	290 (345)	458	Peak A < 260 / 448-480	Terrestrial humic-like substances, widespread Hydrophobic acid fraction (HPOA), suggested as photo-refractory Component 1: 270 (365) / 453 (Zhang et al., 2009b) Component 2: 255 / 380-460 (Luciani et al., 2008) Component 3: 270 (360) / 478 (Stedmon et al., 2003) Component 3: 250 (355) / 461 (Yao et al., 2011)
			Peak C 320-360 / 420-460	Ubiquitous humic-like substances, widespread Hydrophobic acid fraction (HPOA) Component 1: 350 / 400-450 (Luciani et al., 2008) Component 1: 345 / 462 (Yamashita et al., 2010b) Component 4: 350 / 420-480 (Kowalczuk et al., 2009)
2	315	398	Peak M 290-325 / 370-430	Terrestrial humic-like substances Hydrophobic acid fraction (HPOA) Component 3: 260(370) / 490 (Murphy et al., 2008) Component 1: <250(335)/428 (Guo et al., 2011)
3	290	360		

Secondary excitation band is given in brackets.

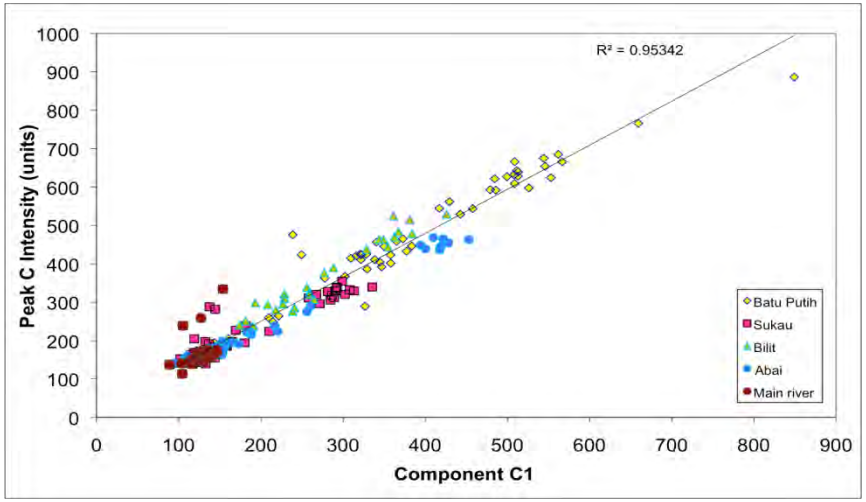
The excitation maximum for C2 occurred below 315 nm at 398 nm emission and the per cent contribution of modelled fluorescence is 43%. The characterisation of C2 has been previously described by Coble (1996) and

Parlanti et al., (2000) as peak M and marine in origin. Stedmon et al., (2003) has suggested that this component was observed in 'terrestrially dominated end-member samples' while more recently, Fellman et al., (2010) identified this peak as ultraviolet A (UVA); a component with low molecular weight, which they attributed to microbial processing. This component is common in marine environments associated with biological activity but is also found in wastewater, wetland and agricultural environments. For example, Pollard and Ducklow (2011) found that the water column in a subtropical river (Bremer River, Australia) was turned over every two days, due to DOC consumption by bacteria with bacterial specific growth rates were found to be ~20 times greater than that previously observed in marine ecosystems. Thus, peak M in the samples is probably derived from microbial and/or photo-degradation processes.

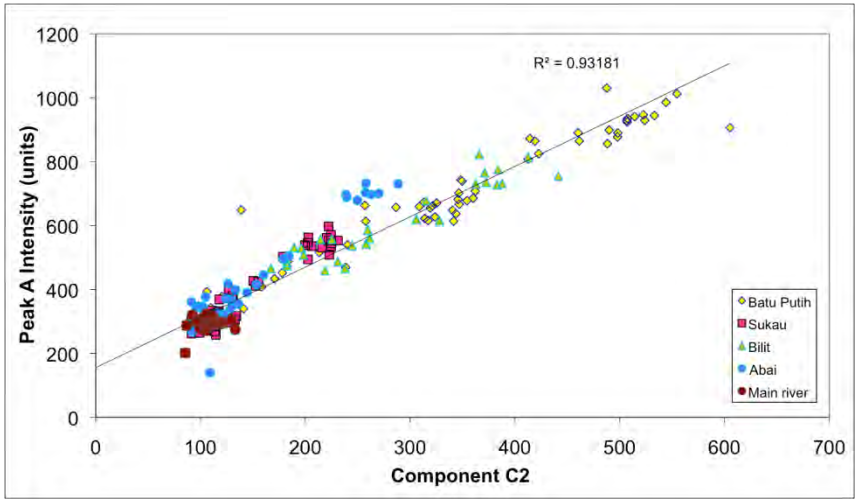
Component C1 contributed 35% of modelled fluorescence for the samples, and is a combination of two non-separated peaks of different excitation. It shows a double excitation maxima at 345 and 290 nm, which correspond to the type A and C; and a single emission peak at 458 nm. The spectral characteristics of C1 are also reported by previous studies: Kowalczuk et al., (2008), Luciani et al., (2008), Stedmon and Markager (2005a) and Yamashita et al., (2008) as ubiquitous, terrestrially derived, which occurs commonly in diverse aquatic environments. Peak A fluorescence has been observed in both marine and terrestrial DOM (Coble 1996). Component C3 occurred at a maximum excitation wavelength of 290 nm and emission wavelength of 360 nm, corresponding to peak M and contributes 22% of modelled fluorescence.

PARAFAC component C2 was observed to be present at the same sites where there is high peak C fluorescence intensity per unit absorbance, while component C1 was present with low spectral slope results. Therefore high peak C intensities are probably due to two overlapping fluorophores, which PARAFAC splits into components C1 and C2, whereas at the other sites, there is just a single component, C1.

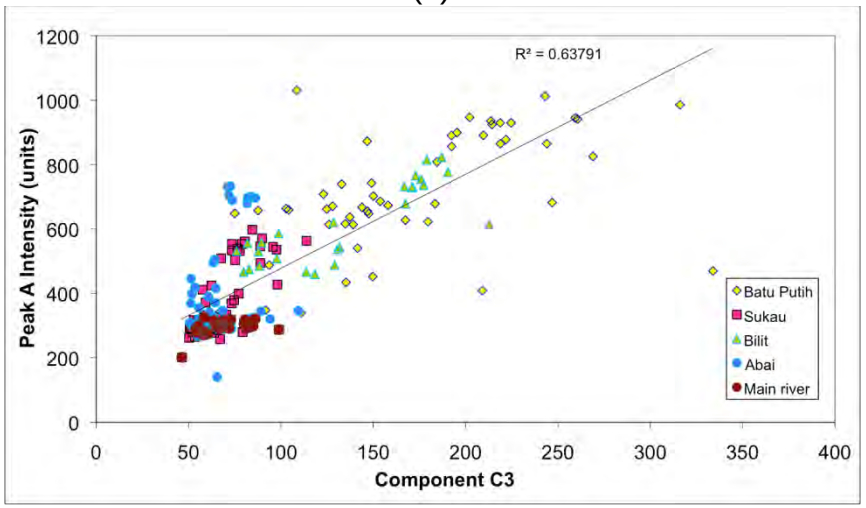
Fig. 4.8 (a) to (c) presents the correlation and comparison graphs between the PARAFAC components C1, C2 and C3 against the peak C and A intensities (r^2 = 0.95; r^2 = 0.93; r^2 = 0.64 respectively), which both show a strong positive correlation. Fig. 4.8 (d) to (g) plot the PARAFAC components C1, C2 and C3 against UV absorbance at 340 nm respectively for both PARAFAC and peak picking results. The PARAFAC results show both components C1 and C2 are in agreement with Fig. 4.7. DOM hydrophilicity was found to decrease as DOM travels from Batu Putih (BP) to Abai (AB), and may also reflect degradation of the DOM from peak C (PARAFAC component C1) to peak A (PARAFAC component C2). This dilution trend can also be seen in Fig. 4.8 (h) to (k) when the PARAFAC components C1, C2 and C3 were plotted against the spectral slope for both PARAFAC and peak picking results. It also showed that the same sampling sites are visible at the same area in each graph (Fig. 4.8 (d) to (k)).


R² = 0.95342
Peak C Intensity (units)
Component C1
Batu Putih
Sukau
Bilit
Abai
Main river

(a)

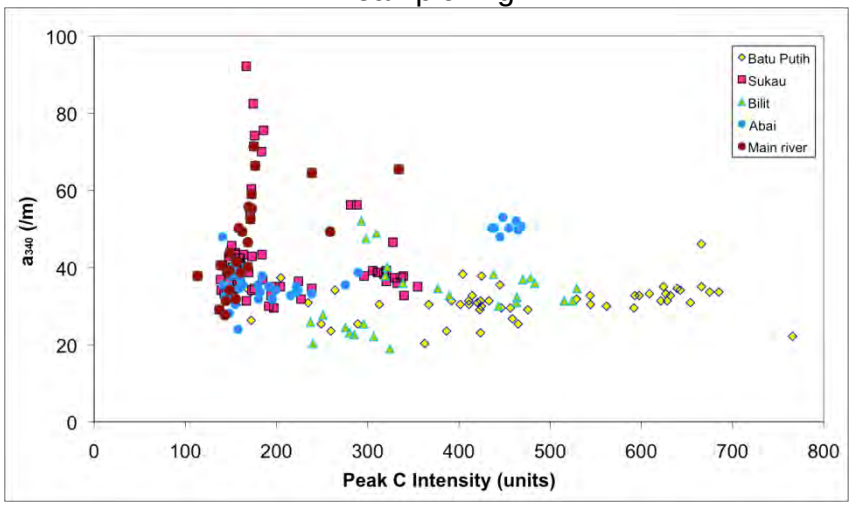

R² = 0.93181
Peak A Intensity (units)
Component C2
Batu Putih
Sukau
Bilit
Abai
Main river

(b)

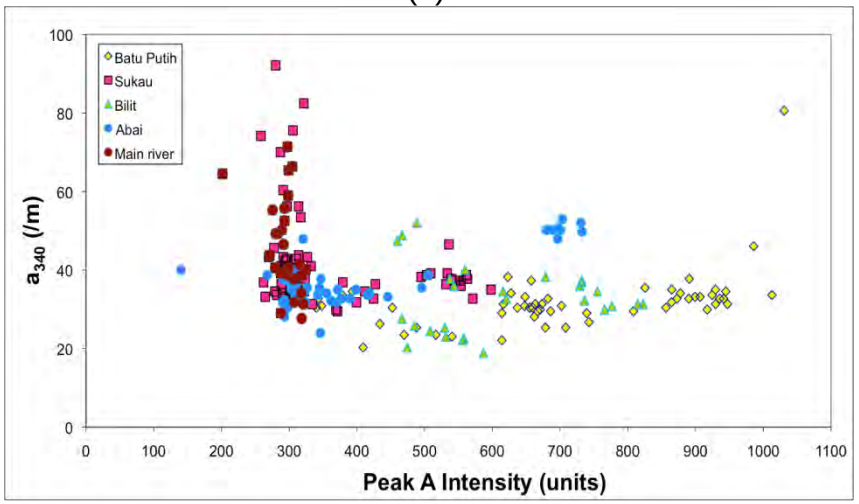

R² = 0.63791
Peak A Intensity (units)
Component C3
Batu Putih
Sukau
Bilit
Abai
Main river

(c)

Peak picking

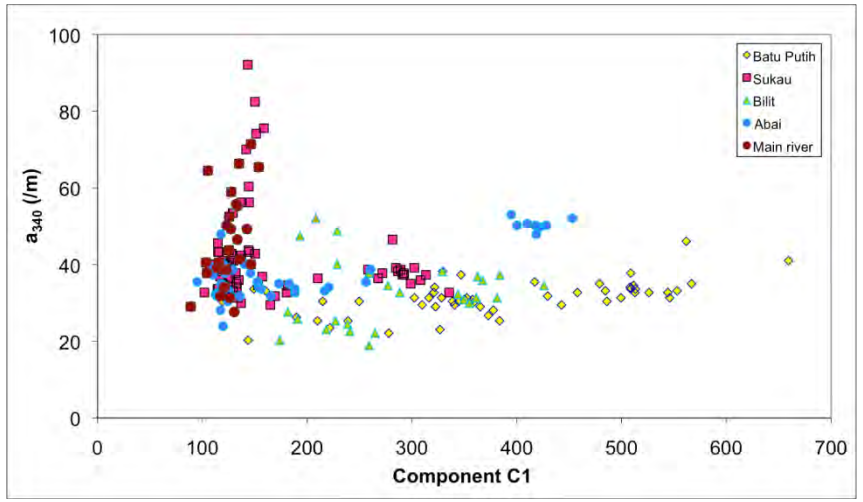


(d)

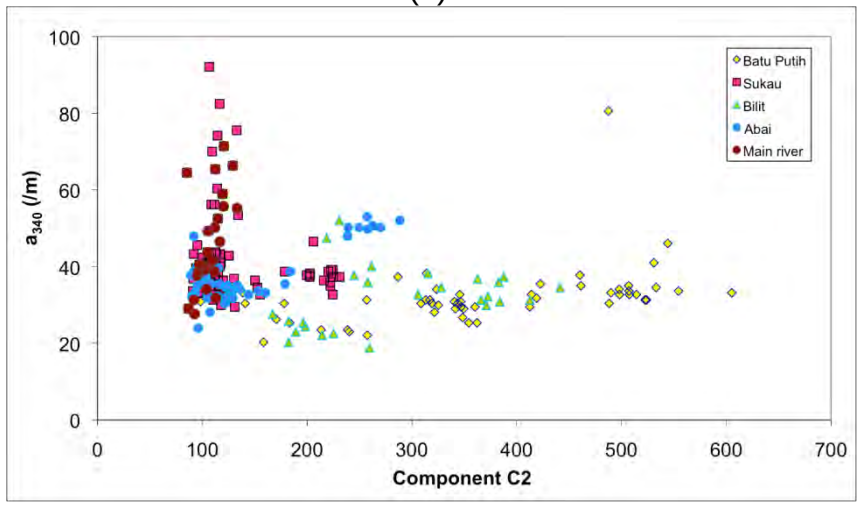


(f)

PARAFAC

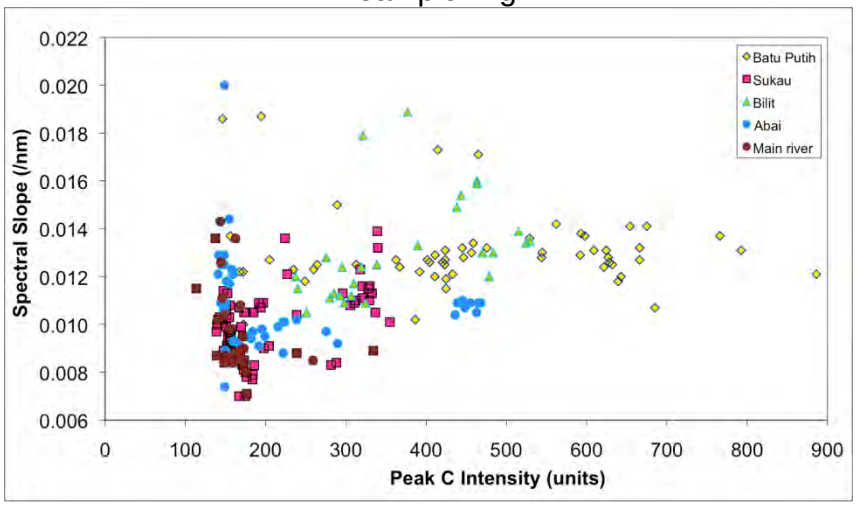


(e)

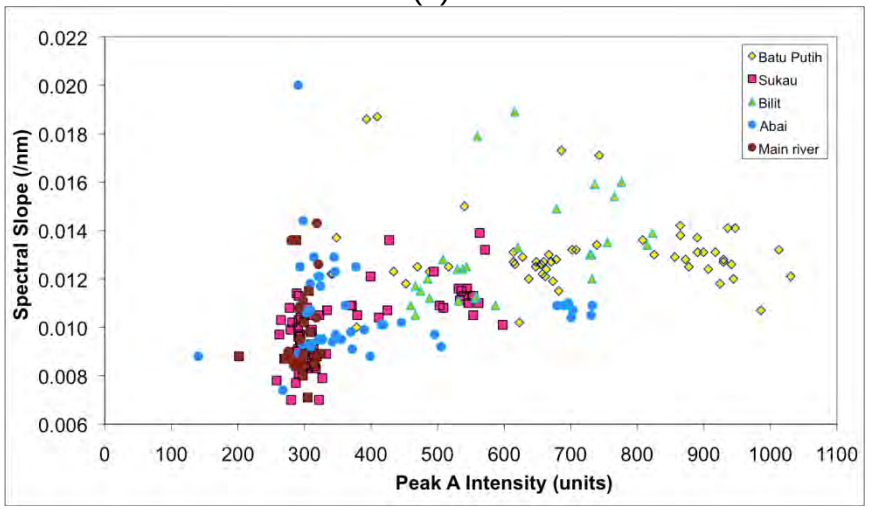


(g)

Peak picking

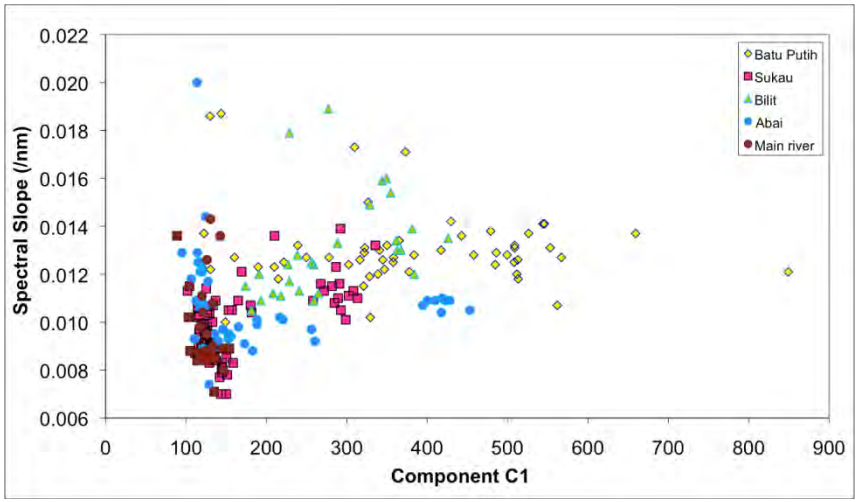


(h)

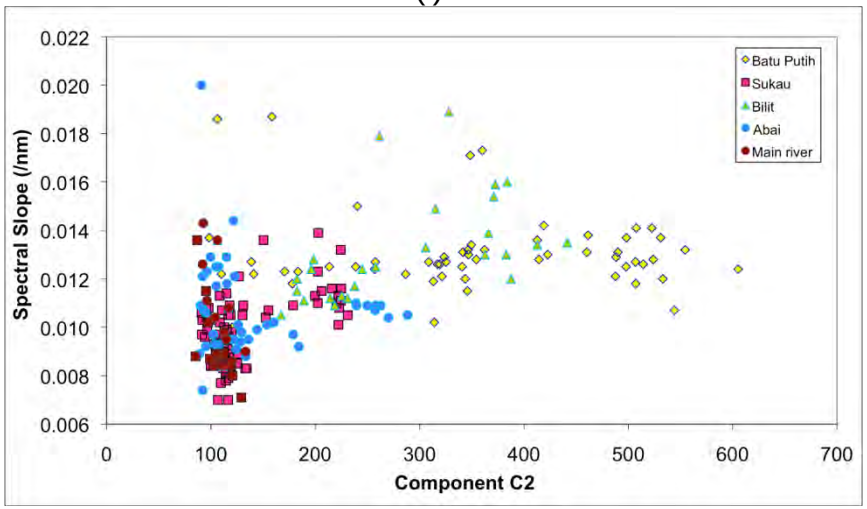


(j)

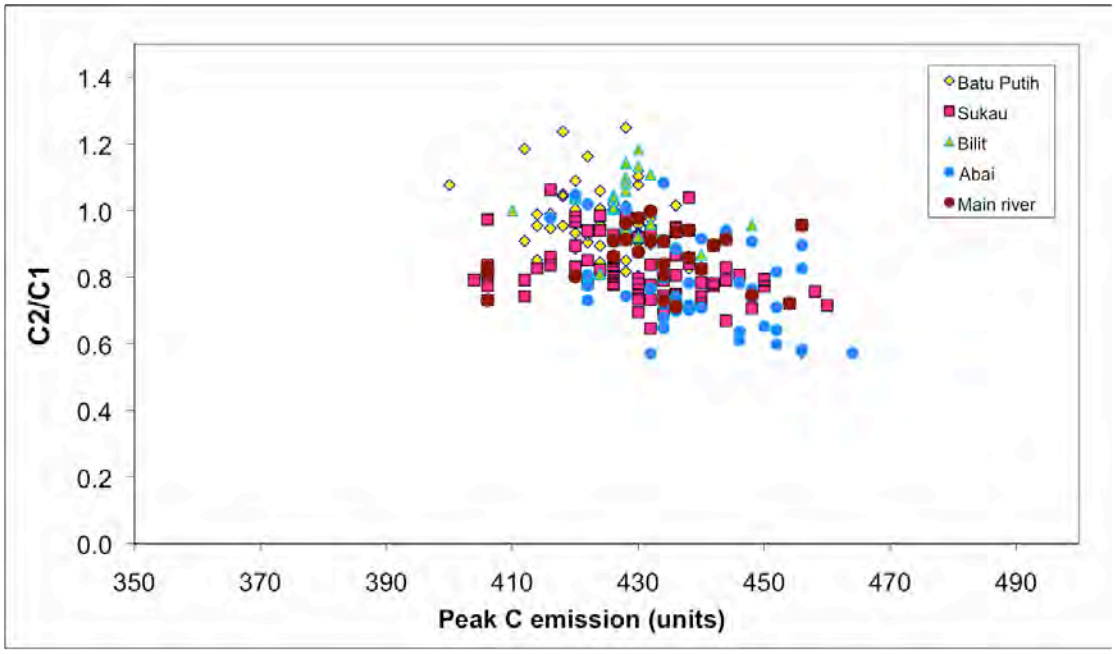
PARAFAC



(i)



(k)



(l)

Fig. 4.8 Correlation and comparison graphs between: (a)-(c) PARAFAC component C1, C2 and C3 vs peak C intensity and peak A intensity respectively; (d)-(g) Comparison between PARAFAC components and peak picking results for a_{340} (/m); (h)-(k) Comparison between PARAFAC components and peak picking results for Spectral Slope (/nm); (l) Ratio of PARAFAC component C2/C1 vs peak C emission.

4.4 DISCUSSION AND CONCLUSIONS

These results provide important baseline data on the variation in DOM quantity and quality in a degraded tropical catchment. In particular, by characterising DOM using absorbance and fluorescence, it is possible to differentiate DOM characteristics between individual sub-catchments. The strong correlation between peak C and peak A fluorescence indicates that the majority of DOM in the Kinabatangan catchment comprises terrestrially derived substances, and

that the relative loss of peak C fluorescence relative to absorbance is due to a change in DOM character. Upstream sites at Batu Putih, including several sites closely associated with oil palm plantations (BP3, BP4, BP6-8) have a high fluorescence intensity per unit absorbance and high spectral slope, which is indicative of relatively low molecular weight organic matter. Downstream sites (e.g. at Sukau) have a high UV-visible absorption coefficient, peak C intensity fluorescence and low spectral slope, which is indicative of a higher molecular weight DOM.

The application of PARAFAC in this study provides further information on the origin and biogeochemical role of the DOM from each sampling site. PARAFAC modelling also helps interpret progressive changes in DOM character in the Lower Kinabatangan River catchment from upstream to downstream. For example, Fig. 4.8 (h) to (k) show that the PARAFAC model is consistent with the dilution trends showed in Fig. 4.8 (d) to (g) determined by peak-picking. In contrast, Fig. 4.8 (l) demonstrates that the ratio of PARAFAC C2 over C1 does not correlate with peak C emission wavelength determined by peak-picking, which is an indicator of the hydrophobicity of DOM (Baker et al., 2008). Peak M could be indicative of microbial (e.g. Pollard and Ducklow, 2011) and/or photodegradation processes, as high amount of sunlight received in the tropical regions.

Significantly, the variation in fluorescence relative to UV-visible absorbance between tributary sites and the main stem of the Kinabatangan, reveals a loss of highly fluorescent DOM within the catchment. This loss, and the general spatial variability of DOM character, reflects the interaction between at

least three sources of variability of DOM within the catchment: i. spatial variation in DOM source; ii. effects of transport (e.g. degradation over time from photo-degradation); and iii. differences among DOM in the propensity for biological and photochemical removal.

It is hypothesised that in the Kinabatangan Catchment, rapid oxidation by photochemical and especially microbial processes to produce carbon dioxide (Cory et al., 2007) preferentially breaks down the aromatic carbon containing molecules which account for the fluorescent properties of DOM. Samples from low-order tributaries would be expected to be dominated by the input of terrestrially derived DOM, which would include in the catchment DOM that reflects activities associated with oil palm plantations. This DOM is regarded as rapidly photo and biodegraded to less fluorescent, stable DOM, probably present as fine colloidal complexes, and where downstream DOM concentration and character will often be hydrologically controlled by rapid transport (Findlay and Sinsabaugh, 1999).

5. SEASONAL VARIATIONS IN THE COMPOSITION OF DISSOLVED ORGANIC MATTER IN A TROPICAL CATCHMENT: THE LOWER KINABATANGAN RIVER, SABAH, MALAYSIA

Scope of Chapter

Dissolved organic matter (DOM) was characterised in waters sampled in the Lower Kinabatangan River Catchment, Sabah, Malaysia between October 2009 and May 2010 (concentrated sampling programmes). This chapter analyses the data collected, seeking: i. to distinguish between the quality of DOM in waters draining palm oil plantations (OP), secondary forests (SF) and coastal swamps (CS) and, ii. to identify the seasonal variability of DOM quantity and quality. Surface waters were sampled during fieldwork campaigns that spanned the wet and dry seasons. DOM was characterised optically by fluorescence Excitation Emission Matrix (EEM), the absorption coefficient at 340 nm and the spectral slope coefficient (S). Parallel Factor Analysis (PARAFAC) was undertaken to assess DOM composition from EEM spectra and five terrestrial derived components were identified: (C1, C2, C3, C4 and C5). Components (C1 and C4) contributed most to DOM fluorescence in all study areas during both the wet and dry seasons. The results suggest that component C1 could be a significant (and common) PARAFAC signal that is found widely in tropical regions. Both wet and dry seasons were dominated by peak M (C2 and C3), which appear to be anthropogenic in origin due to active land use changes in the study area.

5.1 INTRODUCTION

In a recent synthesis and re-evaluation of the global carbon cycle, Cole et al. (2007) suggested that of the 1.9 Pg C per year delivered from land to river, approximately half of the carbon was consumed within river systems before reaching the ocean. This highlights the importance of in-stream processing and corroborates research in South America by Richey et al. (2002) who found that Amazonian rivers outgassed more than ten times the quantity of carbon exported to the ocean in the form of total organic carbon or dissolved organic carbon (DOC). Significantly, determination of the carbon isotopic composition of DOC has suggested that contemporary organic carbon (i.e. that < 5 years in age) was the dominant source of excess carbon dioxide that drives outgassing in Amazonian rivers (Mayorga et al., 2005). Together, these results emphasise the importance of land-derived, biologically available carbon, for heterotrophic microbial processes in river systems.

Tropical wetlands have been estimated to contribute ~60% of total (global) water, sediment and organic carbon input to the ocean (Alkhatib et al., 2007), however, these wetlands are seriously threatened by environmental deterioration as currently evident in S and SE Asia where many catchments have experienced rapid conversion of land to agriculture (Atapattu and Kodituwakku, 2009; Mattsson et al., 2000; Sidle et. al., 2006) and a concomitant reduction in wetland extent. Particularly significant has been the increasing extent of palm oil plantations which have been estimated to cover >13.5 million ha across the Tropics (Fitzherbert et al., 2008). Malaysia and Indonesia produce > 80% of the

world palm oil and increases in oil palm production are associated with the drainage of floodplain wetlands, and loss of primary and secondary forest (Koh and Wilcove, 2008). At present, the majority of oil palm development is confined to SE Asia, however, Fitzherbert et al. (2008) highlight the suitability of areas of Africa (Congo Basin) and S. America (Amazon) for oil palm plantation, and further developments are likely in these areas.

The full implications of these recent and in some places accelerating changes, for carbon export have yet to be considered in detail. However, recent advances in fluorescence spectroscopy have significantly enhanced the ability to quantify organic matter composition in water (e.g. reviews by Blough and Del Vecchio, 2002; Fellman et al., 2010) enabling study of the molecular chemistry of fulvic acid and its interaction with metal ions and organic chemicals (Senesi, 1990). DOM fractions possess fluorescent properties enabling monitoring of DOM in soils (Fuentes et al., 2006), rivers (Ahmad et al., 2002; Williams et al., 2010), lakes (Miller et al., 2009), estuaries and coastal environments (Stedmon and Markager, 2005a; Yamashita et al., 2008). Specifically in a tropical catchment, Spencer et al. (2010) demonstrated the utility of optical determination of DOM composition in a pristine tributary of the Congo where they found significant temporal variations in DOM quantity and quality. Spencer et al. (2010) found DOM export to be greater during the April flush, and they suggest tropical rivers are likely to export more labile DOM during wet periods. These results have implications for downstream and marine ecosystems that receive DOM from these sources, but these ideas have still to be tested in other catchments.

In this study, fluorescence excitation emission matrix (EEM) spectra were reassessed using Parallel Factor Analysis (PARAFAC). PARAFAC enables the decomposition of an EEM dataset into the least squares sum of several mathematically independent components parameterized by concentrations (loadings) and excitation and emission spectra and corresponding, ideally, to a chemical analyte or a group of strongly covarying analytes (Kowalczuk et al., 2009). This modelling technique has been found to be invaluable in characterising and quantifying changes in DOM fluorescence permitting different DOM fractions to be traced through the natural environment (Cory and McKnight, 2005).

Given this context, this paper seeks to characterise DOM quality in a tropical catchment in SE Asia that has experienced recent deforestation and rapid agricultural development. The floodplain of the Lower Kinabatangan River in East Sabah, Malaysia typifies many catchments in this region with an increase in the extent of oil palm plantations. Moreover, conservation of riparian secondary forest and coastal wetlands provides an opportunity to determine the degree to which DOM quantity and quality may firstly be affected by land-use, and secondly vary over time as a result of the seasonal flood pulse (Junk, 2002). Accordingly, the objectives of this study were twofold:

- to characterise the quality of the DOM drained from palm oil plantations, secondary forests and coastal wetlands (the three main land covers in Sabah, Malaysia) using fluorescence spectroscopy and PARAFAC (Bro, 1997; Stedmon et al., 2003);

- to determine the seasonal variability of DOM quantity and quality, and its relationship to land use.

5.2 RESULTS AND DISCUSSION

5.2.1 Characterisation of PARAFAC Components

Five fluorescent components were identified by PARAFAC from the 510 EEMs of samples collected from the study area (Fig. 3.2). The excitation and emission pairs of the main peak positions for each of the components are summarised in Tables 5.1 and 5.2, and individual components are plotted in Fig. 5.1. The Tables also compare the results with components identified by selected studies that have modeled DOM in marine, oceanic and estuarine environments.

Table 5.1 Spectral characteristics of excitation and emission maxima of five components identified by PARAFAC modelling for the whole EEMs data set collected in the Lower Kinabatangan River catchment compared to previously identified sources.

Component in this study	Excitation maximum (nm)	Emission maximum (nm)	Coble et al.,(1996); Coble et al. (1998)	Description and probable source
C1	345	466	Peak C 320-360 / 420-480	Ubiquitous humic-like substances, widespread Hydrophobic acid fraction (HPOA) Component 1: 350 / 400-450 (Luciani et al., 2008) Component 1: 345 / 462 (Yamashita et al., 2010b) Component 4: 350 / 420-480 (Kowalczuk et al., 2009)
C2	305	426	Peak M 290-312 / 370-420	Terrestrial humic-like substances, widespread
C3	325	408		Hydrophobic acid fraction (HPOA), suggested as photo-refractory Component 2: 255 / 380-460 (Luciani et al., 2008) Component 3: 255 (330) / 412 (Zhang et al., 2009b) Component 3: 270 (360) / 478 (Stedmon et al., 2003) Component 3: 250 (355) / 461 (Yao et al., 2011)
C4	290	464	Peak A 260 / 380-460	Terrestrial humic-like substances, widespread Hydrophobic acid fraction (HPOA), suggested as photo-refractory Component 1: 270 (365) / 453 (Zhang et al., 2009b) Component 2: 255 / 380-460 (Luciani et al., 2008) Component 3: 270 (360) / 478 (Stedmon et al., 2003) Component 3: 250 (355) / 461 (Yao et al., 2011)
C5	290	338	Peak M 290-312 / 370-420	Ditto with description for C2.

Table 5.2 Descriptive statistics of environmental conditions and PARAFAC model of selected sampling stations in the Lower Kinabatangan River Catchment.

			pH	Salinity	DOC (mg/l)	a_{340} (/m)	$S_{275-295}$ (/nm)	IC1	IC2	IC3	IC4	IC5	I total
OP	Inter-monsoonal	Mean	6.94	0.07	15.30	42.14	0.0128	8.17	10.93	13.95	8.92	5.72	47.69
		Std. dev.	0.52	0.03	9.50	23.25	0.0018	3.68	3.83	5.75	3.10	2.96	15.88
		Variance	0.27	0.00	90.24	540.63	0.0000	13.53	14.66	33.05	9.59	8.76	252.27
	Wet Season	Mean	6.77	0.06	11.59	62.37	0.0104	10.46	14.94	11.70	25.63	3.39	66.11
		Std. dev.	0.66	0.02	3.58	35.46	0.0016	5.03	6.18	4.96	10.70	0.87	26.85
		Variance	0.44	0.00	12.82	1257.48	0.0000	25.28	38.24	24.64	114.55	0.75	721.17
	Dry Season	Mean	6.90	0.09	7.26	20.28	0.0125	7.13	11.21	9.11	17.61	6.27	51.33
		Std. dev.	0.75	0.03	1.61	5.80	0.0015	1.92	3.44	2.87	5.13	3.26	13.96
		Variance	0.56	0.00	2.58	33.59	0.0000	3.68	11.85	8.23	26.27	10.61	194.99
SF	Inter-monsoonal	Mean	6.89	0.04	10.20	55.75	0.0113	8.06	9.44	13.29	7.62	3.23	41.63
		Std. dev.	0.25	0.01	7.64	13.17	0.0012	3.31	3.64	5.07	2.93	1.66	15.86
		Variance	0.06	0.00	58.35	173.43	0.0000	10.97	13.26	25.75	8.59	2.75	251.64
	Wet Season	Mean	6.93	0.04	11.17	75.88	0.0100	9.90	13.28	10.08	23.59	2.89	59.75
		Std. dev.	0.30	0.02	5.46	65.67	0.0019	6.55	7.69	5.95	13.77	0.75	33.96
		Variance	0.09	0.00	29.79	4312.30	0.0000	42.85	59.07	35.37	189.74	0.57	1153.60
	Dry Season	Mean	6.87	0.07	7.42	28.04	0.0113	7.74	11.48	8.84	18.45	4.51	51.03
		Std. dev.	0.24	0.04	2.40	6.40	0.0012	3.54	5.17	4.09	8.36	3.18	22.99
		Variance	0.06	0.00	5.77	40.93	0.0000	12.52	26.71	16.70	69.90	10.13	528.59
CS	Inter-monsoonal	Mean	6.20	1.33	10.36	45.49	0.0125	8.48	10.34	14.23	8.14	2.83	44.03
		Std. dev.	0.76	2.15	5.03	17.49	0.0018	3.07	3.32	4.88	2.52	0.95	14.16
		Variance	0.57	4.62	25.27	305.76	0.0000	9.41	11.02	23.84	6.35	0.91	200.60
	Wet Season	Mean	5.95	0.08	14.70	100.49	0.0112	14.34	18.16	14.14	33.12	2.71	82.70
		Std. dev.	0.76	0.04	4.14	62.52	0.0023	6.15	6.50	5.45	12.16	0.85	29.65
		Variance	0.57	0.00	17.15	3908.20	0.0000	37.88	42.27	29.74	147.76	0.73	879.15
	Dry Season	Mean	7.11	2.39	6.21	14.03	0.0135	6.16	10.23	7.58	16.66	5.92	46.55
		Std. dev.	0.30	2.09	0.95	4.59	0.0019	1.47	2.57	1.84	4.65	2.58	10.66
		Variance	0.09	4.38	0.91	21.02	0.0000	2.15	6.62	3.40	21.64	6.68	113.55

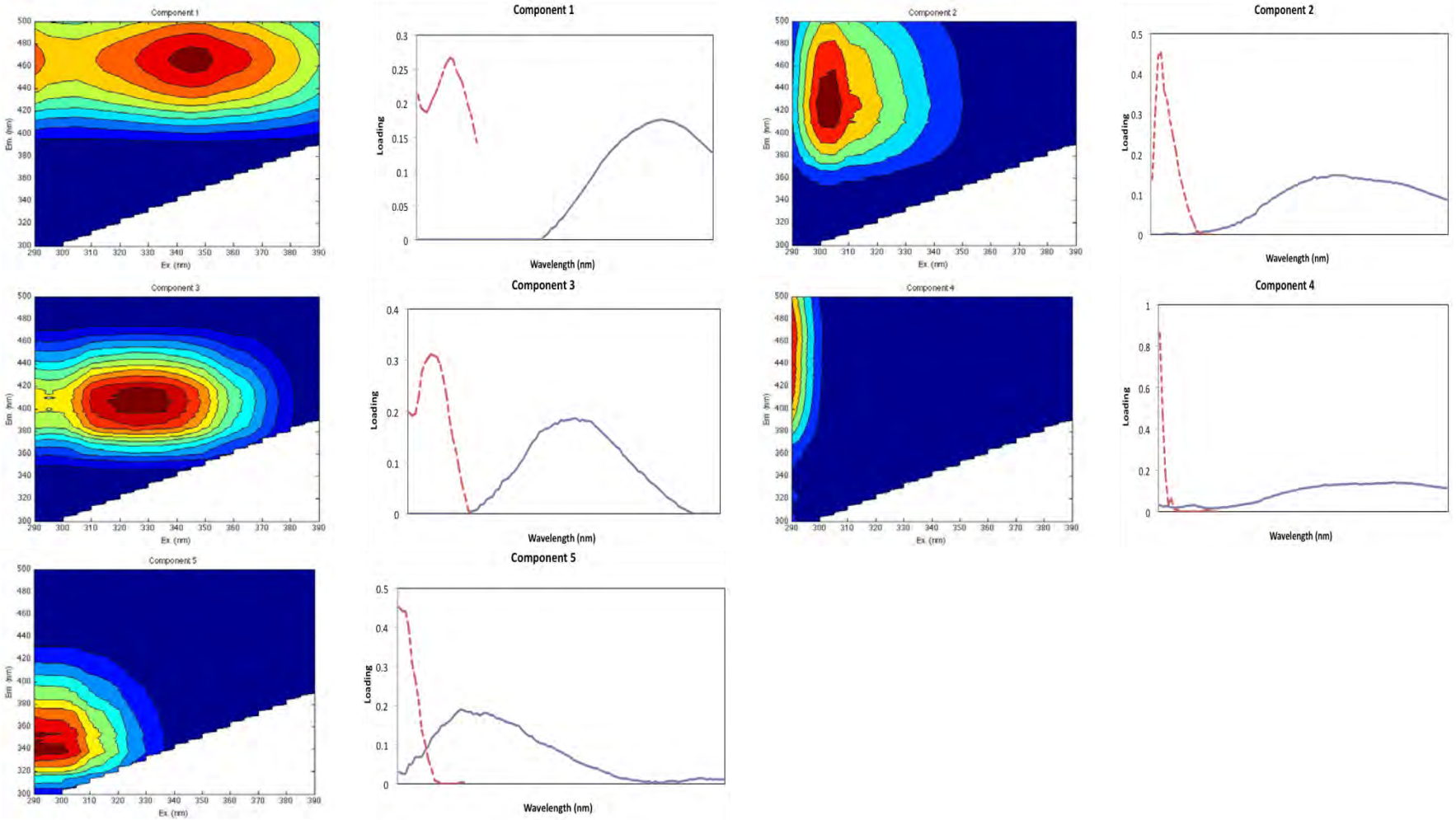


Fig. 5.1 PARAFAC model output showing fluorescence signatures of five components identified. Contour plots present spectral shapes of excitation and emission of derived components. Line plots at right side of each contour plot present split-half validation results for each identified component.

The PARAFAC model identified 5 terrestrial derived substances: component 1 (C1), component 2 (C2), component 3 (C3), component 4 (C4) and component 5 (C5). Components C1 and C4 are common in estuarine, marine and oceanic environments and represent fluorophores that have the longest excitation wavelength and broadest excitation band as well as the longest emission wavelength associated with a broad emission band. Components C2, C3 and C5 with shorter emission wavelengths has been interpreted as representing marine humic substances and also as dissolved organic matter that are microbially-derived.

Terrestrially-derived components C1 (peak C) and C4 (peak A) excitation maximums occurred below 345 nm and 290 nm, at 466 nm and 464 nm emission respectively (Fig. 5.1). The characteristics of C1 and C4 are similar to the previously reported ubiquitous, fulvic acid-like, component which commonly occurs in diverse aquatic environments. This has been observed in tropical and sub-tropical regions: Component 1 of Luciani et al. (2008), Stedmon and Markager (2005b) and Yamashita et al. (2010); Component 2 of Fellman et al. (2009), Component 3 of Yao et al. (2011) and Component 4 of Kowalczuk et al. (2009). The C1 was similar to the humic-like fluorophore in the visible region as defined by Coble (1996).

The excitation maxima for components C2, C3 and C5 occurred below 305 nm, 325 nm and 290 nm at 426 nm, 406 nm and 338 nm emission respectively. The C2 resembles Component 3 of Murphy et al. (2008), and Components 4 and 6 of Stedmon et al., (2003) and Yamashita et al., (2010b)

respectively. Others have also reported this component: Zhang et al. (2011): their Component 1; Luciani et al. (2008): their Component 2; Stedmon et al. (2003): their Component 3; Yao et al. (2011): their Component 3; and Stedmon et al. (2003): their Component 5.

Components C2, C3 and C5 have been reported as peak M and may have a marine source (Coble, 1996; Parlanti et al., 2000). Subsequent study by Stedmon et al. (2003) indicated that this component was found in 'terrestrially dominated end-member samples', and more recently this peak was observed as ultraviolet A (UVA); a low molecular weight component, which associated to microbial activities (Fellman et al., 2010). Peak M is common in marine environments and has been related to biological activity. However, it is also found in wastewater, and in wetland and agricultural environments. For example, Castillo et al. (2004) found that the DOC concentrations from the subtropical lowland rivers of the Orinoco basin, Venezuela was greater in blackwater than clearwater rivers, while inverse results were found for the average bacterial production in respective type of land use. Nedwell et al. (1994) found that the carbon mineralisation in the subtropical Jamaican mangrove swamp was higher compared to other transect area, indicated abundant availability of OM. Consequently, decomposition processes of mangrove leaf litter in Matang, Malaysia was mainly driven by microbes (Sahoo and Dhal, 2009), fungi and small invertebrates, depending on the mangrove species (Ashton et al., 1999). Thus, it is hypothesised that the peak M in the Lower Kinabatangan River catchment with seasonal variations and different type of land use (oil palm plantations, secondary forests and coastal swamps)

could be derived from microbial and/or photo-degradation processes.

I_n which is defined as 'intensity of the *n*th component in sample' has been calculated (Section 3.5.1) and showed that the mean DOM compositional pattern of all samples is as follows: IC4 > IC2 > IC3 > IC1 > IC5, where terrestrial derived peak IC4 has the most abundant spectral characteristics, followed by peak M (IC2, IC3 and IC5) and peak C (IC1). The terrestrial derived peak component has been described as ubiquitous, photo-labile and derived from agricultural activities (Yamashita et al. 2010b). Given the relative land covers in the catchment of the Kinabatangan where forests extend across ~74% of the catchment and ~ 26% of the catchment is permanently cultivated, largely with oil palm plantations (Josephine et al., 2004), this could explain the spectral characteristics and abundance of component IC4.

The PARAFAC components described here, and in other studies of tropical catchments (e.g. Luciani et al., 2008; Yamashita et al., 2010) are similar, suggesting it is possible to identify common attributes in tropical areas. However, DOM characteristics described in most studies to-date, are of DOM with a very different origin to that in NE Sabah. Consequently their results and the implications for both the Kinabatangan catchment, and tropical regions generally, need to be interpreted with caution (Ahmad et al. 2002).

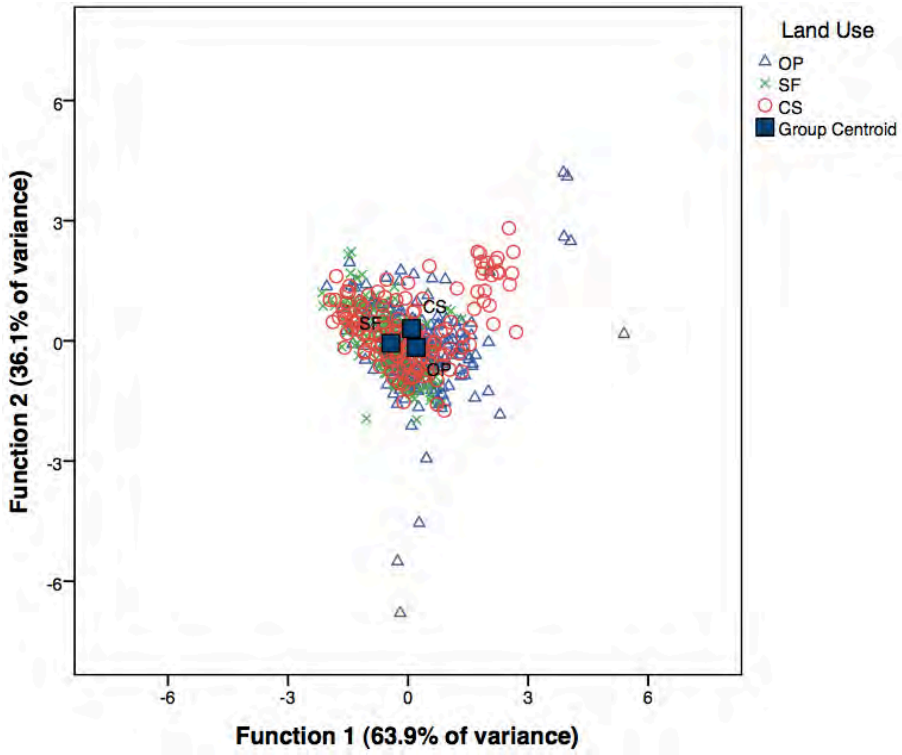
5.2.2 DOM Characterisation

In order to gain more insight on the DOM characterisation, fluorescence indices (FI) were used in this study. Discriminant analysis also has been applied to both the peak picking and PARAFAC data sets to characterise DOM. Values of peak C emission, UV absorbance at 340 nm, spectral slope and different type of ratios have been used to determine the pre-dominance of each parameter in each land use type: peak C/a_{340}, peak A/peak C intensity, IC1/a_{340} (peak C/a_{340}), IC2/IC1 (peak M/peak C), IC3/IC1 (peak M/peak C) and IC5/IC1 (peak M/peak C).

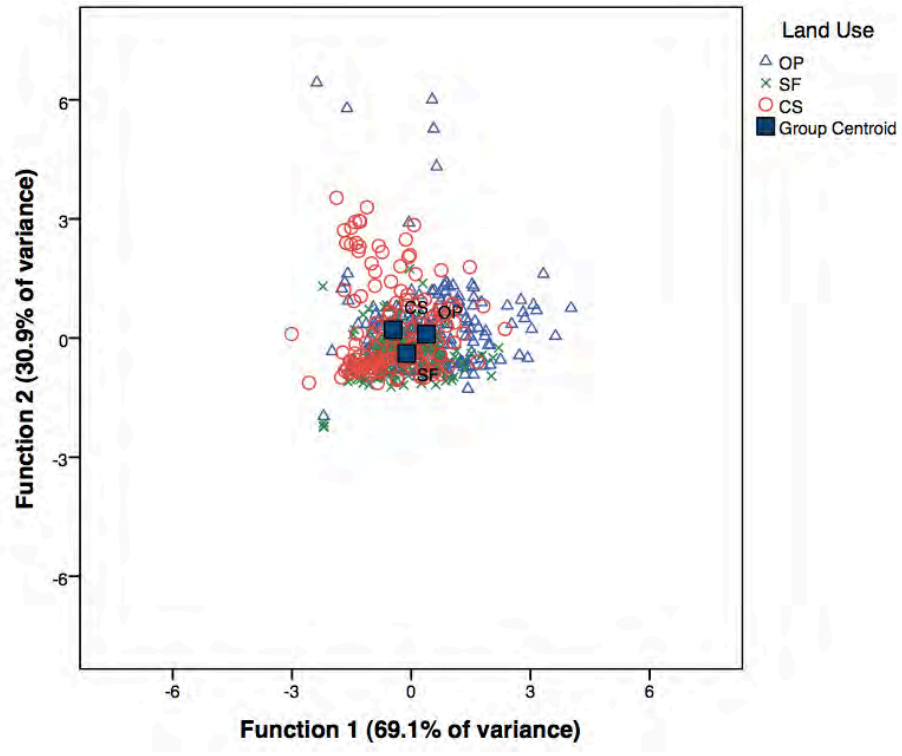
Following a series of discriminant analyses, a total of two discriminant functions were obtained throughout the analysis. Both peak picking and PARAFAC data sets show consistent and equivalent trends (Table 5.3, Fig. 5.2).

Table 5.3 Factor structure coefficients from discriminant analysis for both peak picking and PARAFAC data sets.

Fluorescence indices	**Function**	
Peak picking:	1	2
Peak C/a_{340}	.764*	.474
Peak C Emission	-.762*	.491
Spectral Slope	.456*	.112
Peak A/Peak C	-.031	.568*
47.1% of original group cases correctly classified.		
PARAFAC:	1	2
IC3/IC1 (Peak M/Peak C)	.796*	.334
IC2/IC1 (Peak M/Peak C)	.569*	.247
IC5/IC1 (Peak M/Peak C)	.400*	.203
IC4/IC1 (Peak A/Peak C)	.267*	.180
IC1/a_{340} (Peak C/a_{340})	-.084	.931*
Spectral slope	.077	.514*
47.2% of original group cases correctly classified		



(a)



(b)

Fig. 5.2 Group separation of discriminant analysis for each (a) peak picking and (b) PARAFAC data sets.

This analysis suggests that ratio of peak C to a_{340} and spectral slope was negatively correlated with peak C emission in discriminant function 1 (63.9% of variance explained) (Table 5.3). The PARAFAC analysis demonstrates that the ratios of i. IC2 to IC1 and ii. IC3 to IC1 always correlated positively with IC5/IC1 and were classified in discriminant function 1 with 69.1% of variance explained. Both peak picking and PARAFAC data sets indicate that samples associated with oil palm plantations (OP) were mainly contributing to fresh DOM, while those collected from coastal swamps (CS) largely comprise terrestrial derived DOM. This could also result from DOM degradation (bio- and photo-) in the river reaches downstream near the estuary.

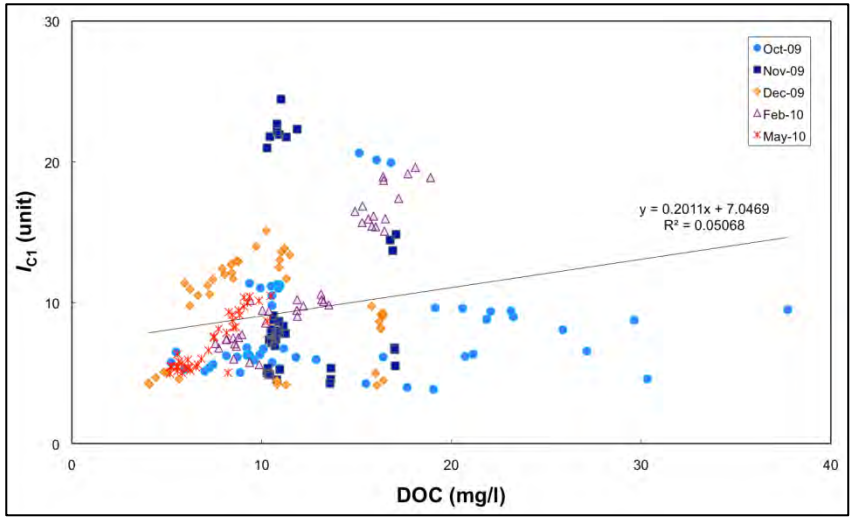
In the case of the PARAFAC data set, the fluorescence indices IC2/IC1, IC3/IC1 and IC5/IC1 were positively correlated and dominated by samples collected from oil palm plantations (OP) (Fig. 5.2). Coastal swamps (CS) were dominated by ratio of IC1/a_{340} and spectral slope. UV absorbance a_{340} and spectral slope approximate DOM molecular weight (Baker et al., 2008; Helms et al., 2008), and thus the ratio of IC1 to a_{340} could be interpreted as the ratio of DOM concentration to molecular weight.

5.2.3 Seasonal and Land Use Variations

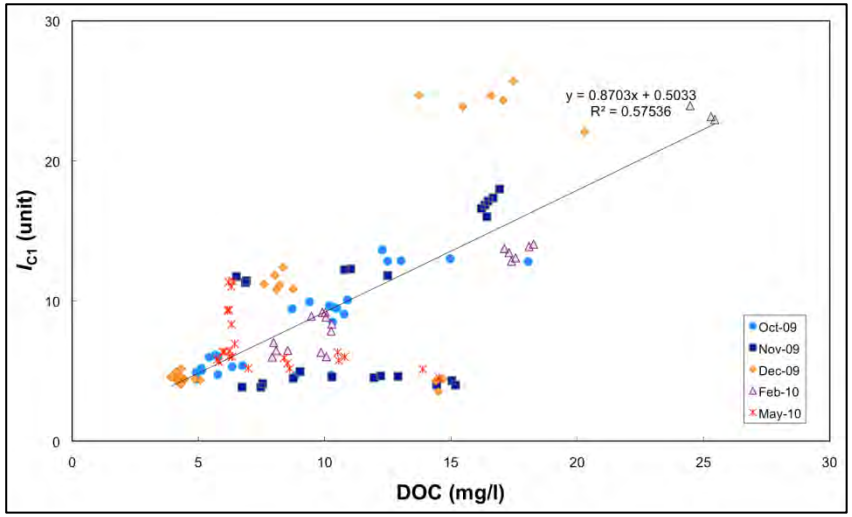
DOC concentrations are presented in Table 5.2 with mean concentrations that range from 9.88 to 12.85 mg/l. Consistent high values of DOC concentrations could indicate high humic materials in the water bodies. Other studies show that DOC concentrations in Jiulong River, a subtropical watershed in China varied from 0.4 to 13.1 mg/l (Hong et al., 2011); while Yamashita et al (2011) found DOC concentrations in three tropical watersheds to vary within the range 142 to 891 μMC (1.71 to 10.7 mg/l).

As an example of the seasonal and land use variations of DOM, Fig. 5.3 plots DOC against PARAFAC component IC1 for each type of land use. Samples from oil palm plantations (OP) showed DOC was strongly and positively correlated with C1 during the dry season (r^2 = 0.8), and this is consistent with the discriminant analysis (Table 5.3), which suggests that microbial and/or photo-degradation processes as well as humic substances are abundant in the OP samples. Dry season water samples from downstream Sg. Langat in Selangor, Malaysia, located also within oil palm plantations, have mean Biochemical Oxygen Demand (BOD) values ranging from 2.1 to 2.6 mg/l (Azrina et al., 2006) while a study conducted by Peduzzi and Schiemer (2004) showed high abundance of virus particles and elevated bacteria counts in tropical freshwater reservoirs in Sri Lanka, during the dry season. DOC concentrations from secondary forests (SF) and coastal swamps (CS) were correlated positively with C1 during both seasons. This is also consistent with the discriminant analysis (Fig. 5.2) where the factor structure coefficients, which indicate peak C, showed

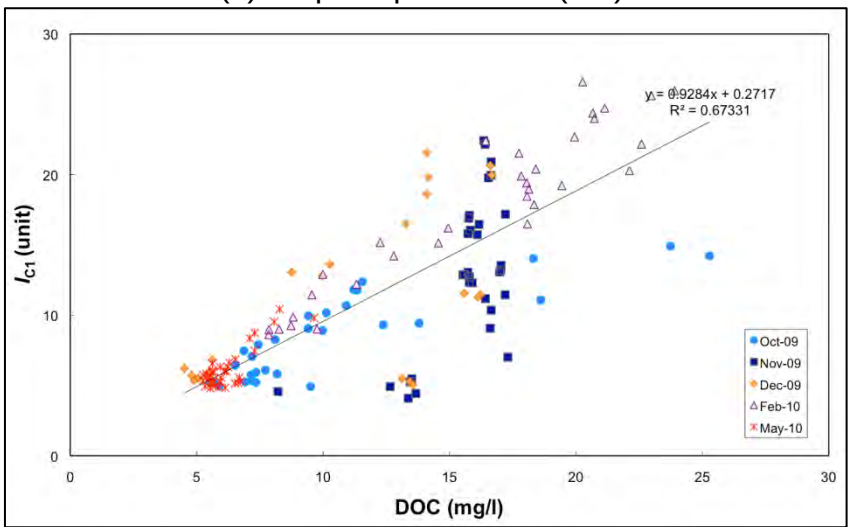
that samples from CS were higher than SF. Mangrove forests tend to have rich tannins, which is likely to be associated with decreasing bacterial counts (Sahoo and Dhal, 2009) and have been identified as hydrophobic acids (Aitkenhead-Peterson et al., 2003). Both peak picking and PARAFAC results also suggest that the inter-monsoonal samples from this study exhibited a correlation between spectral slope and fluorescence ratio of peak A/peak C and IC1/a_{340}. This suggests there are abundant humic materials within this period. It has also been suggested that substantial precipitation might occur during inter-monsoonal period, which is normally in October and April (Desa and Niemczynomicz, 1996; Suhaila et al., 2010), and this would be associated with fresher DOM inputs to the catchment.



(a) Oil palm plantations (OP)



(b) Secondary forests (SF)



(c) Coastal swamps (CS)

Fig. 5.3 DOC against PARAFAC component C1 for each type of land use.

6. SPATIAL AND TEMPORAL VARIATIONS IN THE COMPOSITION OF DISSOLVED ORGANIC MATTER IN A TROPICAL RIVER: THE LOWER KINABATANGAN RIVER, SABAH, MALAYSIA

Scope of Chapter

Dissolved organic matter (DOM) was characterised along the main stem of the Lower Kinabatangan River, Sabah, Malaysia. The objectives of the study were to determine DOM quality along a medium sized tropical river affected by recent deforestation and specifically to determine the seasonal of DOM quantity and quality trends in DOM of waters sampled from different depths, along the main stem of the river. A total of 128 water samples were collected in the Kinabatangan River at three depths (surface, mid-point and riverbed) at nine points in five fieldwork campaigns (between October 2009 and May 2010), three of which corresponded with the wet season, one the dry season, and one the inter-monsoonal period. DOM was characterised optically by fluorescence spectroscopy and parallel factor analysis. Individual Excitation Emission Matrices (EEMs) were generated for each sample, together with the absorption coefficient at 340 nm; and spectral slope coefficient (*S*). A PARAFAC model of the data-set identified three terrestrially derived components (C1, C2 and C3). DOM variations with river depth showed that suspended sediment concentrations were highest at the riverbed (1165.2 mg/l) and correlated positively with all the PARAFAC components. These components were found to contribute most to DOM fluorescence in all study areas, particularly in the wet season. The results imply

that C1 could be a significant PARAFAC signal that can be found in tropical regions. Both seasons (wet and dry) were dominated by peak M (C2), which could be derived from microbial sources and/or photo-degradation processes.

6.1 INTRODUCTION

The riverine transport of dissolved organic matter (DOM) plays a significant role in the global carbon cycle, as it provides a source of atmospheric CO_2 and links terrestrial and marine ecosystems (Baum et al., 2007; Cole et al. 2007). Cole et al. (2007) has suggested that 1.9 Pg C per year is delivered from terrestrial to fluvial systems globally and approximately of half of the carbon was consumed within rivers before reaching the ocean. Evidently, large rivers are contributing actively to the composition, transformation, and processing of DOM and influence its subsequent lability as well as reactivity (Massicotte and Frenette, 2011; Yamashita et al., 2010a). The composition of riverine DOM is highly dependent on various inputs; it could derive from allochthonous and autochthonous sources; as well as biogeochemical processes (Massicotte and Frenette, 2011). Organic carbon and nutrient export from catchments are controlled by a range of environmental factors including hydrology, geomorphology, land use/land cover patterns, aquatic light intensity, microbial activities, vegetation types and soils within individual catchments (McGroddy et al. 2008; Yamashita et al., 2010b; Yang et al., 2012).

DOM dynamics are also known to be characterised by significant spatial and seasonal changes (Findlay and Sinsabaugh, 1999; Ishii and Boyer, 2012;

Jaffe et al., 2008). Normally, DOM will be transformed during transport from the catchment headwaters (Massicotte and Frenette, 2011); thus influencing its quality (Jaffe et al., 2008; Maie et al., 2012). DOM modifications can also be influenced by catchment hydrodynamics, such as flow velocity as well as stream size (Kaplan and Newbold, 2003). From an ecosystem perspective, further downstream the canopy opens, litter inputs decline and higher exposure to sunlight results in greater irradiation of stream water and bed sediments (Battin et al., 2008; Findlay and Sinsabaugh, 1999; Tank et al., 2010). Spatially, Yamashita et al. (2010b) also found that DOC concentrations in the subtropical Everglades decreased as a function of distance travelled and were heavily influenced by the agricultural activities in the area.

In terms of seasonal variations in the tropics, the wet season flushes out much of the litter that has accumulated during the preceding dry season. Frequent inundations may also 'reset' the system and remove DOM before degradation can occur (Wantzen et al., 2008). Coynel et al. (2005) found that highest concentrations of dissolved organic carbon (DOC) and particulate organic carbon (POC) in the Congo Basin were observed during high water periods, whereas the lowest concentrations occurred during the low water periods. Significant temporal variations of DOM export in pristine tributaries of the Congo River observed by Spencer et al. (2010) further suggest that tropical rivers are likely to export more labile DOM during wet periods. Furthermore, a study in Florida Bay showed that the fluorescence index (FI) varied seasonally, ranging from terrestrially influenced DOM (at low values) to strongly microbial influenced DOM (at high values) (Jaffe et al., 2008). The same study also showed that

limited tidal exchange with the Florida Shelf led to less microbial influence particularly during the dry season.

Vertical variations in DOM quantity and quality through the water column are also likely to influence the total carbon content to the oceans globally (Mulholland and Watts, 1982). For example, the concentration of POC from a depth-integrated sample in the Amazon River was found to be twice that of the surface suspended sediment (Thurman, 1985). Both lateral and depth-integrated samples have been shown to be important and a major factor for the carbon fluxes estimations (Lu et al., 2011). Lu et al. (2011) also reviewed a data set which combined surface and bottom samples (in the range of 3.2 to 8.5 mg/l) from the subtropical Yellow River (collected by Zhang et al. (1992)) resulted in much higher organic carbon transport compared to estimates derived using only surface water (in the range of 2.0 to 4.0 mg/l) by Cauwet and Mackenzie (1993). In a well-mixed water column, DOM near the surface will be replenished due to turbulent mixing and will cause limited transport to the deeper regions, and thus, DOM near the riverbed will become depleted (Kaplan and Newbold, 2003).

This chapter seeks to characterise the DOM quality in a tropical river in SE Asia, which has been exposed to various environmental pressures including deforestation and agricultural development. Since the 1980s, the Lower Kinabatangan River has been characterised by extensive development of oil palm plantations within the catchment. The aims of this study were threefold:

- to determine DOM variations between samples collected from the surface, middle and riverbed of the main river;

- to identify any trends in DOM along the axis of the river downstream and;
- to determine the seasonal variability of DOM quantity and quality.

6.2 RESULTS

6.2.1 Water Quality Characteristics and PARAFAC Components

The results of the fieldwork campaigns are summarised in Fig. 6.1, Fig. 6.2 and Fig. 6.3 and Table 6.2 which give descriptive statistics for each parameter and their variation with depth and downstream. During the period of study, suspended sediment concentrations ranged from 33.6 to 9814.0 mg/l, with greatest concentrations in waters sampled from the lowest points in the river profile. Suspended sediment concentrations increased downstream, with maximum values observed in Abai in December 2009.

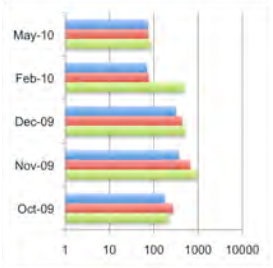
(a) Suspended sediment (mg/l)

BPB (66.9 km)

BPC (42.7 km)

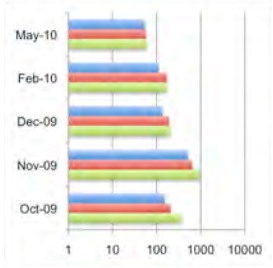
BPA (32.1 km)

SKC (45.1 km)



SKD (42.7 km)

SKB (34.3 km)



SKA (32.1 km)

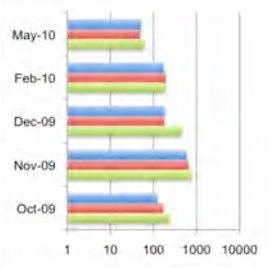
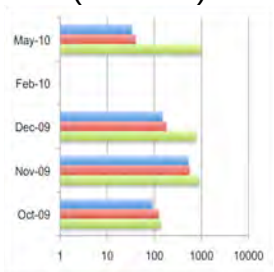


ABB (29.1 km)

ABA (19.6 km)



(b) Dissolved organic carbon (DOC) (mg/l)

BPB (66.9 km)

BPC (42.7 km)

BPA (32.1 km)

SKC (45.1 km)

SKD (42.7 km)

SKB (34.3 km)

SKA (32.1 km)

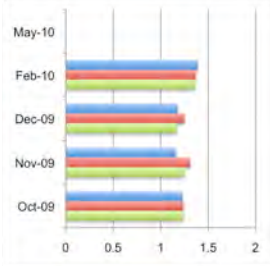
ABB (29.1 km)

ABA (19.6 km)

Fig. 6.1 (a)-(b) Descriptive trends of suspended sediment and DOC for each sampling point. Indicators: Blue = surface; Red = middle; Green = near the base. Distances from the sea are given in brackets.

(a) Peak A/Peak C

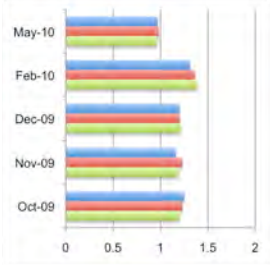
BPB (66.9 km)



BPC (42.7 km)

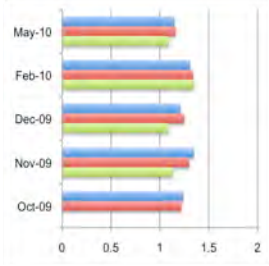
BPA (32.1 km)

SKC (45.1 km)



SKD (42.7 km)

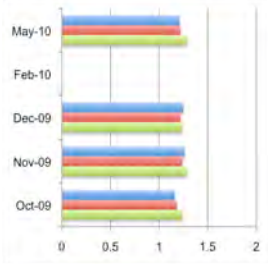
SKB (34.3 km)



SKA (32.1 km)

ABB (29.1 km)

ABA (19.6 km)



(b) Peak C/a_{340}

BPB (66.9 km)

BPC (42.7 km)

BPA (32.1 km)

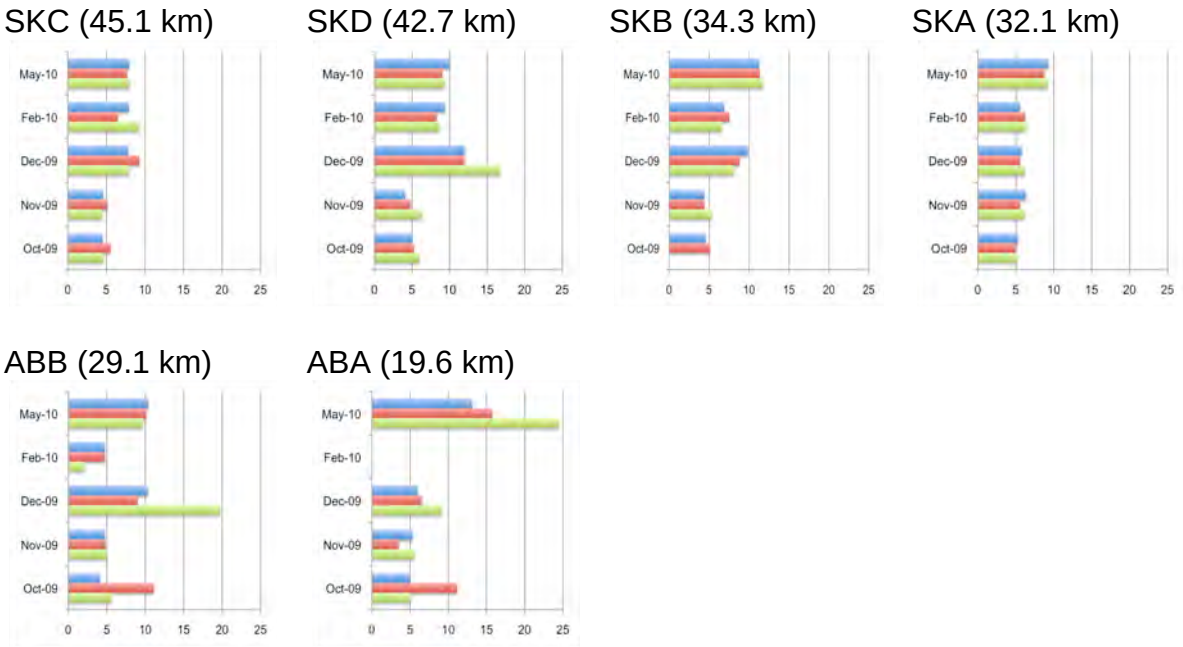


Fig. 6.2 (a)-(b) Descriptive trends of fluorescence ratio for peak picking data at each sampling point. Indicators: Blue = surface; Red = middle; Green = near the base. Distances from the sea are given in brackets.

(a) IC1/IC3

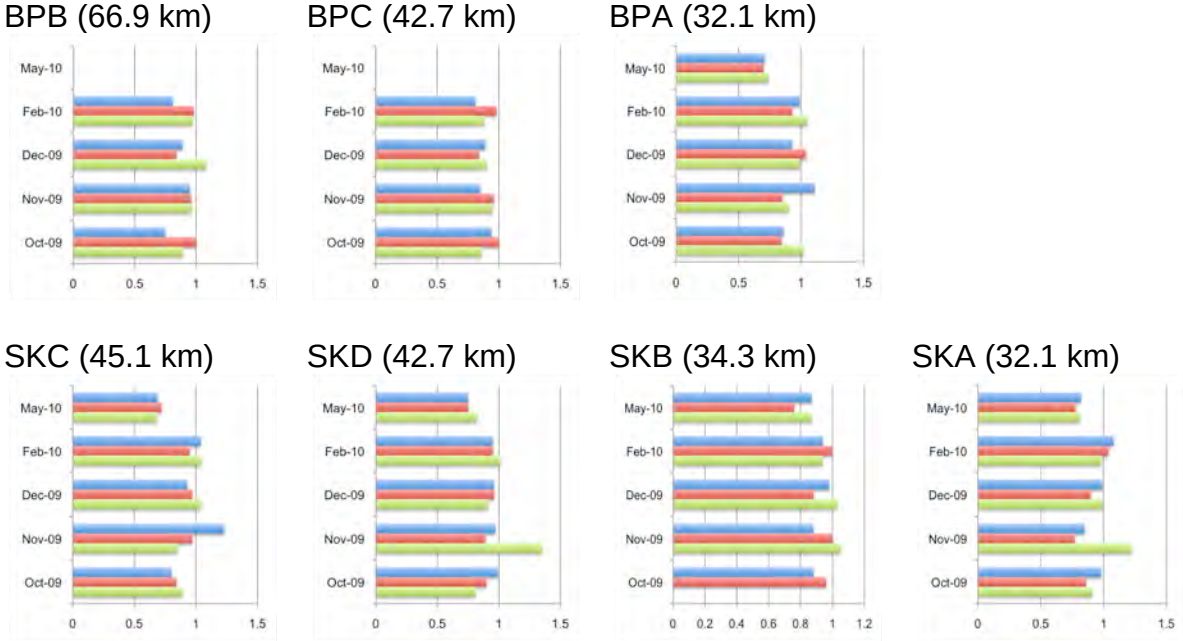


ABB (29.1 km)

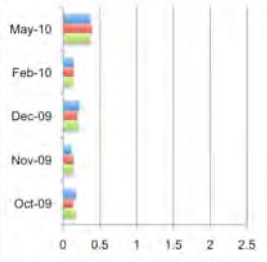
ABA (19.6 km)

(b) IC3/a_{340}

BPB (66.9 km)

BPC (42.7 km)

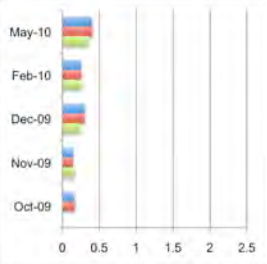
BPA (32.1 km)



SKC (45.1 km)

SKD (42.7 km)

SKB (34.3 km)



SKA (32.1 km)

ABB (29.1 km)

ABA (19.6 km)

(c) IC2/IC3

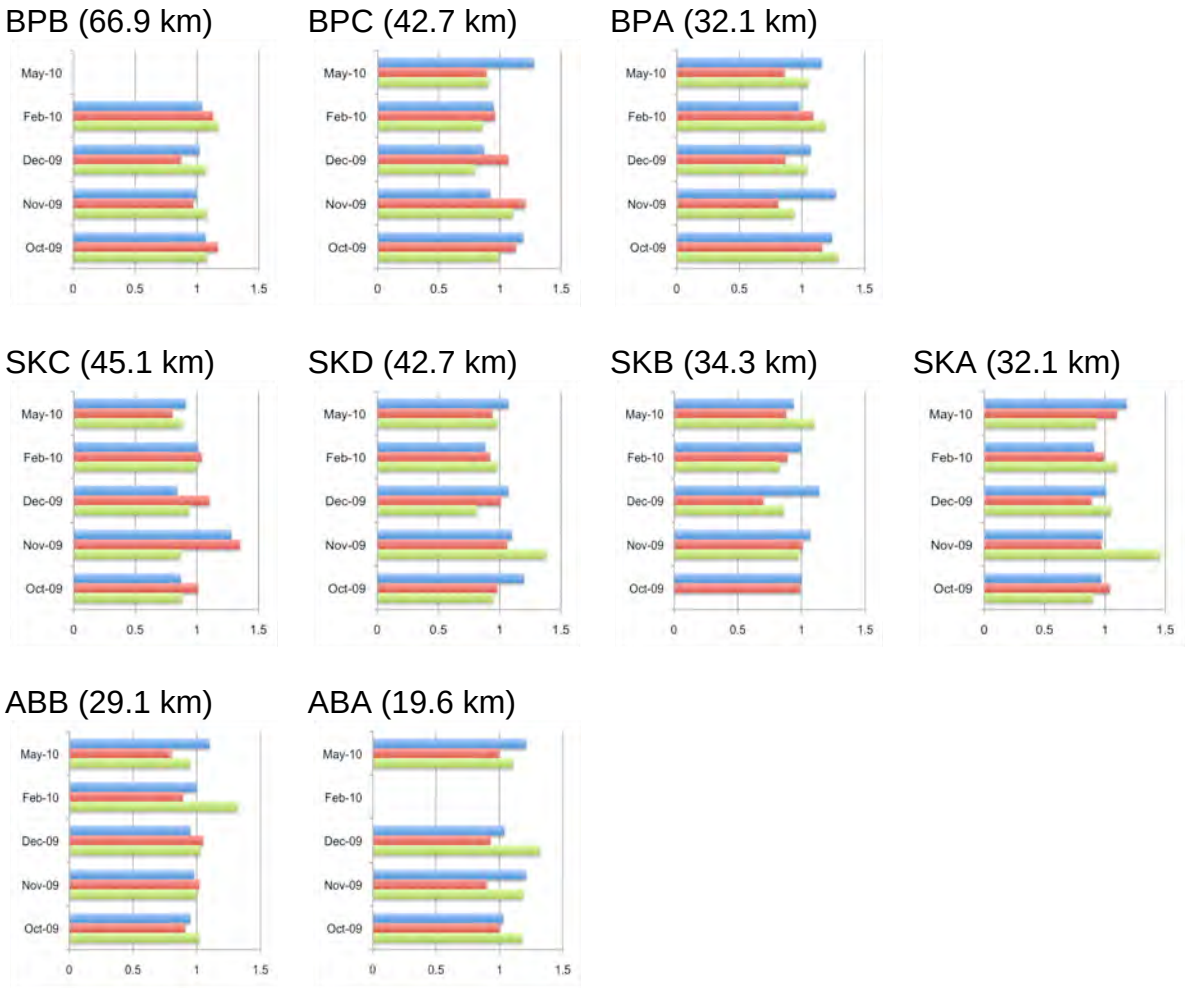


Fig. 6.3 (a)-(c) Descriptive trends of fluorescence ratio for PARAFAC data set at each sampling point. Indicators: Blue = surface; Red = middle; Green = near the base. Distances from the sea are given in brackets.

DOM concentrations varied with depth, and generally greatest values were found in waters sampled from near the river surface, which ranged from 7.4 to 9.5 mg/l. DOC concentrations were consistently low in May 2010 (dry season), and high during the wet season (November 2009), although in December 2009, DOC

concentrations were high in the upper reaches Batu Putih, and lower in Sukau before increasing dramatically at Abai downstream.

As Figs. 6.1-6.3 indicate, there was little variation in the ratio peak C/peak A with sample depth. However, the fluorescence index IC1/IC3, which is equivalent to peak C/peak A, was typically high in waters sampled at the river surface and near the riverbed especially in November 2009 (Fig. 6.3). The ratios peak C/a_{340} and IC3/a_{340} were both consistently dominated by samples collected from near the riverbed. Moreover in December 2009 and May 2010, both ratios gradually increased with distance downstream.

Similarly, IC2/IC3 was also dominated by samples from the river surface and bed (Fig. 6.2 and Fig. 6.3). The ratio IC2/ IC3 did not vary significantly between wet and dry seasons, nor was there a significant variation in samples collected during the inter-monsoonal period (October 2009). Looking at trends downstream, however, in May 2010 the ratio peak C/a_{340} was high at upstream sampling points (i.e. at Batu Putih) and gradually increased downstream to Sukau (with the exception of sample from SKC) and Abai.

Three fluorescent components were identified by PARAFAC from the 128 individual EEMs derived from the data set. The excitation and emission pairs of the main peak positions for each components are summarised in Tables 6.1 and 6.2 which compare the results with components identified by selected studies that have modelled DOM in marine, oceanic and estuarine environments in different environments globally.

Table 6.1 Spectral characteristics of excitation and emission maxima of three components identified by PARAFAC modeling for the whole EEMs data set collected from main stem of the Lower Kinabatangan River catchment compared to previously identified sources.

Component no.	Excitation maximum (nm)	Emission maximum (nm)	Coble (1996); Parlanti (2000)	Description and probable source
1	290	464	Peak A 230-260 / 380-460	Terrestrial humic-like substances, widespread Hydrophobic acid fraction (HPOA), suggested as photo-refractory Component 2: 255 / 380-460 (Luciani et al., 2008) Component 3: 270 (360) / 478 (Stedmon et al., 2003) Component 3: 250 (355) / 461 (Yao et al., 2011) Component 1: 270 (365) / 453 (Zhang et al., 2009b)
2	290	398	Peak M 230-260 / 380-460	Terrestrial humic-like substances, widespread Hydrophobic acid fraction (HPOA), suggested as photo-refractory Component 2: 255 / 380-460 (Luciani et al., 2008) Component 3: 270 (360) / 478 (Stedmon et al., 2003) Component 3: 250 (355) / 461 (Yao et al., 2011) Component 4: <260 (305) / 376 (Yamashita et al., 2010b) Component 1: 270 (365) / 453 (Zhang et al., 2009b)
3	340	418	Peak C 350-360 / 420-480	Ubiquitous humic-like substances, suggested as photo-labile and agricultural land use derived Hydrophobic acid fraction (HPOA) Component 3: 320 / 380-420 (Luciani et al., 2008) Component 4: 325 / 416 (Stedmon et al., 2003) Component 6: 325 / 406 (Yamashita et al., 2010b)

Table 6.2 Descriptive statistics of environmental conditions and PARAFAC model of selected sampling stations in the main stem of the Lower Kinabatangan River catchment.

			pH	Salinity	DOC (mg/l)	Suspended sediment (mg/l)	a_{340} (m^{-1})	$S_{275-295}$ (nm^{-1})	I_{tot}	I_{C1}	I_{C2}	I_{C3}
Surface	Wet Season	Mean	6.87	0.03	9.78	249.6	41.5	0.0123	20.45	6.52 (32%)	6.82 (34%)	7.11 (35%)
		Std. dev.	0.55	0.01	3.39	172.0	16.4	0.0178	6.44	2.25	1.90	2.38
		Variance	0.30	0.00	11.52	29592.1	269.0	0.0003	41.46	5.07	3.62	5.68
	Dry Season	Mean	7.11	0.11	5.88	85.3	22.4	0.0110	21.34	5.97 (28%)	7.97 (37%)	7.40 (35%)
		Std. dev.	0.38	0.14	0.55	72.6	4.87	0.0007	1.03	0.32	0.72	0.66
		Variance	0.14	0.02	0.31	5272.9	23.8	0.0000	1.07	0.11	0.52	0.44
Mid-point	Wet Season	Mean	6.84	0.03	9.26	324.3	42.6	0.0089	20.81	6.66 (32%)	6.81 (33%)	7.33 (35%)
		Std. dev.	0.29	0.01	3.38	226.9	16.4	0.0019	6.49	2.15	2.05	2.42
		Variance	0.08	0.00	11.45	51489.0	267.7	0.0000	42.14	4.64	4.20	5.84
	Dry Season	Mean	7.05	0.35	5.69	88.2	23.5	0.0109	21.62	6.01 (28%)	7.33 (34%)	8.28 (38%)
		Std. dev.	0.20	0.82	0.35	74.7	6.1	0.0009	1.10	0.43	0.68	0.53
		Variance	0.04	0.67	0.12	5576.6	37.2	0.0000	1.21	0.19	0.47	0.28
Riverbed	Wet Season	Mean	6.85	0.03	9.98	1165.2	36.8	0.0091	20.79	6.80 (33%)	6.95 (34%)	7.04 (34%)
		Std. dev.	0.33	0.01	3.49	1950.6	15.9	0.0018	7.97	2.72	2.92	2.52
		Variance	0.11	0.00	12.18	3804972.5	254.1	0.0000	63.50	7.40	8.55	6.34
	Dry Season	Mean	7.04	0.53	5.82	210.5	22.9	0.0114	21.56	6.06 (28%)	7.60 (35%)	7.90 (37%)
		Std. dev.	0.25	1.33	0.52	320.4	7.1	0.0017	1.40	0.37	0.52	0.82
		Variance	0.06	1.76	0.27	102629.8	50.2	0.0000	1.96	0.14	0.27	0.68

The PARAFAC model presented here identified three components: component 1 (C1), component 2 (C2) and component 3 (C3). Components C1 and C2 have been commonly reported in estuarine, marine and oceanic environments while C3 represents fluorophores that have the longest excitation wavelength and broadest excitation band as well as the longest emission wavelength associated with a broad emission band. Individual components are summarised in Fig. 6.4 as contour plots. The intense excitation maxima were: 290-nm at 464-nm emission (C1); 305-nm at 464-nm emission (C2); and 340-nm at 418-nm emission (C3).

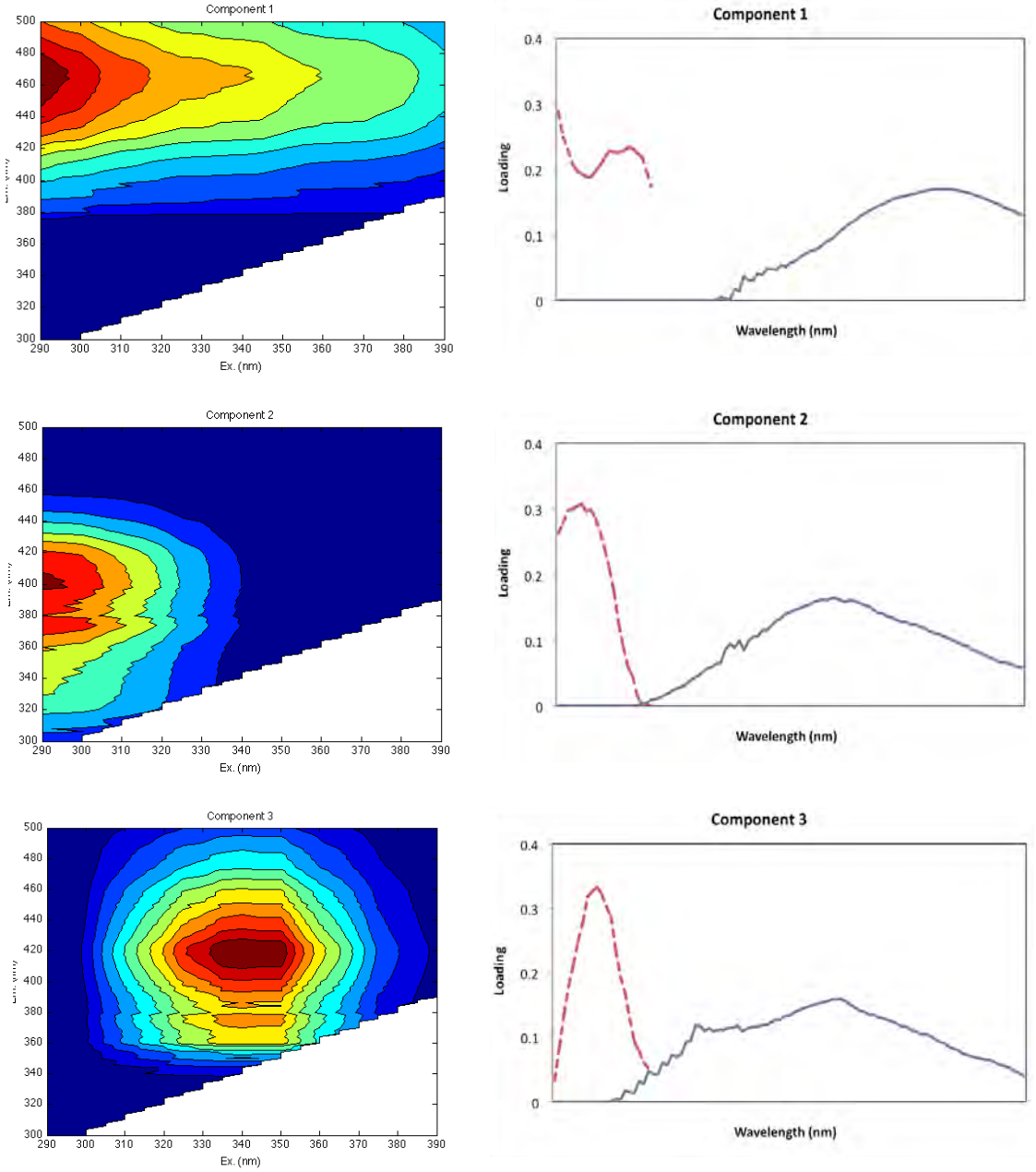


Fig. 6.4 PARAFAC model output representing fluorescence signatures of three components identified. Contour plots present spectral shapes of excitation and emission of derived components. Line plots at right side of each contour plot present split-half validation results for each identified component. Excitation (dotted line) and emission (solid line) loadings for each component, obtained from two independent PARAFAC models on random halves of the data array.

The mean DOM composition of all samples varies considerably: peak M (C2) is the most abundant, followed by peak C (C3) and peak A (C1). Samples from the surface in the wet season and mid-point in both seasons exhibited a similar pattern: C3 > C2 > C1, while different patterns were evident in waters sampled from the surface during the dry season: C2 > C3 > C1. Samples collected from the lowest point of the water column (near the riverbed) in the main stem showed patterns of: C2 = C3 > C1 in the wet season and C3 > C2 > C1 in the wet season. Finally, water samples collected in the inter-monsoonal period exhibited a similar pattern throughout the water column: C2 = C3 > C1.

6.2.2 Discriminant Analysis

Looking first at DOM characteristics with depth, there were only slight differences between the DOM composition of waters sampled from the surface, middle and bottom of the river (Table 6.2). Fig. 6.5 plots the first and second discriminant function of each parameter from both data-sets. A series of discriminant analyses identified two discriminant functions, with identical results for the sets derived from peak picking and PARAFAC analysis. Discriminant function 1 from the PARAFAC and peak picking explains 81.1% and 91.4% of the variance in the data respectively. The results confirmed a positive correlation between suspended sediment and the two fluorescence indices IC1/IC3 and IC3/a_{340} with results that were dominated by samples from the riverbed, followed by the middle and then the river surface. The only exception was for discriminant function 1, where the ratio peak A/peak C (from peak picking) and peak C

emission were negatively correlated. PARAFAC data set also showed that the ratio IC2/IC3 was positively correlated and classified under discriminant function 2. This ratio was mainly dominated by samples collected from the surface of the river profile, followed by bottom and middle samples.

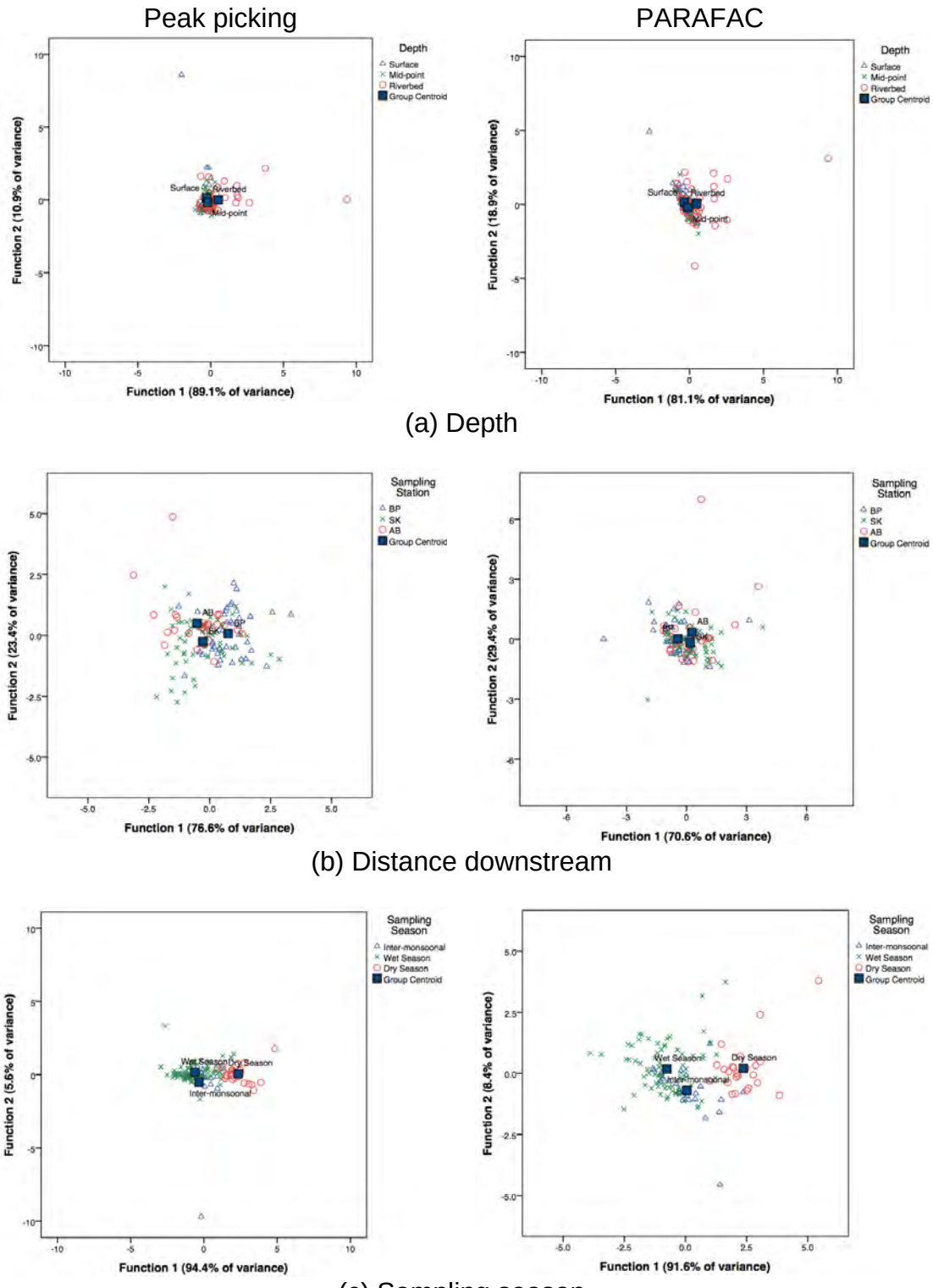


Fig. 6.5 Plots for the first and second discriminant functions of each parameter from peak picking and PARAFAC data-sets according to: (a) Depth; (b) Distance downstream; and (c) Sampling season.

Looking secondly at trends in DOM composition downstream, discriminant functions 1 and 2 for PARAFAC data set explained 70.6% and 29.4% of the variance respectively; revealing that samples from Abai were dominated by the ratio IC3/a_{340} (which is comparable to the fluorescence intensity ratio peak C/a_{340}). They were followed by samples from Sukau and finally Batu Putih. The ratio IC1/IC3 and IC2/IC3 were classified under discriminant function 2 and negatively correlated with the spectral slope. These ratios were dominated by samples collected from Abai, followed by Batu Putih and finally Sukau.

For the peak picking data set, the factor structure coefficients showed that suspended sediment and spectral slope were positively correlated. Discriminant functions 1 and 2 explained 52.8% and 47.2% of the variance respectively. These ratios were also dominated by samples collected from Batu Putih (upstream), followed by Sukau and Abai (i.e. progressively downstream). The analysis also showed that the ratio peak A/peak C was dominated by samples from Abai, followed by Batu Putih and Sukau, which is identical to the PARAFAC data-set.

Discriminant analyses on both the peak picking and PARAFAC showed very similar results to DOM variations during the dry and rainy seasons. The results also consistently indicated a positive correlation between the ratios of IC3/a_{340}, peak C/a_{340}, IC2/IC3, peak A/peak C, peak C/a_{340} and suspended sediment which were all classed under discriminant function 2, and dominated by samples in the wet season.

6.3 DISCUSSION

6.3.1 Characterisation of PARAFAC Components

Table 6.1 compares the characterisation of C1, C2 and C3 components in this study with studies in the literature. The component C1 is similar to the peak A as defined by Coble (1996) and previously reported to be a ubiquitous, component commonly found in various aquatic environments including tropical and sub-tropical waters (Kowalczuk et al., 2009; Luciani et al., 2008; Stedmon and Markager, 2005b; Yamashita et al., 2010b; Yao et al., 2011). Ishii and Boyer (2012) considered this component to be ultraviolet C (UVC) and commonly abundant in terrestrial-derived DOM such as thermokarst, forested streams, wetlands and tree leaves particularly during the dry months or after storm events. Several studies also found that C1 correlated negatively with salinity and hence could indicate aquatic systems transitions from freshwater to seawater (Ishii and Boyer, 2012). Yamashita et al. (2008) suggested that this component was dominant from surface samples of Ise Bay in Japan and that is decreased with depth.

Coble (1996) and Parlanti et al. (2000) have previously interpreted component C2 as peak M and marine in origin. However, Stedmon et al., (2003) indicated that this component was observed in ‘terrestrially dominated end-member samples’. More recently, Fellman et al., (2010) and Yamashita et al. (2010b) identified this peak as ultraviolet A (UVA); a component with low molecular weight, which they attributed to microbial processing. Furthermore, C2 has also been observed as being resistant to photo-degradation (component C3

in Ishii and Boyer, 2012). This component is widespread and common in marine environments; it is associated with biological activity but it also found in wastewater, wetlands and agricultural environments. Thus, the dominance of component C2 (peak M) in the main stem samples (and particularly those collected from the river surface) strengthens the hypothesis that the peak M in samples from the Kinabatangan catchment is DOM which derived from microbial and/or photo-degradation processes.

Pollard and Ducklow (2011) showed that the water column in a subtropical river (Bremer River, Australia) was turned over every two days, as a result of DOC consumption by bacteria. This is supported by bacterial specific growth rates, which were found to be ~20 times greater than that previously observed in marine ecosystems. Abundant sunlight in general has been found to increase microbial activities within water bodies (Alonso-Saez et al., 2006; Wantzen et al., 2008) in particular cyanobacteria (Mortillaro et al., 2012). For example, average bacterial production in was found higher in clearwater rivers than blackwaters, thus, suggesting light penetration play an important role in DOM decomposition (Castillo et al., 2004). Component C3 has been identified in various types of water body including those dominated by DOM from terrestrial and microbial sources (component C2 in Ishii and Boyer, 2012). Similar to C2, this component has been found subject to photo-degradation.

Components C1, C2 and C3 were positively correlated with each other and are possibly to be associated with terrestrially derived organic matter. Peak C has been described as ubiquitous, photo-labile and associated with agricultural

land use (Yamashita et al., 2010b). Given that ~74% of the total catchment of the Lower Kinabatangan River comprises forests (primary and secondary), and the remainder of the catchment (~26%) has been developed for oil palm plantations and is permanently cultivated (Josephine et al., 2004), this could explain the abundance of terrestrial derived peaks in all the main stem samples.

Even though scatter removal has been applied (Section 3.5.1), thus, limited to 290-nm excitation wavelength, PARAFAC components identified in this and other studies (including Hong et al. (2011), Luciani et al. (2008) and Yamashita et al. (2010b) could reflect specific PARAFAC components found in tropical areas. Although given the variation between DOM characteristics described in many studies, comparisons with other regions might not apply locally (Ahmad et al., 2002).

6.3.2 Depth-profiles of DOM Quality

DOC concentrations observed in this study were found to vary with depth with highest values from the river surface and Fig. 6.6 exhibits the conceptual diagram of DOM dynamics within a water column. These are comparable to those reported elsewhere in the literature for tropical watersheds: DOC concentrations in the Jiulong River, China, were found to vary from 0.4 to 13.1 mg/l (Hong et al., 2011), while Yamashita et al (2010a) found DOC concentrations in three Venezuelan rivers to vary between 1.71 to 10.7 mg/l. Suspended sediment concentrations, peak C/a_{340} and $IC3/a_{340}$ were high in samples from near the

riverbed, followed by mid-point and surface of river. This is supported by the discriminant analysis, which revealed that suspended sediment and IC1/IC3 were positively correlated. This could be a result of on-going land clearance in the catchment (Josephine et al., 2004) as agricultural activities are associated with elevated nutrient concentrations and increased suspended sediment (Tank et al., 2010). Interestingly, lower peak C/a_{340} and $IC3/a_{340}$ were observed in samples collected from the mid-point of river (as explained in Methods section). Microbial activities and abundant sunlight in the tropical regions would be expected to accelerate DOM decomposition, thus suggesting decomposition of surface DOM which accounts for the lower peak C/a_{340} and $IC3/a_{340}$ of samples from the mid-points of river. Photochemical reactions have been found to generate low molecular weight organic compounds, trace gases, and also phosphorous and nitrogen rich compounds (Cory et al., 2007; Kowalzuk et al., 2009; Winter et al., 2007). However, light penetration through the water column (~20 m) may be limited for much of the time given the generally high suspended sediment concentrations, and waters sampled close to the riverbed are unlikely to have experienced as much decomposition from photochemical reactions (Pisani et al., 2011).

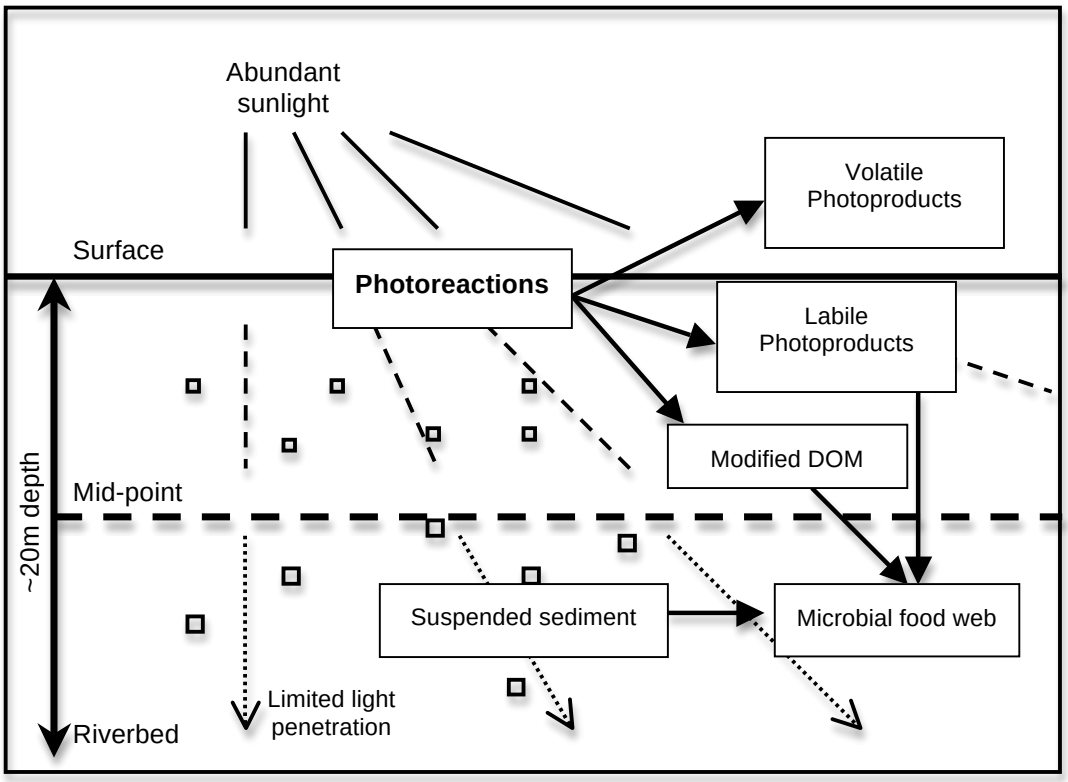


Fig. 6.6 Conceptual model of DOM dynamics in a water column of a tropical river (after Moran and Covert, 2003).

Samples collected from the river surface and immediately above the riverbed were found to dominate the fluorescence ratio IC2/IC3. Peak M has been attributed to microbial processing, and thus, could be associated with high microbial activities at these depths, compared to samples at the river mid-point. Consequently, DOM at the river surface is probably more likely to be degraded by both photochemical reaction, and microbial processes. High suspended sediment concentrations can also contribute to lower photochemical reactions. For example, Yamashita et al. (2010a) suggested that limited light penetration in main river channels reduced photo-degradation of DOM. Although light has been

found to enhance microbial activities within water bodies, Lindell et al. (1996) observed that direct sunlight could negatively affect aquatic bacteria metabolic activity (Westhorpe et al., 2012).

High suspended sediment concentrations might also be a factor explaining high microbial and/or photo-degradation processes at the river surface and bed, as indicated by the fluorescence ratio IC2/IC3. Sediment in the aquatic ecosystems has been suggested as one of the main sources of DOM (Riggsbee et al., 2008), which serves as benthic substrate (Wetzel, 2001), a DOM adsorption sink (Guo et al., 2011; Mortillaro et al., 2012), and also provide nutrient subsidies for bacterioplankton (Lennon and Pfaff, 2005). The chemical composition of DOM, significantly affects microbial processes, and could be an important factor explaining the dominance of IC2/IC3 in samples from near the river surface and bed. Lennon and Pfaff (2005), for example, highlighted that phosphorus content of DOM is a significant determinant of bacterial productivity, and there was no relationship between bacterial growth and bacterial productivity along the DOC gradient. In Rio de Janeiro tropical coastal lagoons, Farjalla et al. (2002) found that bacterial productivity was unaffected by DOC concentrations. The findings in the Kinabatangan River samples showed that both DOC concentration and the fluorescence ratio IC1/IC3 were high in samples from the river surface, which could indicate the dominance of humic materials that could comprise of various chemical components.

6.3.3 DOM Variations Downstream

Fig. 6.7 summarises DOM dynamics in a downstream direction observed in this study. An interesting variation in optical parameters downstream has been revealed, whereby a_{340}, the spectral slope, and ratios peak C/a_{340}, and IC3/a_{340} were low in Batu Putih and gradually increased downstream to Sukau and Abai. However, DOC and suspended sediment concentrations were high in Batu Putih, decreased in Sukau and increased again in Abai. The discriminant analysis of the PARAFAC data, set presented here, also confirms that samples from Abai were dominated by fluorescence ratios of IC1/IC3 and peak A/peak C, thus suggesting that this area was rich in terrestrial derived organic matter, followed by Batu Putih and Sukau. The inference in that DOM was degraded from Batu Putih to Sukau, due to both longer residence time as well as the tidal effect, and DOM was re-exported in Abai. Restoration works in the estuarine Mississippi Delta post-Katrina and Rita hurricanes found out that sediment deposits in leeves ranged from older wood-peat deposits to younger riverine fluvial deposits (Day et al., 2007; Twilley and Rivera-Monroy, 2009). New delta formed, and coarser sediments accumulated at river mouth and as the delta advanced, sand is shifted horizontally to create beach ridges (Day et al., 2007), thus suggesting that riverine deposits were controlled by the tidal effect, exporting the sediments back to the river.

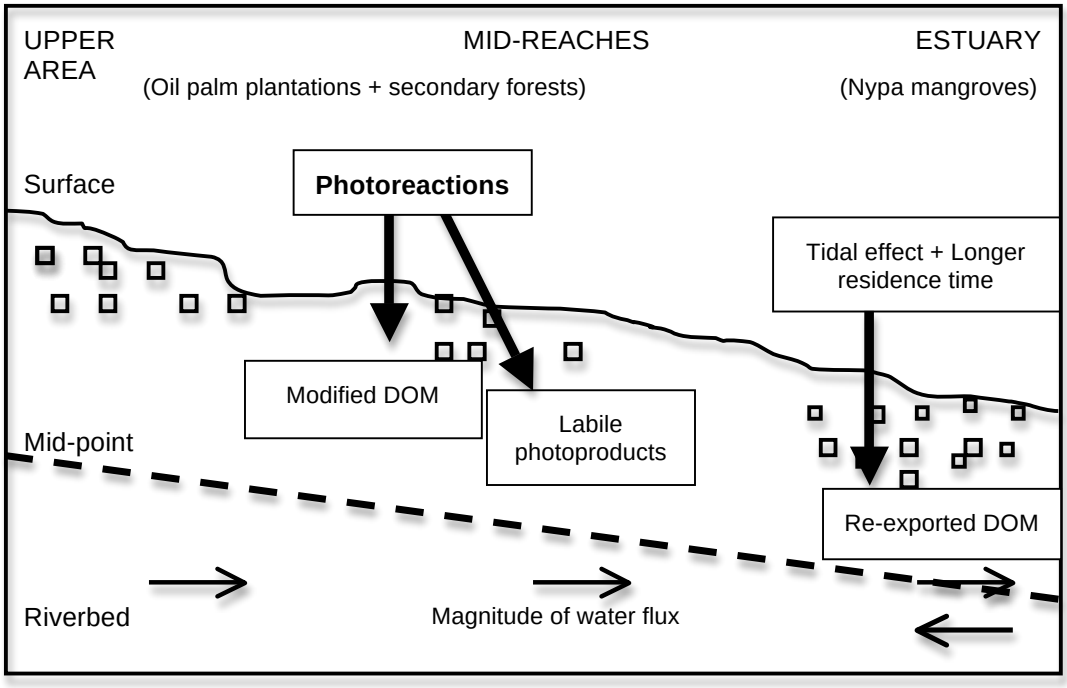


Fig. 6.7 Conceptual diagram of DOM dynamics following the axis downstream of a tropical river.

Highest IC1/IC3 and peak A/peak C were identified in samples from Abai where the highest salinity was observed. This could be associated with high suspended sediment concentrations in this area, although salinity has generally been found to be inversely correlated with DOC (Baum et al., 2007; Moore et al., 2011) and coloured DOM (CDOM) (Murphy et al., 2006). The increasing density of the nypa palm, *Nypa fruticans* in the floodplain downstream could also be a factor. In similar mangrove environments, decomposition of litter falls has been found to occur through a combination of leaching and microbial degradation (Sahoo and Dhal, 2009), and leaching alone is able to generate high levels of DOM (Benner, 1990; Kristensen et al., 2008). Nypa vegetation is known to provide rich polyphenols and tannins (Kathiresan and Bingham, 2001) and is

likely to be associated with decreasing bacterial counts (Sahoo and Dhal, 2009). Thus would be supported by the dominance of fluorescence intensity ratio of IC2/IC3 observed in Abai.

6.3.4 Temporal Variations of DOM

The summary of data from the study presented in Table 6.2 highlights how the total fluorescence intensity I_{tot} as well as the intensity of components C2 and C3 were consistently higher in the dry season, when DOC concentrations were at minimum levels. Fig. 6.8 represents the DOM dynamics from temporal variations perspectives. Discriminant analysis from both PARAFAC and peak picking data-sets also agreed that fluorescence ratios IC1/IC3 and IC2/IC3 were highest during the wet season. As FI IC2/IC3 is equivalent to peak M/peak C, its abundance could indicate the microbial and/or photo-degradation processes in the main stem as well as most active microbial activity (in combination with high amount of sunlight) within this period. In the subtropical North Jiulong River, China, Yang et al. (2013) observed significant increased in the flux of DOC and PARAFAC components that equivalent to peaks A and C (components C1 and C3) during the storm events, which could indicate substantial impact of the storm event on the export of DOM as well as its fluorescent constituents.

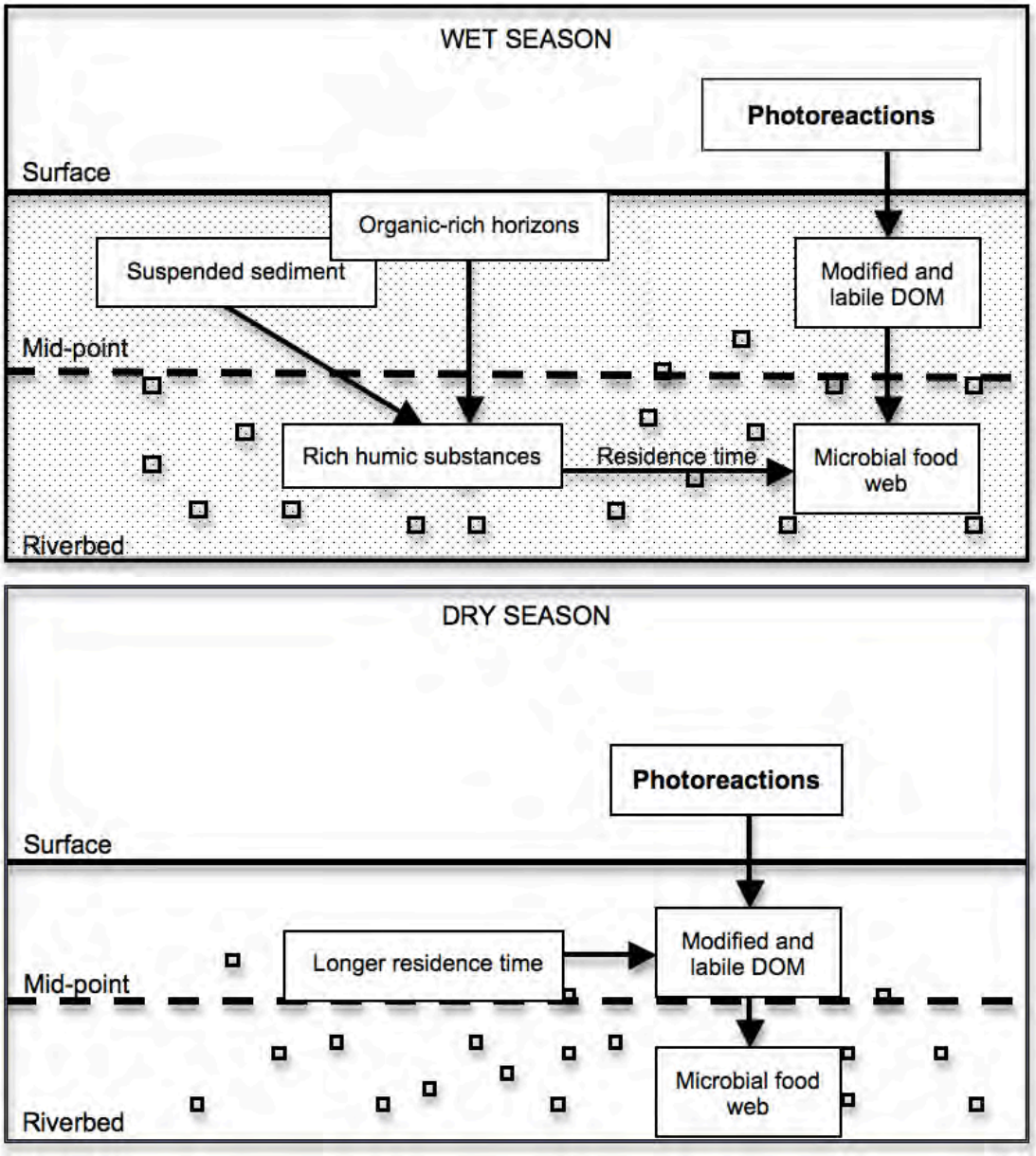


Fig. 6.8 Diagram of DOM dynamics in terms of temporal variations.

In contrast, suspended sediment concentrations were higher in samples collected during the wet season. During storms, the water flowpaths were probably through organic-rich soil horizons (Wiegner et al., 2009), thus, abundant terrestrial-derived DOM. DOC concentrations were also greatest during the wet season, and has been found elsewhere to increase during the rainy season (Hood et al., 2006). Similar results have been found for the spectral

slope $S_{275-295}$, which Helms et al., (2008) suggest can characterise DOM better than absorption values alone (Helms et al., 2008). The spectral slope also correlates strongly with molecular weight (MW) and aromaticity (Helms et al., 2008); thus, low $S_{275-295}$ values for samples collected during the wet season could indicate fresher DOM within this period.

6.4 CONCLUSIONS

It can be concluded that the DOM characteristics in the study area are influenced to a considerable degree by microbial activities and/or photo-degradation processes. This has been reflected by the results, which demonstrates that PARAFAC components peak M were abundant in the upper river reaches (Batu Putih). Interestingly, the discriminant analysis indicated that DOM degradation was higher at river mid-point and near the bed, whilst samples from near the riverbed were characterised by higher molecular weight organic molecules. In terms of temporal variations, the findings showed that fresher DOM in the wet season was subjected to degradation to less fluorescent and stable compounds, in particular by photochemical and microbial activities.

7. DOM DYNAMICS IN THE LOWER KINABATANGAN RIVER CATCHMENT

Scope of Chapter

This chapter draws together the results presented in detail in the preceding Chapters 4, 5 and 6. Three conceptual diagrams were presented in Chapter 6 and used to characterise the DOM in the main stem of the Lower Kinabatangan River and its transformations from the upper catchment (Batu Putih) to reaches downstream (Abai). This chapter aims to present two new conceptual models describing DOM transformations: firstly, with regard to spatial and temporal variations in DOM with differing land use (oil palm plantations, secondary forests and coastal swamps); and secondly, examining the degree to which existing widely used conceptual models (integrating hydrological and biogeochemical processes), can be applied in a degraded tropical catchment. The chapter also highlights the contribution of this study to our understanding of the DOM transformations and fluxes, specifically the effects of recent land degradation in the tropical catchment, by placing the study within the context of recent research. It also identifies some of the limitations of the study and concludes with a summary of current or urgent gaps in the research area.

7.1 SPATIAL AND TEMPORAL VARIATIONS

Tropical floodplains are recognized as sites of intense biogeochemical transformation and fluvial networks in tropical regions are potentially a very important source of global carbon (Yamashita et al., 2010a) with the highest rate of production that normally occur during the regular inundation events (Davies et al., 2008). However, available data are sparse and thus, this thesis draws upon a wide data set to characterise the DOM in a tropical river catchment (the lower Kinabatangan), and a summary of the main conclusions of the research presented in this thesis are shown schematically in Fig 7.1.

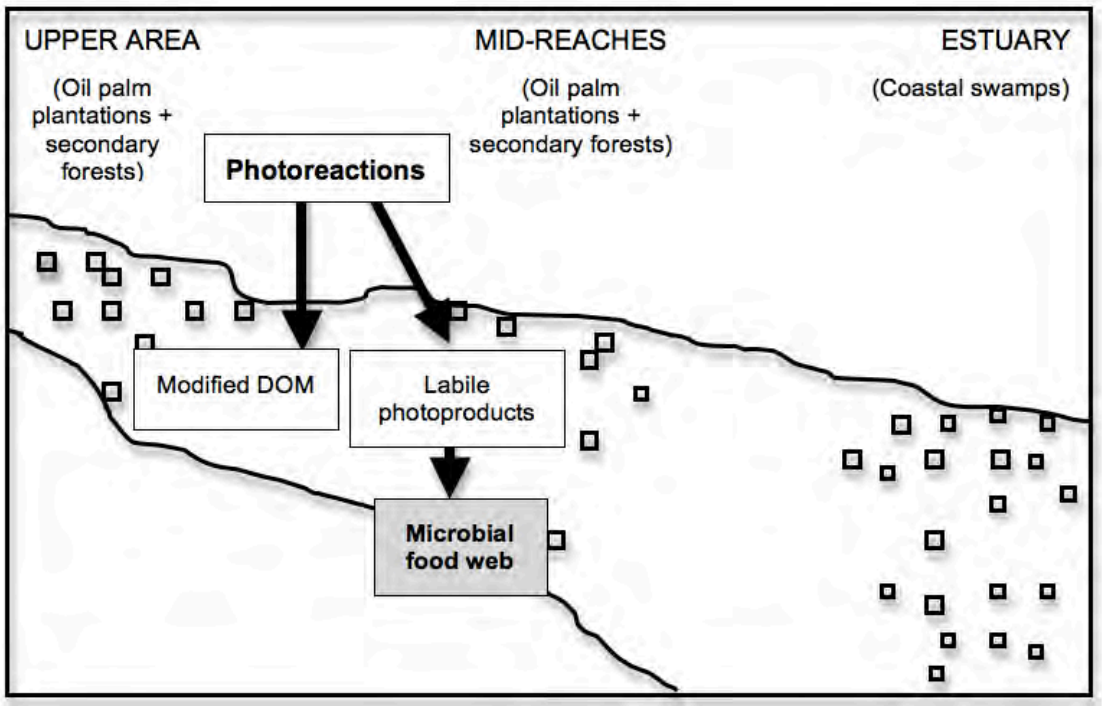


Fig. 7.1 Conceptual diagram of DOM transformations in three different types of land use (oil palm plantations, secondary forests, coastal swamps) in a tropical river catchment.

In the upper reaches (Batu Putih), the land use was pre-dominantly oil palm plantations (~79%) and secondary forests (~10%), in an area that is ~82 km from the coast (Department of Environment Malaysia, 2009). Further downstream, in the mid-reaches of the Kinabatangan (Sukau), the main type of land use was again oil palm plantations (~42%), but also protected and state forests (49%) (Department of Environment Malaysia, 2009). It was hypothesised that oil palm plantations would contribute the majority of the DOM (with respect to the different land use types), and thus, that this land use would constitute the main source of DOM in the Lower Kinabatangan River catchment.

Samples from the preliminary study (Chapter 4), which were collected from areas of the catchment where the land use was predominantly oil palm plantations, showed evidence of significant microbial activities and fluorescence terrestrial-origin characteristics. Other optical parameters, such as UV absorbance at 275 and 340nm and the spectral slope coefficient at 275-295 nm, also indicated that DOM in surface water samples from the upper area (Batu Putih) were fresher (site mean peak A intensity ranged from 499 to 898 units; site mean peak C from 256 to 671 units), compared to samples collected from coastal swamps. These trends were confirmed by PARAFAC modelling where peak M was found to predominate, thus, implying that DOM from the oil palm plantations dominated area was microbial and terrestrial in origin (Fellman et al., 2010). Loss of fluorescence in the peak C intensity region (Fig. 4.5) suggests that DOM in samples collected from the main stem of the Kinabatangan River were degraded compared to those in samples collected from the tributary streams.

DOM degradation, indicated by fluorescence indices peak T/peak C and peak M/peak C from peak picking and PARAFAC analyses respectively, showed high microbial activity in samples from the oil palm plantations (Chapter 5). It has been estimated that every tonne of crude palm oil can produce 2.5 tonnes of palm oil mill effluent (POME) with 10,000 to 25, 000 mg/l BOD (WWF Malaysia, 2000). Untreated POME may severely affect the aquatic system if discharged directly (Abdul Rani, 1995). Palm oil mills also have been identified to become the main pollution load into the rivers in Malaysia (Wu et al., 2009). A total of ~20 palm oil mills and ~292 licensed oil palm plantations are located in the Lower Kinabatangan River catchment (Department of Environment Malaysia, 2009; Hai et al., 2001; WWF Malaysia, 2000). A water quality sampling exercise carried out in early 1999 showed that a number of palm oil mills in this area have failed to conform with the regulatory requirements for effluents discharge into the streams/river (WWF Malaysia, 2000).

The subsequent results presented in Chapters 5 and 6, however, indicate a contradiction whereby DOM abundance was found to be greatest in waters sampled from the coastal swamps (demonstrated by fluorescence indices peak A/peak C from both the peak picking and PARAFAC data sets). DOM abundance was second highest in waters sampled from areas of oil palm plantation, but lower in waters collected in areas of secondary forest. Significantly, the discriminant analysis demonstrated that the fluorescence ratio of peak C to UV absorbance at 340 nm did not correlate with peak C emission (Table 5.3) which could be indicative of DOM hydrophilicity in water samples from the oil palm

plantations. This provides a possible basis for identifying the relative contribution of oil palm to the total carbon budget in tropical catchments.

DOM degradation processes in tropical regions are enhanced by the high temperatures and abundant sunlight received in this area. Photoreactions, in combination with high temperature, modify DOM and produce labile photoproducts which are then taken up by the microbes. The dominance of fluorescence ratio peak A to peak C in the coastal swamps could indicate that the coastal swamps, as normally characterised by acid waters, low dissolved oxygen and leaves resistant to degradation are high in tannins and lignin, thus, restrain the litter decomposition. Furthermore, litter from secondary forests in a Malaysian peat swamp as indicated by Yule and Gomez (2008) rapidly broke down, compared to leaves of peat-swamp trees (Wantzen et al., 2008).

These interpretations are supported by a number of studies in the literature as presented in the Chapter 2. For example, DOM concentration and fluxes have been found to be affected more by climate and land use changes in comparison to internal properties and aquatic ecosystems processes (Mulholland, 2003). Identification of peak M is significant as interactions between the DOM and microbial community are intense in both directions (Findlay and Sinsabaugh, 2003). DOM characteristics influence microbial metabolism and composition, and consequently affect DOM production, characteristics and fate. Peak M initially has been identified as marine in origin (Coble, 1996; Parlanti et al., 2000) and Stedmon et al. (2003) later suggested it was observed in ‘terrestrially dominated end-member samples’ (Fellman et al., 2010), and it

predominates in all the PARAFAC components (as summarised in Chapters 4, 5 and 6). Microbial processes in tropical rivers are recognised as more important in this region compared to the temperate zone (Wantzen et al., 2008), which mainly comprise shallow rivers, and thus, shredding invertebrates play an important role in the DOM decomposition processes (Boulton et al., 2008). Furthermore, the absence of *Ephemeroptera*, *Plecoptera* and *Trichoptera* (EPT) groups of aquatic macroinvertebrates in study area (Harun, 2006) also indicate that the DOM dynamics is very highly dependent upon photoreactions and microbial processes.

DOM transformation was also found to vary significantly seasonally. Chapters 5 and 6 demonstrated that post-flood DOM in the study area was rich in terrestrial derived substances, which were most probably of low molecular weight (as found in other studies in tropical and sub-tropical regions: Spencer et al. 2010; Yamashita et al., 2010b). The DOM of water samples collected in the inter-monsoonal period exhibited a similar pattern to those from the wet season. Results from the preliminary survey (Chapter 4), undertaken during the summer, were comparable with the DOM quality of samples from areas of oil palm plantations during the wet season (Chapter 5). However, presuming that peak M has a uniquely microbial source, microbial activity and/or photo-degradation processes is likely to have been greater during this period, as peak M pre-dominated in the water column during the wet season.

The results presented in this study demonstrate that anthropogenic disturbances to the aquatic system can regulate DOM biochemical cycling. Previous studies have showed that the highest rate of production normally occurs

during the regular inundation events (Davies et al., 2008). Frequent flooding events in the Lower Kinabatangan River catchment also more likely to modify the ecosystem by disrupting the DOM degradation processes (Wantzen et al., 2008). In tandem, annual pulsing events have also been identified as increasing riverine sediment deposition, enhanced nutrient inputs and increased primary and secondary production (Day et al., 2007; Junk et al., 1989).

7.2 CHARACTERISING THE DOM FLUXES OF THE KINABATANGAN MAIN RIVER

Fluvial systems integrate both hydrological and biogeochemical cycles, and large conceptual frameworks for rivers such as River Continuum Concept (RCC), the Flood Pulse Concept (FPC) and the Nutrient Spiralling concept were identified in Chapter 2 as providing further insight into carbon transport. Both the RCC and FPC have been challenged by the Riverine Productivity Model (RPM), which considers that autochthonous production in the river itself provides a large amount of organic carbon, and that consequently the upper area of the catchment (the headwaters) and the floodplain downstream contribute smaller amounts (Thorp and Delong, 1994). The data collected in this study provide the opportunity to consider the degree to which these concepts can be applied in a degraded tropical catchment.

Fig. 7.2 presents a conceptual diagram of DOM fluxes in the Lower Kinabatangan River catchment, by taking the DOM variations with depth into

consideration. At the estuary, which is dominated by coastal swamps (*Nypa fruticans*), the measuring stations are located ~20 km from the coast. Although it was suggested in Chapter 6 that the DOM downstream had been degraded and transformed, the presence of coastal swamps could possibly restrain the decomposition of riverine DOM, as reflected by the dominance of fluorescence index peak A/peak C. The loss of fluorescence peak C intensity to indicate DOM degradation from the main stem of the Kinabatangan River is showed in Fig. 7.3. Longer residence time, coupled with abundant of sunlight and microbial activities could lead to riverine DOM degradation which became less fluorescent. In combination with hydrological factors such as the tidal effect this has caused the DOM transported (re-export) back to the estuary area.

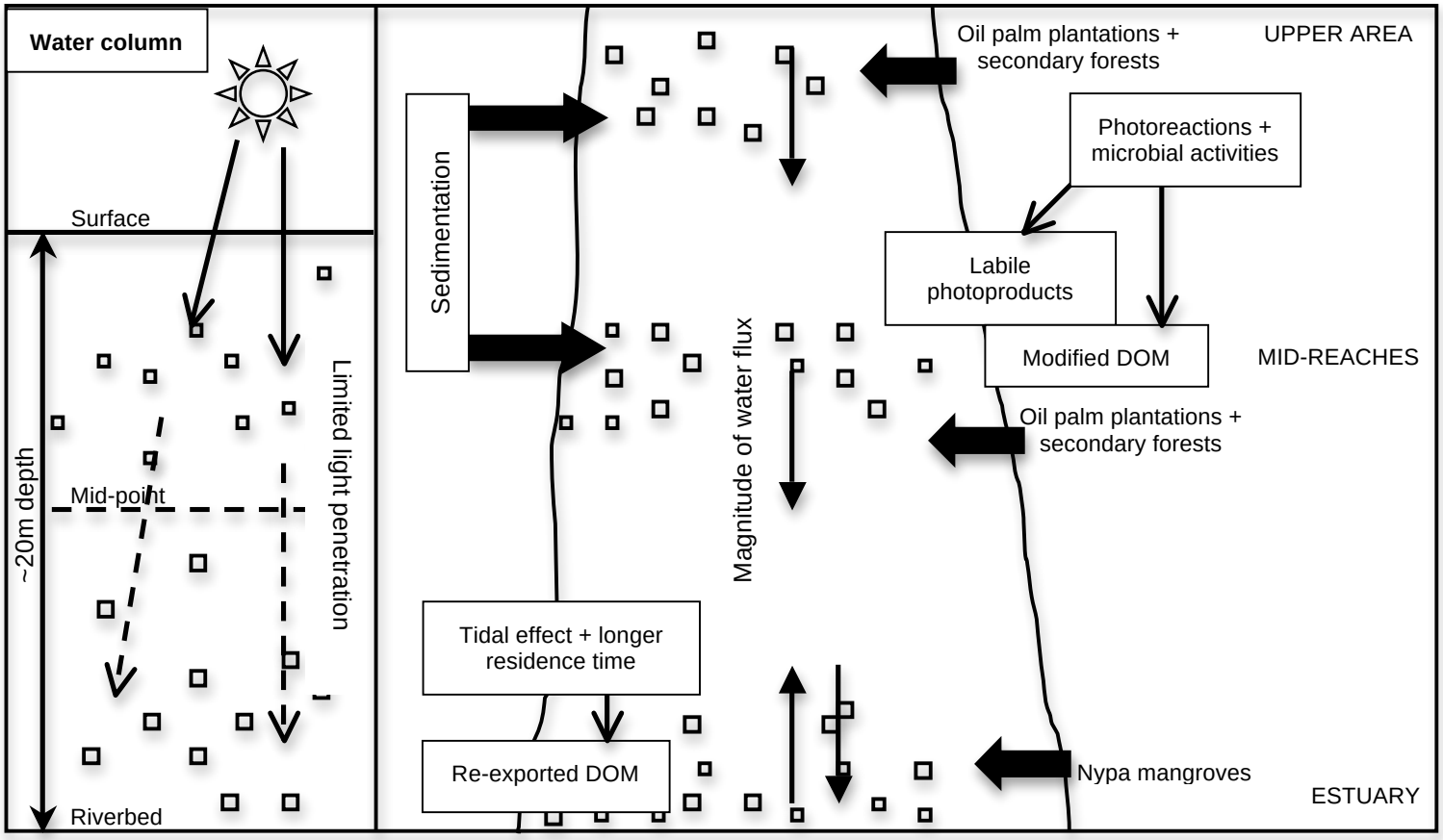


Fig. 7.2 Conceptual figure of the DOM dynamics in the Lower Kinabatangan River catchment.

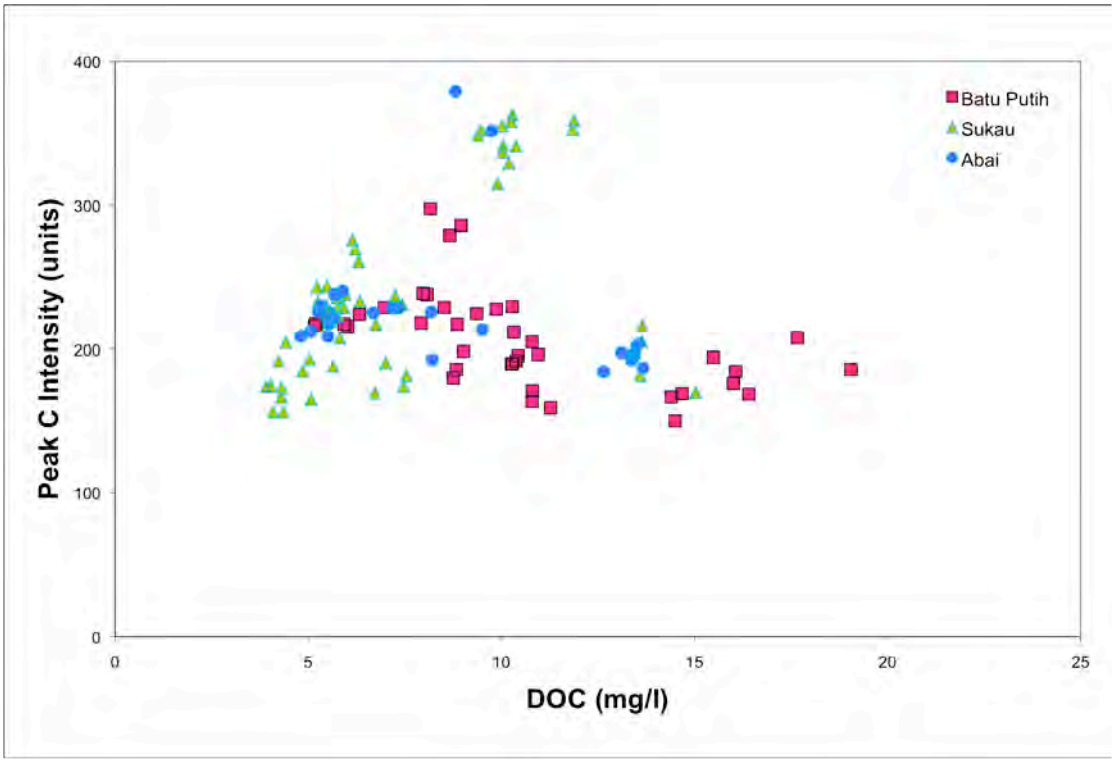


Fig. 7.3 DOC against fluorescence peak C intensity for main stem samples.

It was initially hypothesised in this study that the Lower Kinabatangan River catchment would follow the RCC, the FPC and the nutrient spiralling concepts. Some elements of these concepts were found to be relevant and helped to explain DOM transport in the study area. For example, the results presented in Chapters 4, 5 and 6 indicated DOM degradation from the upper reaches downstream, particularly during the wet season when river water levels were highest; thus, both RCC and FPC are relevant in this context. The nutrient spiralling concept, which supports the RCC by translating the in-stream dynamics in particular to retain and transform OM, has also been supported in this study: Chapter 6 demonstrated that the depth of the river is very important and should be taken into account in future studies.

The results presented in both Chapters 5 and 6 showed that quantities of degraded DOM in coastal swamps were higher compared to the other land use types (oil palm plantations and secondary forests). This suggests that the coastal swamps produced fresh DOM, and the main DOM inputs were not limited to the catchment headwaters. Consequently, the relative loss of fluorescence peak C relative to absorbance is indeed indicative of changes in DOM characteristics with transport from the upper reaches of the river towards the estuary. DOM sources in this area were also not limited to autochthonous sources, and could be mainly derived from allochthonous and specifically anthropogenic sources. Thus, the FPC, which considers that DOM inputs predominantly occur in the upper part of catchment, does not fully apply in this area.

This is supported by several other studies. For example, Greathouse and Pringle (2006) have identified uncertainties in applications of the RCC to tropical rivers, due to their unique characteristics. In the tropical regions, RCC applications by using longitudinal patterns could be curtailed, as in other regions which are dominated by small streams that flowed directly into the sea. Furthermore, tropical river systems have been found generally to have poor retention of organic matter due to unpredictable and frequent flash floods (Greathouse and Pringle, 2006). Thus, these three concepts were found to be not fully applicable in this study area, which is known to experienced annual floods particularly during the northeast monsoon (between October and March).

In order to structure a DOM fluxes model in the Lower Kinabatangan River catchment, the study took a careful look and consideration at the prominent

Mississippi Delta case study. Restoration works post-Katrina and Rita hurricanes showed that this area had been significantly altered where new delta had been formed (Day et al., 2007; Twilley and Rivera-Monroy, 2009). This resulted in the inundation of land, which caused sediment accumulation at the river mouth. Consequently, as the delta advanced, sand was vertically shifted and beach ridges were created, showing evidence of significant tidal effects, which regulated the riverine deposits by exporting the sediments back to the river. By applying information from the Mississippi Delta restoration works, DOM dynamics in the Lower Kinabatangan river catchment may also possibly be controlled by tidal effects, thus, the DOM was transported back into the river.

This study is one of the first to have looked at the DOM trends with depth, and the results provide invaluable baseline data to characterise DOM transformations. Due to the depth of the Lower Kinabatangan River which is relatively deeper, peak M discoveries in this study are very significant in providing a baseline hydrological study particularly for tropical rivers with equivalent depth. Whereas shallow rivers provide a suitable habitat for macroinvertebrates, which therefore play a significant role in the biogeochemical cycle; they are relatively absent in the study area. Therefore, the DOM decomposition of the Lower Kinabatangan River catchment is thought to be almost fully dependant on the microbial activities and/or photochemical processes.

In terms of DOM at different depth levels, there is a positive relationship between DOC in the main stem of the river with runoff. The latter is characterized by extremely high suspended sediment concentrations at the riverbed, compared

to the surface and mid-point of the depth profile. Due to active and on-going land development in Kinabatangan in particular in the upper areas, runoff is speculated to become the main control on organic matter export (sedimentation), as well as hydrological processes.

7.3 SIGNIFICANCE OF FINDINGS

Although various ecological and socio-economic researches have been undertaken in this region of Sabah, mainly in Sukau (reviewed by Harun and Mohamed, 2008), the region still lacks hydrological and biogeochemical data. This is the **first study seeking to investigate DOM dynamics in one of the most poorly understood tropical regions globally**. The significance of this study lies in: i. DOM characterisation in a hitherto poorly studied environment; ii. developing our understanding of DOM dynamics; iii. identifying the limitations of current conceptual models when applied to smaller or degraded catchments. In tandem, similar issue also exists whether the models are transferable to tropical pristine areas.

There have been a number of studies in tropical regions, for example, in the Amazon which showed the dominance of heterotrophic respiration over photosynthesis particularly in turbid waters and canopy-covered streams with variations over wet and dry seasons (Mayorga and Aufdenkampe, 2002; Saunders et al., 2006). However, these studies were limited and have not taken new technologies approach into account. Nevertheless, it has been showed that river metabolism in the tropical regions generally is greatly influenced by

photochemical reactions and the activity of microorganisms, although restricted by light penetration in highly turbid waters (Mayorga and Aufdenkampe, 2002).

It is also important to consider the extent to which the conclusions of studies specifically conducted in temperate environments can be applied to tropical regions. For example, Sobczak and Findlay (2002) found that DOC concentrations in 82 streams in New York state, USA declined, due to a combination of decreased activity of heterotrophic bacteria and low levels of dissolved oxygen. The predominance of peak M in this study evidently supersedes earlier conceptions that DOM generally is refractory, and related to retention by the hydrological and microbial dynamics (Findlay and Sinsabaugh, 2003). Furthermore, Pollard and Ducklow (2011) indicated that the water column of subtropical Bremer River in Australia was turned over every two days.

As much as studies on the lateral variability of DOM are important, it is equally important to look at vertical variations in DOM. The results of this study suggested that DOM in the water column (at depths of ~20m below the surface) were dominated by peak C at the riverbed, compared to waters sampled from near the surface and at mid-points (i.e. intermediate points of the water column) of the Kinabatangan River. Consequently, extremely high suspended sediment concentrations at points close to the riverbed, specifically during the wet season, suggest a significant contribution from on-going land development in the Kinabatangan catchment. Interestingly, the results also indicate that DOM decomposition in the main stem of the Lower Kinabatangan predominantly occurred near the surface, followed by mid-point and finally at the riverbed.

Large tropical rivers are often characterised by variable water level, high concentrations of suspended sediments loads and turbidity, high current velocities and mobile bed materials (Davies et al., 2008). Positive relationships between annual runoff and watershed export of DOC have been identified by various studies as demonstrated in Fig. 7.4. Suspended sediment concentrations in the lowland Amazon were consistently high throughout the year and depended on the precipitation events. Thus they may indicate the significant effect of local climate on OM fluxes in the Amazon River (Townsend-Small et al., 2008). A study on pollution prevention found low level of phytoplankton density (16.96 to 169.54 cells/ml), which could be attributed to high suspended sediment concentrations (108 to 1,630 mg/l). Suspended sediment also has been identified as one of the main pollutants of the river with an approximate load of 6 million tonnes per year (Department of Environment Malaysia, 2009).

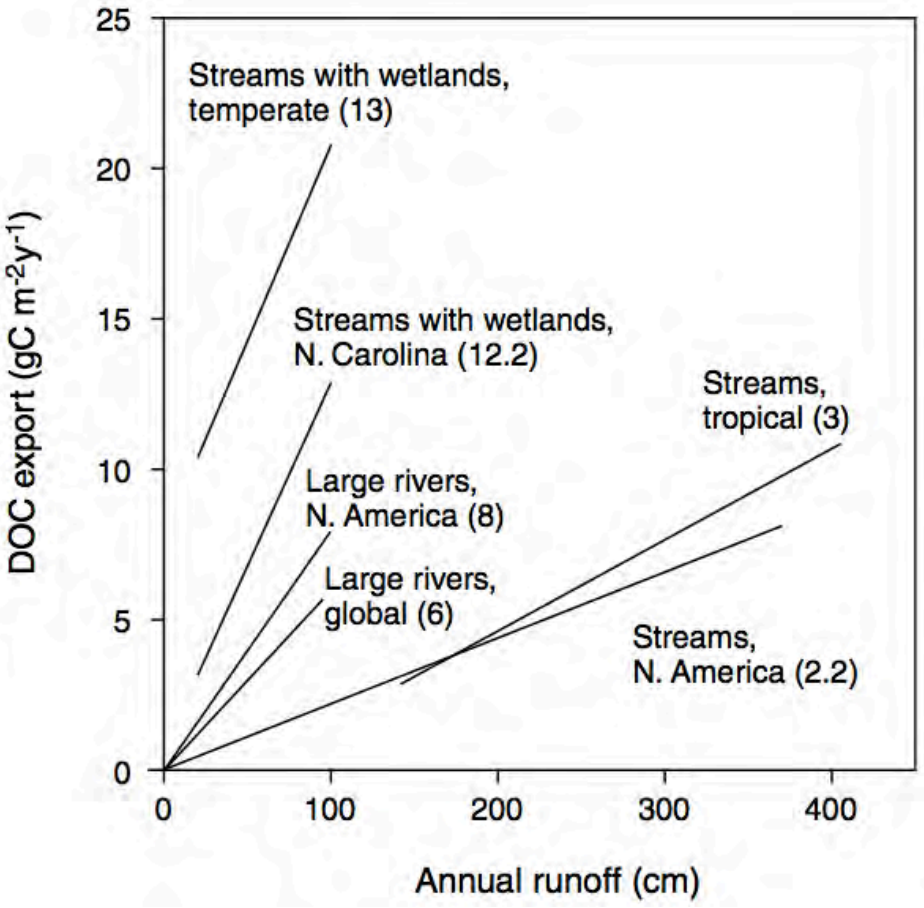


Fig. 7.4 Positive correlations between annual runoff and watershed export of DOC in streams as reported in the literature. Slopes of each line is corresponding to the mean annual DOC concentration for that particular group (in parentheses) (Mulholland, 2003).

7.4 RESEARCH LIMITATIONS

Despite the significance of the results outlined above, there several limitations in the study, which hindered the conduct of research. Logistics were a major limitation, as some of the stations were not accessible by road e.g. in Abai area,

thus, prolonging the period before which samples could be analysed in the UK. Unfortunately also the international courier company lost one entire set of samples, collected in March 2010. This presented a number of problems as it included test samples for data comparison (preliminary survey in 2008). Therefore, in-situ fluorescence would improve the time consuming of sample processes and analyses, which has been successfully carried out in West Florida (Del Castillo et al., 2001). Moreover the lack of temperature, rainfall and river discharge data in each sampling station has constrained the research areas. Permanent installations of meteorological instruments in the study area would certainly improve the rigour of research in future with the ability to monitor the local precipitation and temperature patterns.

7.5 FUTURE RESEARCH QUESTIONS

Future plans particularly in the upper part of this catchment indicate that oil palm plantations conversion and rehabilitation works are going to continue to strengthen the connectivity in the Lower Kinabatangan Wildlife Sanctuary (Department of Environment Malaysia, 2009). However, the major challenges are that the oil palm industry continues to demand land resources in the area. Nevertheless, wider overview on the DOM fluxes and dynamics are important to gain further understanding. Future research potentials should concentrate on:

1. Characterisation of DOM from the upper reaches which consisting of primary forests / pristine areas and make comparison with data from this study.

2. Determination of the flood magnitude and its correlation with the DOM dynamics.
3. Application of the conceptual models in other degraded tropical catchment.

The study presented in this thesis has showed significant results to determine and model the DOM sources as well as fluxes in the Lower Kinabatangan River catchment. However, local sample analysis would certainly enhance the research with more precise real-time monitoring. Furthermore, rapid sample analysis after collection is significant, since OM in the tropical regions may be degraded more quickly.

8. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Scope of Chapter

This concluding chapter summaries the principal results of the research that has been described in the thesis. The principal findings of the research are discussed, before reviewing the initial objectives as outlined in Chapter 1, and, then presenting recommendations for future work in this area.

8.1 PRINCIPAL FINDINGS

The research undertaken at the Lower Kinabatangan River catchment, Sabah, Malaysia, presented in this thesis provides relevant, significant and essential additional knowledge by which the complexity of DOM dynamics particularly in the tropical regions can be further understood. The combined application of fluorescence spectroscopy and PARAFAC modelling were found very useful providing valuable information on the characterisation of DOM, according to the specific objectives as described in sections 1.3 and 8.1 of the thesis.

Preliminary sampling conducted over the period from August to September 2008 in areas of the catchment where the land use was predominately oil palm plantations demonstrated that EEMs peaks A, C and T_{280} were dominant in surface water samples collected from rivers, streams and ditches in the area. Decomposition of EEMs by PARAFAC modelling indicated that the peak M

component was predominant in these samples. Significant positive correlations were found between PARAFAC components and peaks A, C and T_{280} intensities. Peak T_{280} has been shown to be characteristic of labile OM and to correlate positively with BOD a measure of biodegradable organic matter (Hudson et al., 2007). Significantly in this area, the Department of Environment Malaysia (2009) has reported that a total of 29 palm oil mills discharge effluent into the river and they also report that 9 mills out of 15 surveyed separately (i.e. >50% of those surveyed) failed to meet approved effluent discharge limits. POME produced by palm oil mills in this area has been recognised as a significant point sources and contributed BOD of 3,459 kg/day. Untreated POME could affect the aquatic system severely if discharged directly (Abdul Rani, 1995). Thus, the predominance of the peak M component and peak T_{280} intensity could reflect the dominance of microbial activities and/or photo-degradation. These baseline data also indicated continuous DOM degradation in samples collected from Batu Putih downstream, as demonstrated by the loss of fluorescence peak C intensity relative to UV absorbance at 340 nm.

The intensive sampling programme which was undertaken from October 2009 to May 2010 showed significant variations in DOM that reflected: i. seasonal trends; and, ii. differences according to the predominant type of land use. DOM was found to be dominant in the coastal swamps, followed by secondary forests and oil palm plantations. Fresh DOM was evident in waters sampled from (or in the vicinity) of oil palm plantations, while DOM in waters sampled from the coastal swamps predominantly comprised terrestrial derived DOM, as indicated by discriminant analysis whereby the fluorescence indices IC2/IC1 and IC3/IC1

(both were peak M/peak C) were found to be dominant in samples from oil palm plantations and coastal swamps. Lower peak M in waters sampled from the coastal swamps could reflect high concentrations of tannic acids. Tannic acids have been found to reduce bacterial counts (Sahoo and Dhal, 2009), and although their concentrations may vary seasonally (Kathiresan and Bingham, 2001), this could possibly decrease the microbial activities in this area. In terms of seasonal variations, DOM was significantly higher in samples collected during the wet season. This has been observed in previous studies (Coynel et al., 2005; Spencer et al., 2010), although a few studies have reported the reverse. For example, Guo et al. (2011) reported high DOC concentrations in the freshwater subtropical River Jiulong in February, May and June (dry season) compared to the wet season. DOC concentrations in mangrove wetlands along Shark River, Florida were also found to be higher during the dry season (Romigh et al., 2006).

The findings in this study, of the use of peak M to characterise DOM at different depths of the river, provide important baseline data to further understand the DOM transformations particularly for tropical rivers of equivalent depth (i.e. ~20 m). DOM concentrations were highest in waters sampled from close to the riverbed, followed by near the surface and at mid-depths. Photochemical degradation of DOM has been previously demonstrated to result in decrease in aromaticity, although it is not as significant as temperature-dependant degradation processes in surface waters (Cory et al., 2007). For rivers of corresponding depth to the Lower Kinabatangan River, limited light penetration could play a significant role in DOM degradation. A comparison of surface and deep-water samples demonstrated that biological lability of surface-water DOM

was significantly depleted as result of irradiation, while the deep-water DOM remained consistently high even after exposure to sunlight (Benner and Biddanda, 1998). This may be related to the presence of organic-rich waters at (or near) the riverbed, where DOM accumulates as suggested in a number of studies. For example, a pooled reach in the Tualatin River in Oregon was found to be an area of DOM deposition that accumulates abundant organic-rich sediments (Bonn and Rounds, 2010). It also has been demonstrated that DOC concentrations in the Green Lakes Valley, Colorado, were mainly derived from organic-rich sediments and benthic algal mats after flushing of DOC from near-surface soil layers and snowmelt runoff (McKnight et al., 2003). For freshwater rivers, particularly in the tropics that are characterised by depths of ~20 m, the availability of labile DOM in terms of different level of depths could produce comparable results.

Suspended sediments concentrations display a similar trend to DOM with the highest concentrations at the riverbed during the wet season. Large tropical river systems are known to transport the majority of the world's runoff and sediment (Hudson, 2003) and consequently, Mulholland (2003) suggested that there will be a positive correlation between annual runoff and DOC export, and evidently river discharge also plays important role in DOC export (Restrepo and Kjerfve, 2000). For example, strong positive correlations between water discharge and sediment load were observed in the Magdalena River, in the Caribbean particularly during the El Niño and La Niña cycle (Restrepo and Kjerfve, 2000).

The patterns of water movement through the Lower Kinabatangan River catchment suggest that tidal effects are a significant factor in DOM transformations and processes within the catchment. It was initially hypothesised that the study catchment would conform to existing conceptual models such as RCC, FPC and nutrient spiralling concept, although the applicability of RCC in tropical forested rivers is uncertain (Greathouse and Pringle, 2006; Winterbourn et al., 1981) and the concept is limited in the degree to which it takes into account the spatial variability in processes related to drainage networks (Lohse et al., 2009). A study of a tropical stream in Puerto Rico showed that allochthonous DOM from macroinvertebrate grazing followed an opposite trend to that anticipated by the RCC (Greathouse and Pringle, 2006). Other issues related to existing conceptual models showed that both the RCC and nutrient spiralling concept initially disregarded the floodplain dynamics, such as temporal variations in hydrologic drivers, and concentrated on baseflow conditions (Bouwman et al., 2013), although subsequent revisions to the concept have resolved this to some degree (Tockner et al., 2000). The RCC and FPC also over-emphasised the contribution of refractory DOM from headwaters (Roach, 2013; Thorp and Delong, 1994). Results from the current study showed that DOM in coastal swamps were abundant in comparison to oil palm plantations and secondary forests; suggesting that DOM inputs were not restricted from the catchment headwaters. Consequently, the relative loss of fluorescence peak C intensity relative to absorbance could be an indication of DOM characteristics as it is modified by transported through the catchment. The RCC, FPC and nutrient spiralling concept were found not to be fully applicable in the study area in

Sabah, which is: i. experiencing progressive development (with ongoing land clearance for oil palm plantations); ii. receiving abundant sunlight throughout the year; and iii. experiences annual floods during the northeast monsoon (Boonratana, 2000). A comparison of the results presented herewith those of a case study from the Mississippi Delta restoration works (post-Katrina and Rita hurricanes) suggests that the Lower Kinabatangan River catchment could be controlled by tidal effects as degraded DOM is transported from the upper reaches towards the estuary, and then re-exported back to the river; as indicated by salinity, which was consistently high in both wet and dry seasons.

8.2 CONCLUSIONS

Rivers in the tropical regions are well known to play a significant role in the global carbon cycle. However, knowledge of carbon export rates from catchments in this area is still inadequately understood, due in part, to the complex ecosystem, but also reflecting the significance of DOM pathways, fate and transformation. DOM dynamics are complex and this is crucially important particularly in tropical wetlands such as those in the Lower Kinabatangan River catchment studied here. These wetlands experience annual flooding and are characterised by intense precipitation, rapid weathering of inorganic and organic substances and rapid flowing of large volumes of water and sediment (cf. Wohl et al., 2012). The situation is further complicated by recent anthropogenic changes, including continuous and active land development throughout the catchment which has many environmental implications.

Fluorescence excitation-emission spectroscopy and PARAFAC modeling have been found to be very useful in characterising DOM in a number of recent studies. In particular, advances in spectroscopy allow the rapid assessment of bulk OM properties. This thesis presents, for the first time, the results of work that utilised fluorescence spectroscopy to characterise the DOM of the Lower Kinabatangan River catchment. This study had four initial objectives and the conclusions are as follows:

Objective 1: To quantify DOM in areas of land where the land use is predominately oil palm plantations using optical parameters as a tool.

DOM quantities in waters sampled from areas of the catchment where the land use is mainly oil palm plantations have been successfully determined using fluorescence spectroscopy and ultraviolet-visible absorbance spectroscopy (UV-vis). Both peak picking and PARAFAC techniques have been applied and revealed the dominance of terrestrial-origin substances which could be affected by microbial and/or photo-degradation processes. Loss of fluorescence peak C relative to UV absorbance showed progressive DOM degradation from lower order tributaries towards the estuary.

Objective 2: To characterise and interpret the DOM quantity and quality in waters draining three different land use types (oil palm plantations, secondary forests and coastal swamps) and examine the effects of seasonal variability (wet and dry seasons).

Significant DOM transformation was exhibited in waters sampled throughout the catchment: from the upper headwater reaches to the coastal swamps near the Sulu Sea. With respect to land use variation, the results also showed that DOM in the coastal swamps was dominant, although there was a lower peak M, which could reflect high concentrations of tannic acids. The latter are known to be produced in high quantities in swamp and coastal areas although concentrations may vary seasonally (Kathiresan and Bingham, 2001). Seasonally, DOM was significantly higher in samples which were collected in the wet season. At this time, Peak M was found to be dominant, as indicated by both peak picking and PARAFAC techniques.

Objective 3: To characterise and interpret both DOM quantity and quality of the Kinabatangan main river according to depth and seasonal variability (wet and dry seasons).

With respect to waters sampled from the main stem of the river; DOM dynamics showed a clear trend with depth. Samples collected from near the riverbed had higher DOM concentrations, with a decrease in waters sampled from near the surface and at mid-depths. There was also a clear difference in DOM between the wet and dry seasons: with higher DOM concentrations in waters collected in the wet season. Both peak picking and PARAFAC techniques

confirmed the dominance of terrestrial derived peaks, which could be derived from terrestrial and affected by microbial and/or photo-degradation processes.

Objective 4: To infer differences in the pattern of water movement through the catchment using fluorescence as a tool, from three different types of land use (oil palm plantations, secondary forests and coastal swamps) and two types of seasonal variability (wet and dry).

Information from the Mississippi Delta restoration works post-Katrina and Rita hurricanes has demonstrated the possibility of applying this technique in the Lower Kinabatangan River catchment. Lower reaches of the Kinabatangan are heavily influenced by tidal effects as demonstrated by its salinity, which is continuously present even during the wet season, when water levels were high. Degraded DOM was transported from the upper reaches of the catchment towards the estuary and then transported (re-exported) back into the river.

8.3 RECOMMENDATIONS FOR FUTURE WORK

Realistically, the research presented in this thesis represents only the first step in understanding DOM dynamics in catchments such as the Kinabatangan in N. Borneo. Chapter 7 identified a number of outstanding research questions which represent a logical development of the work described here. In particular:

1. It is important to determine and monitor the DOM fluxes within the catchment, to quantify their spatial and temporal variability and determine

the importance to the global carbon budget of carbon fluxes from partially degraded tropical catchments, such as the Kinabatangan.

2. Develop a local sampling programme, sub-sampling within the catchment, as to establish a clearer link between land use and DOM (recognising that there is unlikely to be a clear association between oil palm plantations and DOM characteristics).
3. Examine and quantify the age of DOM, for example, using carbon isotopes.
4. Develop a more rigorous method/protocols to analyse samples more quickly in areas where access to power / laboratory facilities is problematic.
5. Identify the most meaningful parameters (i.e. from EEMs) to provide more concise information on the DOM characteristics.
6. Investigate DOM characteristics in areas of pristine rainforest.
7. Examine in more detail, the transferability of the results of the Kinabatangan to other degraded/pristine catchments (in SE Asia).

APPENDIX A

Fluorescence maxima of three components identified by PARAFAC models (from samples presented in Chapter 4) before and after removal of excitations <280 nm:

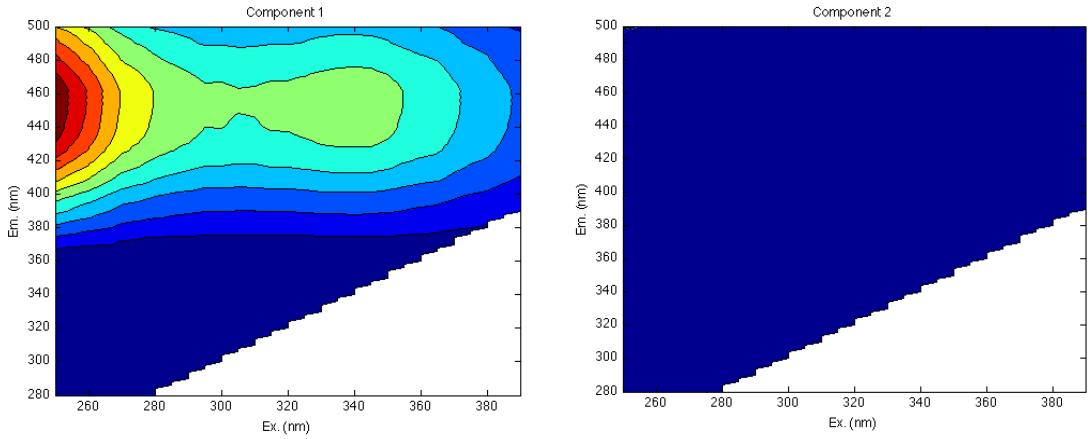
Before removal:

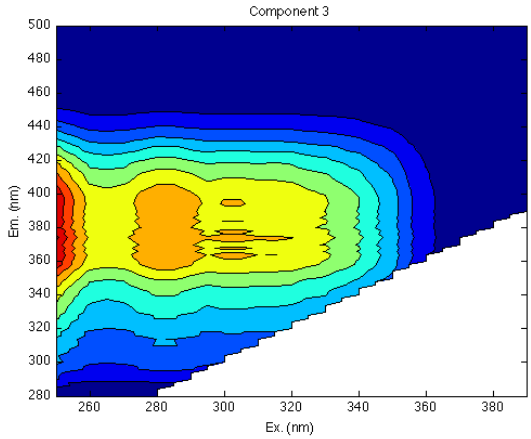
	C1	C2	C3
Excitation	250	250	250
Emission	454	500	374

After removal:	**C1**	**C2**	**C3**
Excitation	290 (345)	315	290
Emission	458	398	360

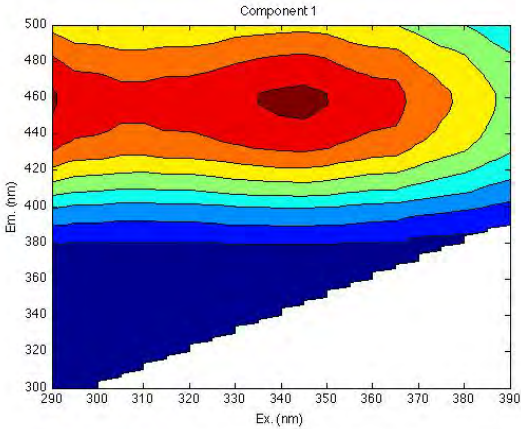
Examples of PARAFAC components before and after removal of excitations <280 nm:

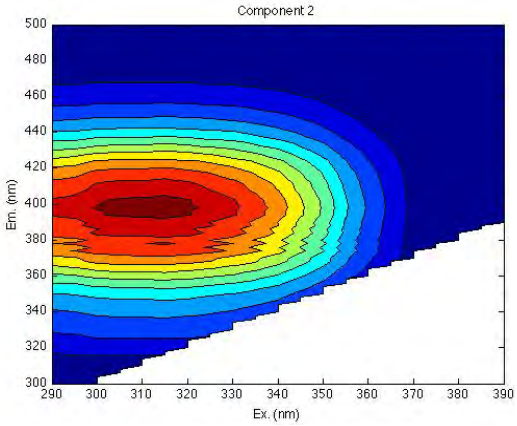
Before removal:

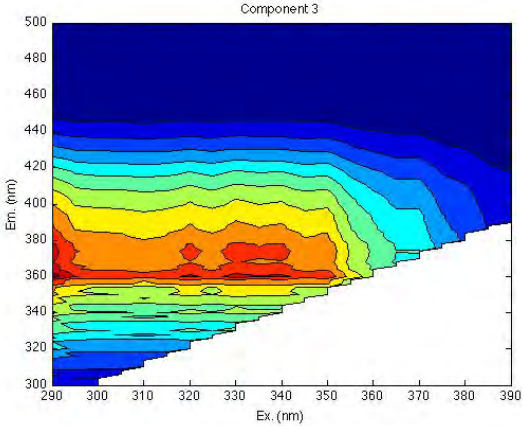




After removal:







APPENDIX B

Isotope δD and δO results of the Lower Kinabatangan River catchment for sampling stations dominated by oil palm plantations.

Station ID	#1	#2	δD	STDEV		δO	expected O	residual O	expected D	residual D	total residuals
BP1	-46.89	-46.25	-46.57	0.45	MAL001	-6.72	-7.686282027	0.96	-39.48442227	7.09	5.010944369
	-46.12	-46.66	-46.39	0.38	MAL002	-6.66	-7.661935743	1.00	-38.99882951	7.39	5.227602713
	-46.43	-46.19	-46.31	0.17	MAL003	-6.74	-7.650824098	0.91	-39.59732273	6.71	4.746580315
	-45.56	-46.85	-46.20	0.92	MAL004	-6.80	-7.636463131	0.83	-40.07362489	6.13	4.335048908
	-46.52	-46.71	-46.61	0.14	MAL005	-6.71	-7.692103712	0.98	-39.38356237	7.23	5.112559948
	-46.35	-46.48	-46.42	0.09	MAL006	-6.73	-7.665473657	0.93	-39.55246414	6.87	4.854539879
	-47.36	-47.67	-47.52	0.22	MAL007	-7.00	-7.814774202	0.82	-41.48436026	6.03	4.265494389
BP2	-49.30	-48.63	-48.96	0.47	MAL008	-7.24	-8.011089949	0.77	-43.31745796	5.64	3.99098841
	-49.57	-49.00	-49.28	0.41	MAL009	-7.39	-8.054842619	0.67	-44.37825106	4.91	3.468601704
	-49.19	-49.15	-49.17	0.03	MAL010	-7.39	-8.039293133	0.65	-44.41479013	4.75	3.361841426
	-49.00	-49.70	-49.35	0.50	MAL011	-7.27	-8.063388891	0.79	-43.52563599	5.82	4.115962812
	-48.78	-49.35	-49.06	0.40	MAL012	-7.19	-8.024602125	0.83	-42.94855662	6.11	4.322159369
	-49.50	-49.82	-49.66	0.23	MAL013	-7.43	-8.105823753	0.68	-44.67719719	4.98	3.522535765
BP3	-43.96	-43.82	-43.89	0.10	MAL015	-6.65	-7.321700334	0.67	-38.97136026	4.92	3.476354055
BP4	-43.96	-43.82	-43.89	0.10	MAL015	-6.65	-7.321700334	0.67	-38.97136026	4.92	3.476354055
	-47.32	-47.71	-47.52	0.28	MAL016	-7.38	-7.814740566	0.43	-44.35256806	3.16	2.237209606
	-44.12	-43.51	-43.82	0.43	MAL017	-6.55	-7.31210708	0.77	-38.17753229	5.64	3.987744061
	-50.43	-50.61	-50.52	0.12	MAL018	-7.81	-8.223151989	0.41	-47.47870031	3.04	2.152199092
	-50.64	-50.06	-50.35	0.40	MAL019	-7.82	-8.199859782	0.38	-47.54907952	2.80	1.981215344
	-25.10	-25.76	-25.43	0.46	MAL014	-3.98	-4.813982936	0.83	-19.28566889	6.15	4.345303107
BP5	-44.20	-43.50	-43.85	0.50	MAL024	-6.28	-7.316423019	1.04	-36.1850804	7.66	5.419068044
BP6	-39.22	-40.17	-39.69	0.67	MAL021	-5.05	-6.75202023	1.70	-27.17488988	12.52	8.852877161
BP7	-43.55	-44.01	-43.78	0.33	MAL022	-6.65	-7.306946604	0.65	-38.96224458	4.82	3.406017559
BP8	-44.55	-44.22	-44.39	0.23	MAL023	-6.98	-7.389683839	0.41	-41.39535003	2.99	2.116154452
	-7.32	-7.97	-7.64	0.45	MAL025	-2.43	-2.397404962	-0.04	-7.905872178	-0.26	-0.184533057
	-8.09	-8.36	-8.23	0.20	MAL026	-2.64	-2.476263841	-0.16	-9.405227142	-1.18	-0.83432516
	-7.56	-8.07	-7.81	0.36	MAL045	-2.86	-2.420167878	-0.44	-11.02575967	-3.21	-2.272141465
	-36.52	-36.41	-36.47	0.07	MAL064	-6.49	-6.31320241	-0.18	-37.78735895	-1.32	-0.934919994

Station ID	#1	#2	δD	STDEV		δO	expected O	residual O	expected D	residual D	total residuals
	-60.77	-60.88	-60.82	0.08	MAL067	-9.68	-9.622575681	-0.06	-61.24407527	-0.42	-0.298338403
SK1	-48.22	-47.75	-47.98	0.33	MAL027	-7.60	-7.878362046	0.27	-45.96298638	2.02	1.429585277
	-49.64	-48.85	-49.25	0.56	MAL028	-7.98	-8.05009778	0.07	-48.70339824	0.55	0.385596775
	-50.79	-50.06	-50.42	0.51	MAL029	-7.86	-8.20969833	0.35	-47.8427231	2.58	1.824782291
	-50.17	-50.15	-50.16	0.01	MAL030	-7.98	-8.17335123	0.20	-48.71983732	1.44	1.015415211
	-49.65	-50.66	-50.15	0.71	MAL031	-7.92	-8.173151552	0.25	-48.27906399	1.88	1.326046854
	-50.84	-50.42	-50.63	0.29	MAL032	-8.02	-8.237884204	0.21	-49.05405117	1.58	1.114938714
	-50.50	-50.40	-50.45	0.07	MAL033	-8.00	-8.2136812	0.22	-48.85469052	1.60	1.129948002
	-50.77	-50.29	-50.53	0.34	MAL034	-8.03	-8.223937103	0.19	-49.12869644	1.40	0.989572757
	-50.23	-50.59	-50.41	0.26	MAL035	-8.05	-8.20760988	0.15	-49.27356528	1.13	0.802164956
SK2	-51.01	-50.96	-50.99	0.04	MAL042	-7.98	-8.286422265	0.30	-48.75694556	2.23	1.577626588
	-51.30	-51.27	-51.28	0.02	MAL043	-7.97	-8.326633991	0.36	-48.64201562	2.64	1.868165661
	-50.57	-51.29	-50.93	0.51	MAL044	-7.85	-8.278281707	0.43	-47.76818992	3.16	2.234410154
	-51.21	-50.73	-50.97	0.34	MAL036	-7.85	-8.283684381	0.43	-47.79475632	3.17	2.243741952
SK3	-50.13	-49.31	-49.72	0.58	MAL038	-7.89	-8.114041122	0.22	-48.07675849	1.64	1.161471266
	-50.99	-50.93	-50.96	0.04	MAL039	-7.92	-8.282329137	0.36	-48.32684611	2.63	1.860448225
	-52.18	-53.18	-52.68	0.71	MAL091	-7.90	-8.51676154	0.62	-48.13787776	4.55	3.214113983
	-50.03	-50.69	-50.36	0.47	MAL040	-8.05	-8.201297002	0.15	-49.226204	1.14	0.802800282
	-50.73	-50.97	-50.85	0.17	MAL041	-7.80	-8.267631875	0.47	-47.41833152	3.43	2.426370572
	-50.61	-50.57	-50.59	0.03	MAL037	-8.05	-8.232109785	0.18	-49.23928733	1.35	0.953906671
SK4	-47.57	-48.42	-48.00	0.60	MAL068	-7.27	-7.879763304	0.61	-43.50366431	4.49	3.175864421
	-49.40	-49.24	-49.32	0.12	MAL069	-7.41	-8.05972147	0.65	-44.55031531	4.77	3.372325859
	-49.55	-49.17	-49.36	0.27	MAL070	-7.41	-8.065691036	0.66	-44.52974787	4.83	3.417936248
	-48.89	-49.64	-49.27	0.53	MAL087	-7.56	-8.052689161	0.50	-45.61840091	3.65	2.5804846
SK5	-46.56	-47.11	-46.84	0.39	MAL071	-6.98	-7.722267804	0.74	-41.40129953	5.43	3.842799652
	-46.92	-46.92	-46.92	0.00	MAL072	-7.03	-7.73348991	0.71	-41.72828118	5.19	3.66999364
	-47.43	-47.47	-47.45	0.03	MAL073	-6.94	-7.805889122	0.87	-41.07754141	6.37	4.506915769
	-47.65	-47.64	-47.64	0.01	MAL074	-7.16	-7.832160687	0.67	-42.70452447	4.94	3.493199998
	-49.51	-49.46	-49.49	0.04	MAL075	-7.42	-8.082330585	0.67	-44.59155306	4.89	3.460830276
	-49.77	-49.31	-49.54	0.33	MAL086	-7.33	-8.090120137	0.76	-43.9270754	5.62	3.97122125
SK6	-40.95	-39.46	-40.20	1.05	MAL089	-6.29	-6.821299846	0.53	-36.31696599	3.89	2.749064004
	-40.65	-40.45	-40.55	0.14	MAL090	-6.34	-6.867961982	0.53	-36.63008969	3.92	2.770495936
BT1	-37.56	-36.95	-37.25	0.43	MAL079	-5.64	-6.420358955	0.78	-31.50441197	5.75	4.06542191

Station ID	#1	#2	δD	STDEV		δO	expected O	residual O	expected D	residual D	total residuals
	-38.62	-38.69	-38.66	0.05	MAL080	-5.87	-6.610761922	0.75	-33.17033792	5.48	3.878351452
	-40.94	-40.78	-40.86	0.11	MAL081	-5.84	-6.910233441	1.07	-33.01250966	7.85	5.548478268
	-43.90	-43.99	-43.95	0.06	MAL082	-5.94	-7.329811941	1.39	-33.69792135	10.25	7.247417589
	-46.97	-48.32	-47.64	0.95	MAL083	-6.59	-7.832179657	1.24	-38.53211761	9.11	6.443607611
	-47.12	-48.80	-47.96	1.19	MAL084	-6.90	-7.875304984	0.98	-40.75374967	7.21	5.097126824
	-47.12	-48.80	-47.96	1.19	MAL084	-6.90	-7.875304984	0.98	-40.75374967	7.21	5.097126824
BT2	-42.23	-40.97	-41.60	0.89	MAL076	-6.05	-7.011145125	0.96	-34.55133426	7.05	4.985545624
	-41.33	-40.99	-41.16	0.24	MAL077	-6.05	-6.95157929	0.90	-34.50714675	6.66	4.706794765
	-41.14	-41.08	-41.11	0.04	MAL078	-6.01	-6.94489861	0.93	-34.25200022	6.86	4.852440905
	-50.29	-50.61	-50.45	0.23	MAL085	-7.54	-8.213199038	0.68	-45.47211777	4.98	3.519255894
AB1	-45.50	-45.16	-45.33	0.25	MAL046	-7.13	-7.517564956	0.39	-42.48353111	2.85	2.012227685
	-45.02	-45.63	-45.33	0.43	MAL047	-6.87	-7.517018882	0.65	-40.57391741	4.75	3.359673617
	-45.72	-45.94	-45.83	0.16	MAL048	-7.11	-7.585503412	0.48	-42.3178723	3.51	2.482934136
	-50.02	-50.72	-50.37	0.50	MAL049	-7.85	-8.202746585	0.35	-47.78601357	2.59	1.828702937
	-50.47	-50.61	-50.54	0.10	MAL050	-7.90	-8.225264445	0.32	-48.16036107	2.38	1.681190528
	-51.00	-50.93	-50.96	0.05	MAL051	-7.85	-8.282785662	0.43	-47.79913386	3.16	2.235969423
	-50.82	-50.79	-50.80	0.02	MAL052	-7.72	-8.261249468	0.54	-46.79510364	4.01	2.833839324
	-51.22	-51.03	-51.12	0.14	MAL053	-8.03	-8.304911056	0.28	-49.08998267	2.03	1.438356447
	-51.54	-52.45	-52.00	0.65	MAL054	-7.88	-8.423715305	0.55	-47.96509301	4.03	2.852053656
	-51.64	-50.98	-51.31	0.46	MAL055	-7.98	-8.330027973	0.35	-48.76057665	2.55	1.801994308
	-51.92	-52.21	-52.07	0.21	MAL057	-8.06	-8.433045262	0.38	-49.28991873	2.78	1.963824865
	-50.03	-51.40	-50.71	0.97	MAL065	-7.82	-8.249108138	0.43	-47.57672929	3.14	2.217965238
AB2	-50.21	-49.99	-50.10	0.15	MAL058	-7.82	-8.166004067	0.35	-47.53734821	2.56	1.813316748
	-50.92	-50.42	-50.67	0.36	MAL059	-7.72	-8.242907712	0.52	-46.84162832	3.83	2.705486535
	-50.92	-50.62	-50.77	0.21	MAL060	-7.70	-8.256167528	0.56	-46.67652212	4.09	2.891240605
	-51.31	-50.20	-50.75	0.79	MAL061	-7.89	-8.254669905	0.37	-48.05998503	2.69	1.905199965
	-50.85	-51.30	-51.08	0.32	MAL062	-7.76	-8.298303492	0.54	-47.08896596	3.99	2.818887908
	-50.80	-50.94	-50.87	0.10	MAL063	-7.77	-8.269821301	0.50	-47.17464771	3.69	2.61007373
	-51.04	-50.13	-50.58	0.65	MAL066	-7.71	-8.23153782	0.52	-46.77482679	3.81	2.693550061

Regression for Rainfall

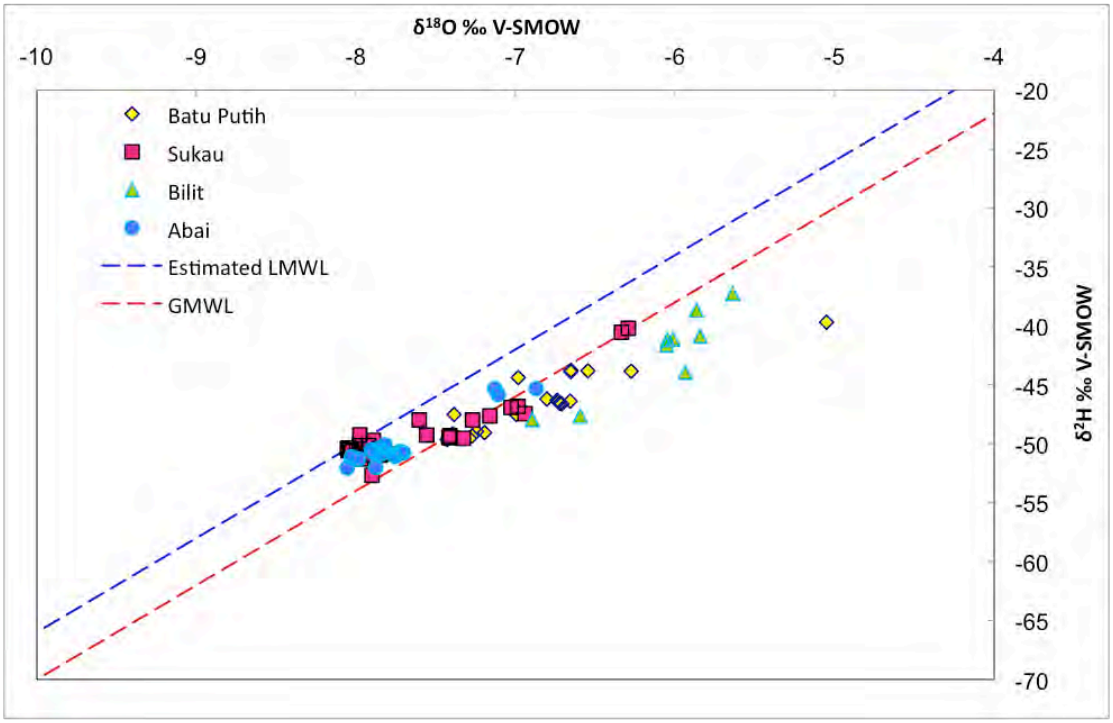
Sample	#1	#2	δD	STDEV	δO
DGFC Rainfall	-25.10	-25.76	-25.43	0.46	-3.98
Rainfall1 27/8/08	-7.32	-7.97	-7.64	0.45	-2.43
Rainfall2 27/8/08	-8.09	-8.36	-8.23	0.20	-2.64
Rainfall 28/8/08	-7.56	-8.07	-7.81	0.36	-2.86
Rainfall 29/8/08	-36.52	-36.41	-36.47	0.07	-6.49
Rainfall 30/8/08	-60.77	-60.88	-60.82	0.08	-9.68

SUMMARY OUTPUT

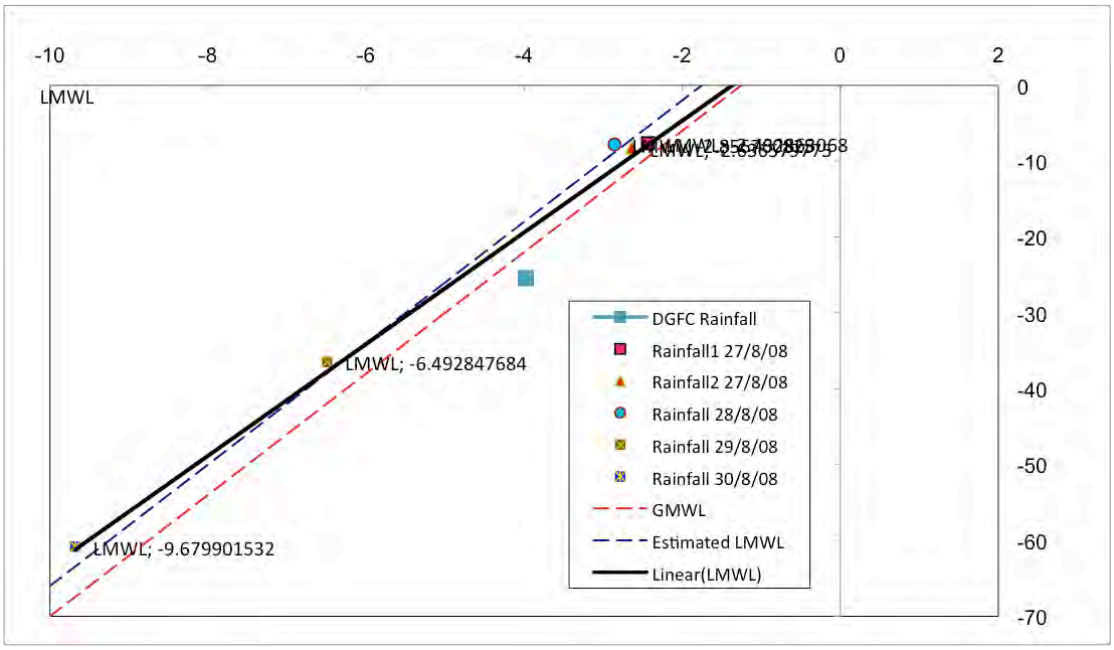
Regression Statistics	
Multiple R	0.988702683
R Square	0.977532995
Adjusted R Square	0.971916244
Standard Error	3.586966182
Observations	6

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	2239.240833	2239.240833	174.0388643	0.000190723
Residual	4	51.46530557	12.86632639		
Total	5	2290.706138			



Plot of $\delta^{18}O$ versus $\delta^{2}H$ for sampling sites at the Lower Kinabatangan River catchment, and comparison with the estimated local meteoric water line (LMWL) and the global meteoric water line (GMWL) for local precipitation.



Plot of local meteoric water line (LMWL) for local precipitation.

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