



CrossMark
click for updates

Cite this: DOI: 10.1039/c5em00462d

Spatial and seasonal variations in the composition of dissolved organic matter in a tropical catchment: the Lower Kinabatangan River, Sabah, Malaysia

Sahana Harun,^{*ab} Andy Baker,^c Chris Bradley^d and Gilles Pinay^e

Dissolved organic matter (DOM) was characterised in water samples sampled in the Lower Kinabatangan River Catchment, Sabah, Malaysia between October 2009 and May 2010. This study aims at: (i) distinguishing between the quality of DOM in waters draining palm oil plantations (OP), secondary forests (SF) and coastal swamps (CS) and, (ii) identifying 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 using the 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 the DOM composition from EEM spectra and five terrestrial derived components were identified: (C1, C2, C3, C4 and C5). Components C1 and C4 contributed the most to DOM fluorescence in all study areas during both the wet and dry seasons. The results suggest that component C4 could be a significant (and common) PARAFAC signal found in similar catchments. Peak M (C2 and C3) was dominant in all samples collected during wet and dry seasons, which could be anthropogenic in origin given the active land use change in the study area. In conclusion, there were significant seasonal and spatial variations in DOM which demonstrated the effects of land use cover and precipitation amounts in the Kinabatangan catchment.

Received 17th September 2015
Accepted 3rd December 2015

DOI: 10.1039/c5em00462d

rsc.li/process-impacts

Environmental impact

The research presented in this paper seeks to characterise dissolved organic matter (DOM) in a tropical catchment in North Borneo that has been affected by significant (and recent), development of oil palm plantations. This paper also examines the variations in DOM according to the land use (specifically secondary forests, oil palm plantations and coastal swamps), and seasonal variations in DOM (during the inter-monsoonal period, wet and dry seasons). We emphasize, in the paper, the potential of fluorescence spectroscopy to determine the environmental impacts of active land use change including deforestation and commercial agricultural activities on water resources. To-date there has been very little work published on catchments that have been affected in this way and particularly with respect to the application of fluorescence spectroscopy. We hope that the research will be of wider interest, and believe that the research is a precursor to solving problems of ecosystem loss for energy production associated with oil palm plantations in tropical regions.

Introduction

A recent synthesis and re-evaluation of the global carbon cycle suggested that approximately 3 Pg C per year of CO₂ is out-gassed from global inland waters,¹ while the estimated global

riverine total carbon flux is 0.80–1.33 Pg C per year.² Given that it has been estimated that approximately half of the carbon is consumed within river systems before reaching the ocean,³ in-stream and near-stream processing of organic matter is a fundamental component of the carbon cycle. This corroborates the research which 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).⁴ Significantly, the determination of the carbon isotopic composition of DOC suggests that contemporary organic carbon (*i.e.* carbon <5 years in age) was the dominant source of excess CO₂ that drives outgassing in Amazonian first order streams and large rivers.⁵ Together, these results emphasize the importance of land-derived, biologically available carbon, for heterotrophic microbial processes in river systems.

^aInstitute for Tropical Biology and Conservation, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia. E-mail: sahana@ums.edu.my

^bWater Research Unit, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia

^cConnected Waters Initiative Research Centre, UNSW Australia, Sydney, NSW 2052, Australia. E-mail: A.Baker@unsw.edu.au

^dSchool of Geography, Earth and Environmental Sciences, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom. E-mail: C.Bradley@bham.ac.uk

^eECOBIO, OSUR, University of Rennes 1, campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: Gilles.Pinay@univ-rennes1.fr

Tropical wetlands provide important ecosystem services including flood mitigation, coastal and wildlife protection, carbon sequestration and respiration.⁶ Tropical wetland ecosystems include a variety of landforms such as lowland floodplains, forested peatlands, swamps and mangroves.⁷ The latter are particularly important carbon sinks which have been reported to store ~49–98% ecosystem carbon in the organic soils.⁸ Tropical wetlands also experience periodic (prolonged) inundation,⁹ reflecting marked seasonal variations in precipitation,¹⁰ while evapotranspiration rates are high.¹¹ Tropical wetlands have been associated with the release of an estimated ~60% of total (global) water, sediment and organic carbon input to the ocean.¹² However, these wetlands are seriously threatened by environmental deterioration as many catchments have experienced rapid conversion of land to agriculture^{13–15} with a concomitant reduction in wetland extent.

Among other agricultural threats, conversion of tropical forest to oil palm (*Elaeis guineensis*) cultivation is a major concern given the recent growth of the palm oil industry.¹⁶ Oil palm plantations are now estimated to extend over >13.5 million ha of the tropics¹⁷ and have contributed to the drainage of floodplain wetlands, and the loss of primary and secondary forest.¹⁸ At present, the majority of oil palm plantations are confined to South East Asia, as Malaysia and Indonesia produce ~80% of the world's palm oil. However, substantial areas of the Congo and Amazon Basin are suitable for oil palm plantation, and further plantation developments are likely in these areas. This situation emphasizes the urgent need to understand the environmental implications of oil palm development. This is particularly important as the full implications of recent and, in some places accelerating, changes in oil palm cover have yet to be considered in detail and these land use changes are likely to affect the quantity and quality of dissolved organic matter (DOM) and DOC.^{19,20}

Recent advances in fluorescence spectroscopy have considerable potential as we seek to address this research gap, as they have significantly enhanced our ability to characterize DOM.²¹ DOM fractions possess fluorescent properties enabling DOM monitoring in soils,²² rivers,^{23,24} lakes,²⁵ estuarine and coastal environments.^{26,27} Reassessment of fluorescence excitation emission matrix (EEM) spectra using Parallel Factor Analysis (PARAFAC) has been invaluable in characterising and quantifying the changes in DOM fluorescence. By decomposing an EEM dataset into several, mathematically independent components parameterized by concentrations (loadings) and excitation and emission spectra, different DOM fractions have been traced through the natural environment.²⁸ For example, in southern Ontario, Canada, DOM production and transformation processes were successfully studied in areas of different use.²⁴ Specifically in a tropical catchment, DOM export was found to be greater during the April flush (inter-monsoonal period), and it has been suggested that tropical rivers are likely to export more labile DOM during periods of high precipitation.²⁹ This is supported by a study in the sub-tropical Jiulong River catchment, China, where increased DOM concentrations were observed after storms, as a result of terrestrial DOM export to the river; with a decrease in the protein-like fraction of DOM

over the same period.³⁰ In sub-tropical Uruguay also, DOM characteristics have been found to vary temporally in catchments with intensive farming practices which was positively related to microbial processing.¹⁹ These results have implications for downstream and marine ecosystems, however, the importance of this research has yet to be more widely established.

The potential utility of fluorescence spectroscopy, specifically in SE Asia, was demonstrated in a preliminary study that sought to characterize spatial trends in DOM in the Lower Kinabatangan River Sabah, Malaysian Borneo.³¹ River flow and photodegradation were found to have a significant effect on DOM properties, however, the extent to which DOM varies seasonally was not considered. This provides the motivation for this paper particularly as, in common with other catchments in this region, there has been a rapid recent increase in the areal extent of oil palm plantations. This, and the conservation of riparian secondary forest and coastal wetlands within the catchment, provides an opportunity to determine the degree to which DOM quantity and quality is affected: first by land-use change, and second by the seasonal flood pulse.³² Accordingly, the objectives of this study were to: (i) characterize DOM quality in waters associated with palm oil plantations, secondary forests and coastal wetlands using fluorescence spectroscopy and PARAFAC;^{33,34} and (ii) determine the seasonal variability of DOM quantity and quality, and its attribution to each land cover type.

Methods and analytical procedures

Study area

DOM characteristics were determined in selected downstream reaches of the Kinabatangan River and tributaries in Sabah, Malaysia. The Kinabatangan River (560 km in length), is the largest river in Sabah, with a total catchment area of 16 800 km² (Fig. 1).³⁵ Geologically, the Kinabatangan area 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.³⁶ Four groups of soil parent materials were identified by surveys conducted in the early 1950s: undifferentiated alluvium, peat, sandstone and mudstone and limestone.^{37,38} Recent alluvium, originating mainly from sedimentary rocks, is found widely on floodplains and in freshwater swamps.³⁸

The area has a humid tropical climate with mean daily temperatures ranging from 22 °C to 32 °C and a mean annual rainfall of 2500–3000 mm.^{35,39} Rainfall is greatest between November and March particularly during the northeast (NE) monsoon, and to a lesser degree during the southwest (SW) monsoon.^{39,40} Transition periods, referred to as the 'inter-monsoonal periods', normally occur in April and October and generally correspond to the period of lowest rainfall⁴¹ although significant precipitation events may still occur at this time.^{40,42} Typically, the floodplain and coastal plain are widely inundated during the rainy season but rainfall totals exhibit considerable inter-annual variability.

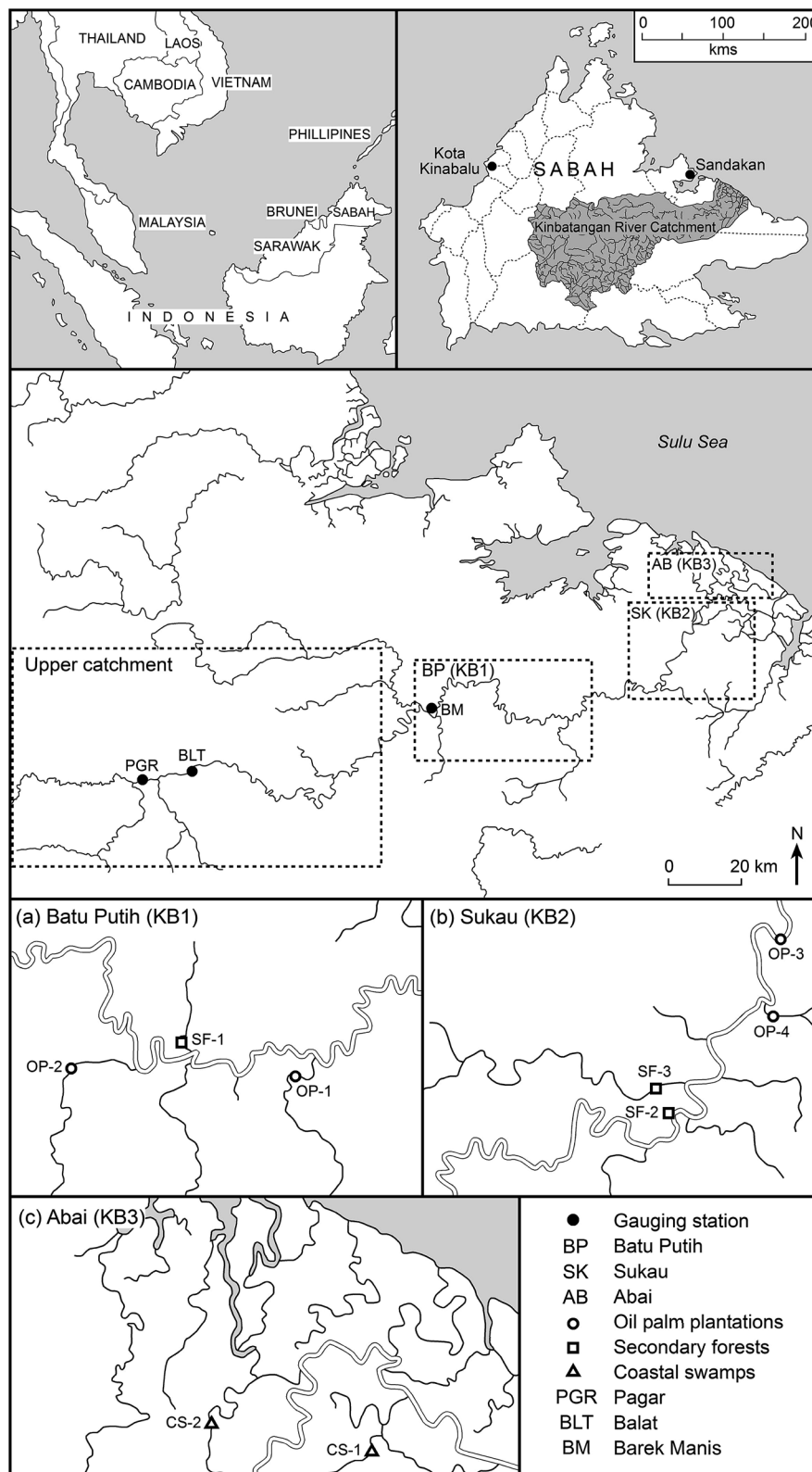
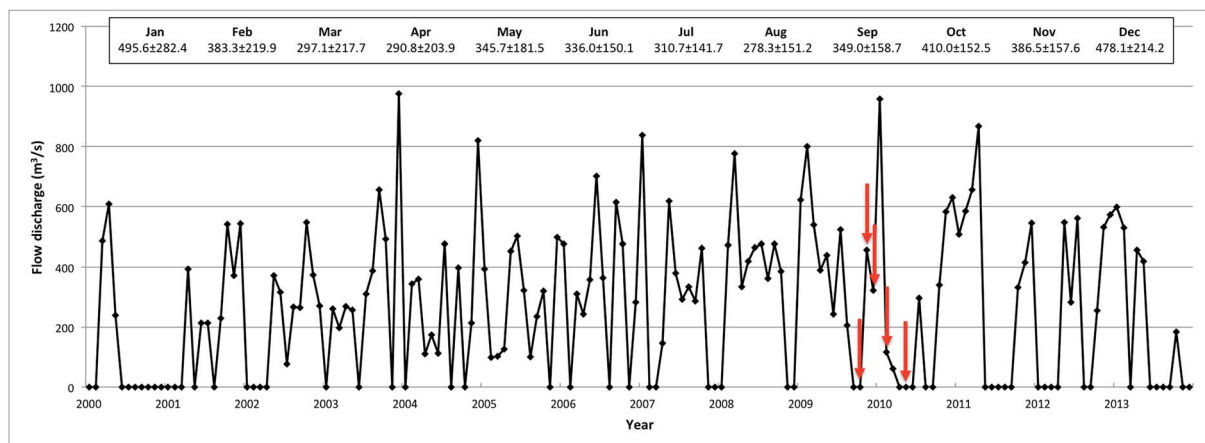


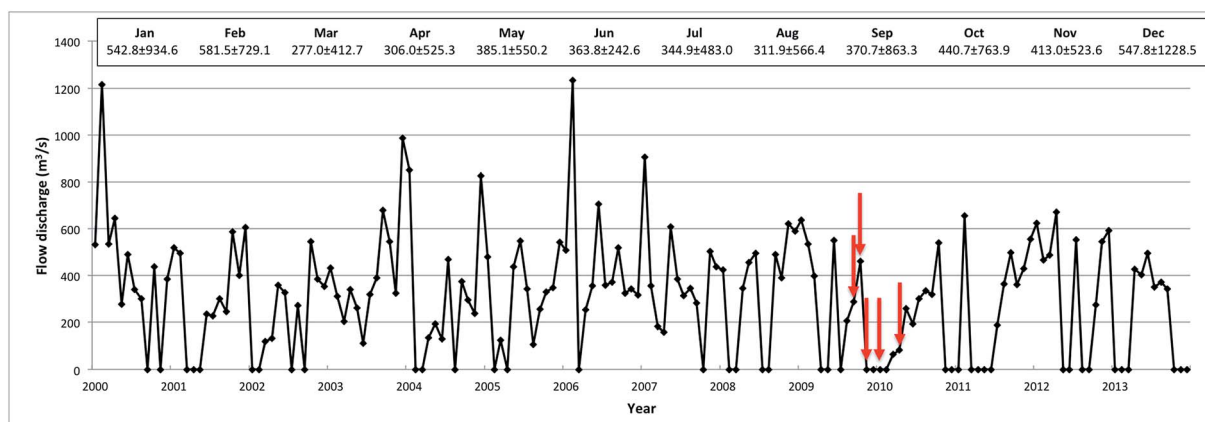
Fig. 1 Location of sampling stations in the Lower Kinabatangan River catchment.

The lower floodplain of the Kinabatangan is $>2800 \text{ km}^2$ in area (Fig. 1) with two principal land uses: (i) forest (mangroves and peat swamps); (ii) agriculture (primarily oil palm

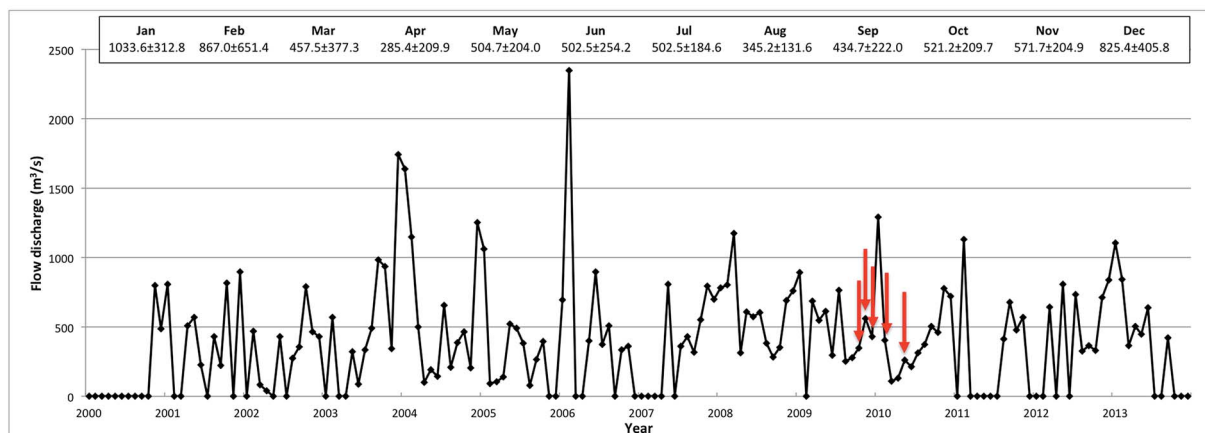
plantations and other crops); with relatively little urban development and only occasional small water bodies.⁴³ Approximately 74% of the Kinabatangan catchment is tropical forest,



(a) Pagar (PGR)



(b) Balat (BLT)



(c) Barek Manis (BM)

Fig. 2 Long-term mean monthly flow discharge for three gauging station at Kinabatangan. The catchment area for each station is 9430 km², 10 800 km² and 12 300 km², respectively. Arrows indicate flow discharges during fieldwork campaign.

including floodplains with open reed swamp, and lowland dipterocarp forest in areas that are inundated frequently.^{39,43} The mean river flow in the upper catchment, recorded at Pagar

(PGR) and Balat (BLT) (Fig. 2) varied from ~14.0 to 1944 m³ s⁻¹ (26–1944 m³ s⁻¹) between 1979 and 2013 (peak daily discharge was recorded in January 1986 at BLT; the lowest flow was

Table 1 Descriptive statistics of environmental conditions, average monthly discharge at the BM station and PARAFAC model of selected sampling stations in the Lower Kinabatangan River Catchment

Inter-monsoonal (IM)	Average of monthly discharge at Berek Manis (BM) ($\text{m}^3 \text{s}^{-1}$)		Land cover	pH	Salinity	DOC (mg l^{-1})	a_{340} (m)	$S_{275-295}$ (nm)	IC1	IC2	IC3	IC4	IC5	I total
	Oct. 2009, 346.6	Nov. 2009, 561.4												
OP	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		
SF	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		
CS	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 (WS)	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		
SF	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		
CS	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 (DS)	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	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	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		

Table 2 List of sampling stations based on land cover and its vegetation characteristics (after Abram *et al.*⁴⁵)

Sampling station	Vegetation characteristics
Oil palm plantation	Palm oil classes
Sg. Pin (OP-1) Sg. Koyah (OP-2)	(i) Young mature: palms were planted from 3–6 years (ii) Prime mature and full stand: prime yield and planted within the range from 7–24 years
Malbumi plantation (OP-3)	(iii) Underproductive at 75%: palm capacity is within 51–75% palms per ha. Older palm with natural mortality start to occur
Sg. Resang (OP-4)	(iv) Underproductive at 50%: palm capacity is ranged from 26–50% palms per ha
Sampling station	Vegetation characteristics
Secondary forest	Forest type
Danau Kaboi (SF-1) ^a	(i) Lowland dry forest: secondary forest, preceding dipterocarp forest with species include <i>Nauclea subdita</i> , <i>Neolamarckia cadamba</i> , <i>Glochidion rubrum</i>
Danau Kalinanap (SF-2) ^b	(ii) Lowland dry dipterocarp forest: preceding logged lowland mixed dipterocarp forest, dominated by <i>Dipterocarp</i> sp.
Sg. Menanggol (SF-3)	
Sampling station	Vegetation characteristics
Coastal swamp	Mangrove forest
Balat Damit (CS-1) Sg. Merah (CS-2)	Nipah palm forest: <i>Nypa fruticans</i> are dominant within the mangrove system. Can be found either in mono-stand or coexist with <i>Rhizophora apiculata</i>

^a SF-1 is oxbow lake. ^b SF-2 is oxbow lake.

observed at PGR in June 1998). Only limited sediment data are available, but a survey at Sukau (at points upstream of coastal swamps) (Fig. 1) in 2005 and 2006 indicated that maximum sediment concentrations were 96 mg l⁻¹ equating to Class IIB of the Malaysian Interim National Water Quality Standard (INWQS).^{43,44} This appears to reflect commercial logging in the catchment since the 1980s and the development of oil palm plantations which currently extend over ~4200 km² which represents approximately 25% of the basin.⁴³

Sampling and analyses

Water was characterized throughout the lower catchment through the manual collection of 510 water samples during five sampling periods in 2009–2010. One period corresponded to the inter-monsoonal period (IM), October 2009; three corresponded to the wet season (WS), November, December 2009 and February 2010; and one the dry season (DS), May 2010. Fieldwork design was constrained by difficulties of access; however, water was sampled along a freshwater – estuarine gradient to determine the seasonal trends in DOM in the Lower Kinabatangan floodplain including across the freshwater–marine interface between the Kinabatangan River and the Sulu Sea. The nearest gauging station was at Berek Manis (BM), situated ~11 km from sample point SF-1, at which point the upstream catchment is 12 300 km² (Fig. 1).

Monthly mean discharges during the fieldwork campaign are presented in Table 1.

Water was sampled from streams or creeks situated entirely within: (i) oil palm (*Elaeis guineensis*) plantations: OP-1, OP-2, OP-3 and OP-4 (220 samples); (ii) secondary forests: SF-1, SF-2 and SF-3 (139 samples) and (iii) coastal swamps of *Nypa fruticans* (nipa palm): CS-1 and CS-2 (151 samples) (Fig. 1). The vegetation characteristics for each land cover type are summarised in Table 2 (after Abram *et al.*⁴⁵). At each point, a 200 ml water sample was collected from the middle of the river/stream from a boat at three points in the water profile: the surface, the mid-point and near the riverbed using a WaterMark Horizontal Polycarbonate water sampler. Samples were stored in high-density polyethylene (HDPE) bottles, pre-washed with hydrochloric acid 10% and deionised water. The pH and salinity were determined using a Hanna Water Quality Multiparameter (Model HI 9828) immediately prior to filtering the water samples (within six hours of sample collection) using 47 mm pre-combusted Whatman glassfiber GF/C filter papers (nominal pore size 1.2 μm). Filtered water samples were kept in the dark and stored at 4 °C before shipment to the UK for laboratory analysis, which occurred within seven days of the end of the field-campaign.

Spectral measurements and DOC

Fluorescence analyses of samples were performed at the University of Birmingham, UK, using a Varian Cary Eclipse spectrophotometer. Excitation–emission matrices (EEMs) were generated for each sample over excitation wavelengths 250 to 400 nm at 5 nm intervals and emission wavelengths 280 to 500 nm at 5 nm intervals, with 2 nm bandwidths on excitation and emission modes. The spectrophotometer output was monitored by regular determination of the Raman intensity of ultra pure water in a sealed 10 × 10 mm cuvette at 348 nm excitation and 5 nm bandpass. No significant changes were observed in the EEMs, particularly in samples associated with the secondary forest and coastal swamps (the mean salinity for all samples collected was 1.27‰), although Yang & Hur⁴⁶ suggested the potential impact of salinity on fluorescence DOM peaks A and M. An inner-filter effect (IFE) correction was applied to the dataset:⁴⁷

$$I = I_0(10^{-b(A_{\text{ex}} + A_{\text{em}})}) \quad (1)$$

where I is the 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 excitation wavelength; and A_{em} is absorbance at emission wavelength.

Absorption coefficients at 340 nm and spectral slope over the interval of 275–295 nm ($S_{275-295}$)⁴⁸ were determined using a Lightwave (WPA) spectrophotometer in a 10 mm quartz cuvette. Absorption measurements were corrected against Milli-Q water blanks and the slope of the absorption curve was calculated by linear regression of the log-transformed spectra.

Dissolved organic carbon (DOC) was 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 collection. The acidified samples (pH ~ 2) were sparged for 8 minutes at 75 or 100 ml min⁻¹ with ultra-pure oxygen to remove all inorganic carbon from samples prior to measurement.

PARAFAC modelling

Fluorescence excitation emission matrix (EEM) spectra were reassessed using Parallel Factor Analysis (PARAFAC).^{33,34} Fluorescence EEMs were combined into a 3-dimensional data array and decomposed to a set of trilinear terms and a residual array:

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + e_{ijk} \quad i = 1, \dots, I \quad j = 1, \dots, J \quad k = 1, \dots, K \quad (2)$$

where x_{ijk} is the fluorescence intensity for sample i at emission wavelength j and excitation wavelength k ; a_{if} , b_{jf} and c_{kf} are the loading matrices. F is the number of components in the model, and e_{ijk} is the residual noise (*i.e.* the variability that is not explained by the model). Despite the use of a 250–395 nm excitation filter, the initial PARAFAC analysis was confounded by scatter in individual EEMs, which occurred within the excitation (emission) wavelength ranges of 250 to 280 nm (280 to 290 nm). In this study, mean suspended sediment

concentrations of the Lower Kinabatangan River varied between ~7 and ~9800 mg l⁻¹ (data not presented). As a result of filtration the signal/noise ratio for excitation wavelengths <290 nm was not acceptable and consequently the microbial peak, which corresponds to an excitation wavelength of 280 nm excitation, was removed in the PARAFAC analysis.

A PARAFAC model with non-negativity constraint on all modes (samples, emission and excitation) was implemented in MATLAB. The data were split into two random halves each comprising 254 EEMs, 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 components between the calibration and validation data arrays and from split-half analysis, a total of five components were validated. Two categories of independent datasets were successfully validated: first, an inter-seasonal comparison between the wet and dry season, and second a land use comparison: oil palm plantations (OP), secondary forests (SF) and coastal swamps (CS). This compares with an earlier PARAFAC model for the Kinabatangan catchment which had validated three components.³¹ In the earlier model, however, all sampling stations were situated in the immediate vicinity of oil palm plantations while in the current study, sampling sites distinguished between three land use types (oil palm plantations, secondary forests and coastal swamps). Thus the five components presented in this study could potentially reflect differences in DOM composition according to land use.

The PARAFAC model returns the relative intensities of derived components, and the intensity of the n th component in a given sample remains unknown. Hence I_n was estimated by determining the fluorescence intensity at the peak excitation and emission maximum of the n th component:⁴⁹

$$I_n = \text{score}_n \times \text{Ex}_n(\lambda_{\text{max}}) \times \text{Em}_n(\lambda_{\text{max}}) \quad (3)$$

where: score_n is the relative intensity of the n th component, $\text{Ex}_n(\lambda_{\text{max}})$ is the maximum excitation loading of the n th component, $\text{Em}_n(\lambda_{\text{max}})$ is the maximum emission loading of the n th component derived from the model. The total fluorescence intensity (I_{tot}) was calculated as the sum of the components.

Statistical analysis

Precipitation data were analysed using a paired-sample t test to determine whether there were significant differences between inter-monsoonal period (IM), wet (WS) and dry seasons (DS). The p -values ($p < 0.05$) for pairs of IM-WS, IM-DS and WS-DS were 0.950, 0.142 and 0.018, respectively. This analysis was also sought to verify whether the rainfall data used in the study were free from precipitation anomalies, potentially caused by irregular synoptic forcing associated with the El Niño Southern Oscillation (ENSO) and changes in the seasonality of the monsoon in SE Asia.⁴⁴ Discriminant analysis was applied to characterise DOM according to the land use type and seasonal variations. Calculations of the fluorescence intensities (I_n) of the individual components indicated that: IC4 > IC2 > IC3 > IC1 > IC5, suggesting that the terrestrially derived peak A had the most abundant spectral characteristics, followed by peak M (IC2

and IC3), peak C (IC1) and peak M (IC5). UV absorbance at 340 nm and fluorescence DOM (FDOM) were normalized to IC4 and fluorescence indices (FI) (ratios as detailed below) were used to determine the pre-dominance of each parameter in each land use type to gain more insight into DOM characterisation: IC4/ a_{340} (peak A/ a_{340}), IC2/IC4 (peak M/peak A), IC3/IC4 (peak M/peak A) and IC5/IC4 (peak M/peak A). Both paired-sample *t* test and discriminant analysis were undertaken using SPSS version 21.0.

Results and discussion

The data presented here provide the first evidence of seasonal changes in DOM composition in a catchment affected by the recent development of oil palm plantations. In the following section we compare our results with recent studies of other tropical catchments and consider the wider significance of this work.

Characterisation of PARAFAC components

Five fluorescent components were identified by PARAFAC from analysis of the 510 sample dataset (Fig. 3). The excitation and emission pairs of the main peak positions for each component are summarised in Table 3, and the individual components are plotted in Fig. 3. Table 3 also compares the results with components identified in selected studies that have modelled DOM in marine, oceanic and estuarine environments.

Our PARAFAC model identified five terrestrially-derived substances: component 1 (C1) to component 5 (C5). Our terrestrially-derived components (C1 and C4) have been observed in other tropical and sub-tropical studies: these are ubiquitous, fulvic-acid representing fluorophores that have the longest excitation (and emission) wavelength and broadest excitation (and emission) band. Our components were found to relate specifically to the Component 1 described by Luciani *et al.*,⁵⁰ Stedmon and Markager⁵¹ and Yamashita *et al.*,⁵² to the Component 2 of Fellman *et al.*,²¹ Component 3 of Yao *et al.*⁵³ and to Component 4 of Kowalczyk *et al.*⁴⁹ Our earlier DOM characterisation study in the Lower Kinabatangan also reported terrestrial-derived Component 1 (peak A and C).³¹ Our C1 (identified here) is similar to the humic-like fluorophore in the visible region defined by Coble.⁵⁴

Our components C2, C3 and C5 have been previously reported as peak M; they have shorter emission wavelengths and were initially attributed to a marine source of DOM.^{54,55} Subsequently Stedmon *et al.*⁵⁶ suggested that this component is found in 'terrestrially dominated end-member samples', and Fellman *et al.*⁵⁷ described this peak as ultraviolet A (UVA), a low molecular weight component related to microbial activities. While peak M is common in marine environments and is apparently related to biological activity, it is also found in wastewater, in wetlands and agricultural environments. Peak M production could be partly due to the photobleaching of terrestrial FDOM or autochthonous production from microbial processes.⁵⁸ Our C2 resembles Component 3 found by Murphy *et al.*,⁵⁹ and

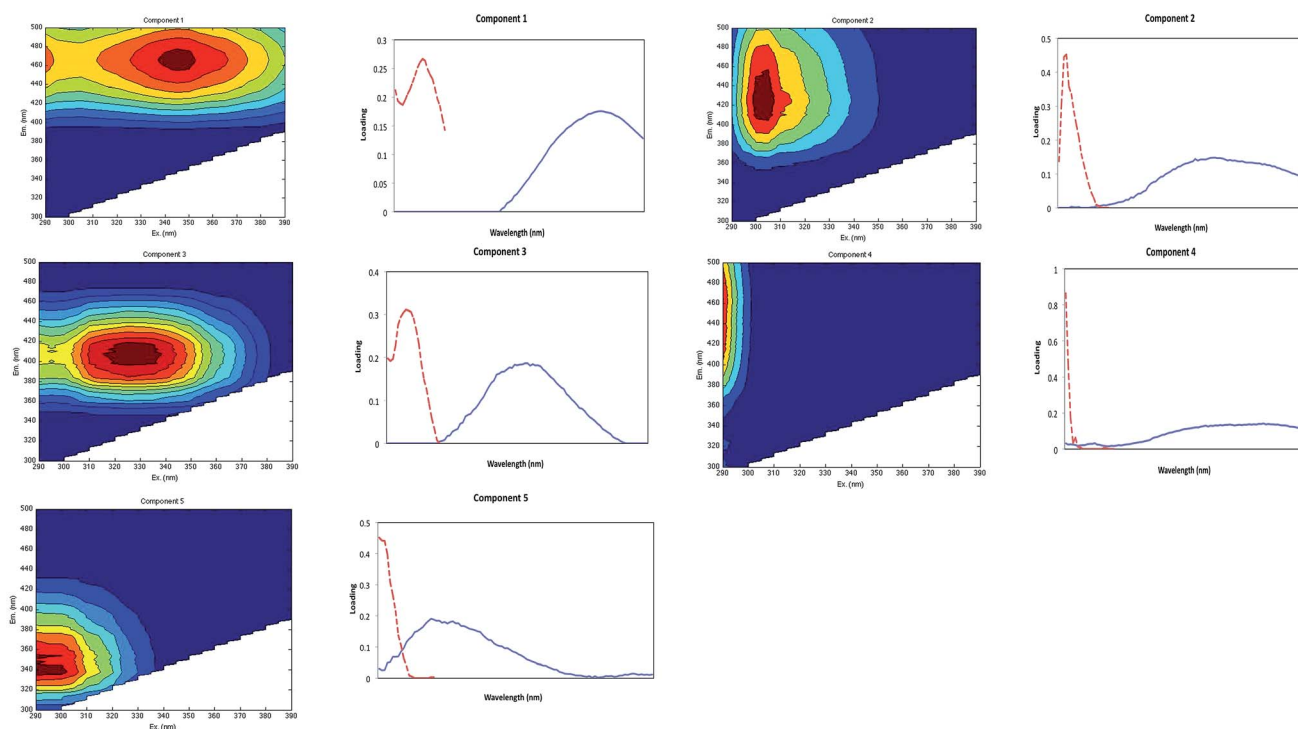


Fig. 3 PARAFAC model output showing fluorescence signatures of the five components identified. Contour plots present spectral shapes of excitation and emission of derived components. Line plots to the right of each contour plot present split-half validation results for each identified component. Excitation (dotted line) and emission (solid line) loadings for each component, obtained from two independent PARAFAC models on random halves of the data array.

Table 3 Spectral characteristics of excitation and emission maxima of five components identified by PARAFAC modelling for the whole EEMs dataset collected in the Lower Kinabatangan River catchment compared to previously identified sources

Component in this study	Excitation maximum (nm)	Emission maximum (nm)	Coble <i>et al.</i> ⁵⁴	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, ⁵⁰ Component 1: 345/462, ⁵² Component 4: 350/420–480 (ref. 49)
C2	305	426	Peak M 290–312/370–420	Terrestrial humic-like substances, widespread, hydrophobic acid fraction (HPOA), suggested as photo-refractory, Component 2: 255/380–460, ⁵⁰ Component 3: 255 (330)/412, ⁶⁰ Component 3: 270 (360)/478, ⁵⁶ Component 3: 250 (355)/461 (ref. 53)
C3	325	408		
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, ⁶⁰ Component 2: 255/380–460, ⁵⁰ Component 3: 270 (360)/478, ⁵⁶ Component 3: 250 (355)/461 (ref. 53)
C5	290	338	Peak M 290–312/370–420	Ditto with description for C2

Components 4 and 6 of Stedmon *et al.*⁵⁶ and Yamashita *et al.*⁵² This component was also reported by Zhang *et al.*⁶⁰ their Component 1; Luciani *et al.*⁵⁰ their Component 2; Stedmon *et al.*⁵⁶ their Component 3; Yao *et al.*⁵³ their Component 3; and Stedmon *et al.*⁵⁶ their Component 5.

Comparison of the fluorescence intensities, I_n , indicated that terrestrially-derived peak IC4 (peak A) had the most abundant spectral characteristics. The peak component has been described as ubiquitous, photo-labile, terrestrially-derived OM which originates from agricultural activities⁵² but it could also represent a photodegradation processing pathway.⁶¹ Natural forest cover in the Lower Kinabatangan river catchment has declined from ~91% in the 1970s to ~47% in 1995;⁶² and at present ~25% of the catchment is largely cultivated with oil palm plantations,³⁹ which could explain the spectral characteristics and abundance of component IC4.

The PARAFAC components summarised in this paper are similar to those outlined in other studies of tropical catchments^{31,50,52} indicating that common attributes can be identified. However, the DOM characteristics described in most previous studies are of DOM that has a very different origin (including subtropical wetlands⁵⁰ and enclosed coastal water bodies⁵²) to that found in our study in NE Sabah.³¹ Consequently the results and the implications for both the Kinabatangan catchment, and tropical regions generally, should be interpreted with caution, as there might be site-specific

contributions of natural organic matter from other land use and vegetation types might be only applicable in a local context.²³ It might also be possible for the fluorescence characteristics to

Table 4 Factor structure coefficients from the discriminant analysis for both land use and seasonal datasets

Fluorescence indices	Discriminant function (DF)	
	1	2
Land use		
IC3/IC4 (peak M/peak A)	0.913*	−0.015
IC2/IC4 (peak M/peak A)	0.618*	0.095
IC5/IC4 (peak M/peak A)	0.405*	−0.054
IC1/IC4 (peak C/peak A)	−0.285*	−0.043
IC4/ a_{340} (peak A/ a_{340})	−0.374	0.746*
Spectral slope	0.144	−0.626*
45.9% of original group cases correctly classified		
Seasonal		
IC5/IC4 (peak M/peak A)	0.678*	0.003
IC4/ a_{340} (peak A/ a_{340})	−0.672*	0.133
IC2/IC4 (peak M/peak A)	0.538*	0.503
IC3/IC4 (peak M/peak A)	0.406	0.586*
IC1/IC4 (peak C/peak A)	−0.108	−0.384*
Spectral slope	0.205	0.253*
63.9% of original group cases correctly classified		

appear 'identical' in different catchments, albeit associated with a different DOM composition.⁶³

Seasonal and land use variations

Discriminant analyses of the DOM dataset and land use type yielded two discriminant functions as summarised in Table 4

and Fig. 4. The ratios of (i) IC3/IC4 and (ii) IC2/IC4 were found to always correlate positively with IC5/IC4. They were classified in discriminant function 1 (DF1) and explained 79.2% of the variance. These results suggest that DF1 corresponds to fluorescence properties arising through photodegradation thus representing a DOM processing signature. Moreover, samples

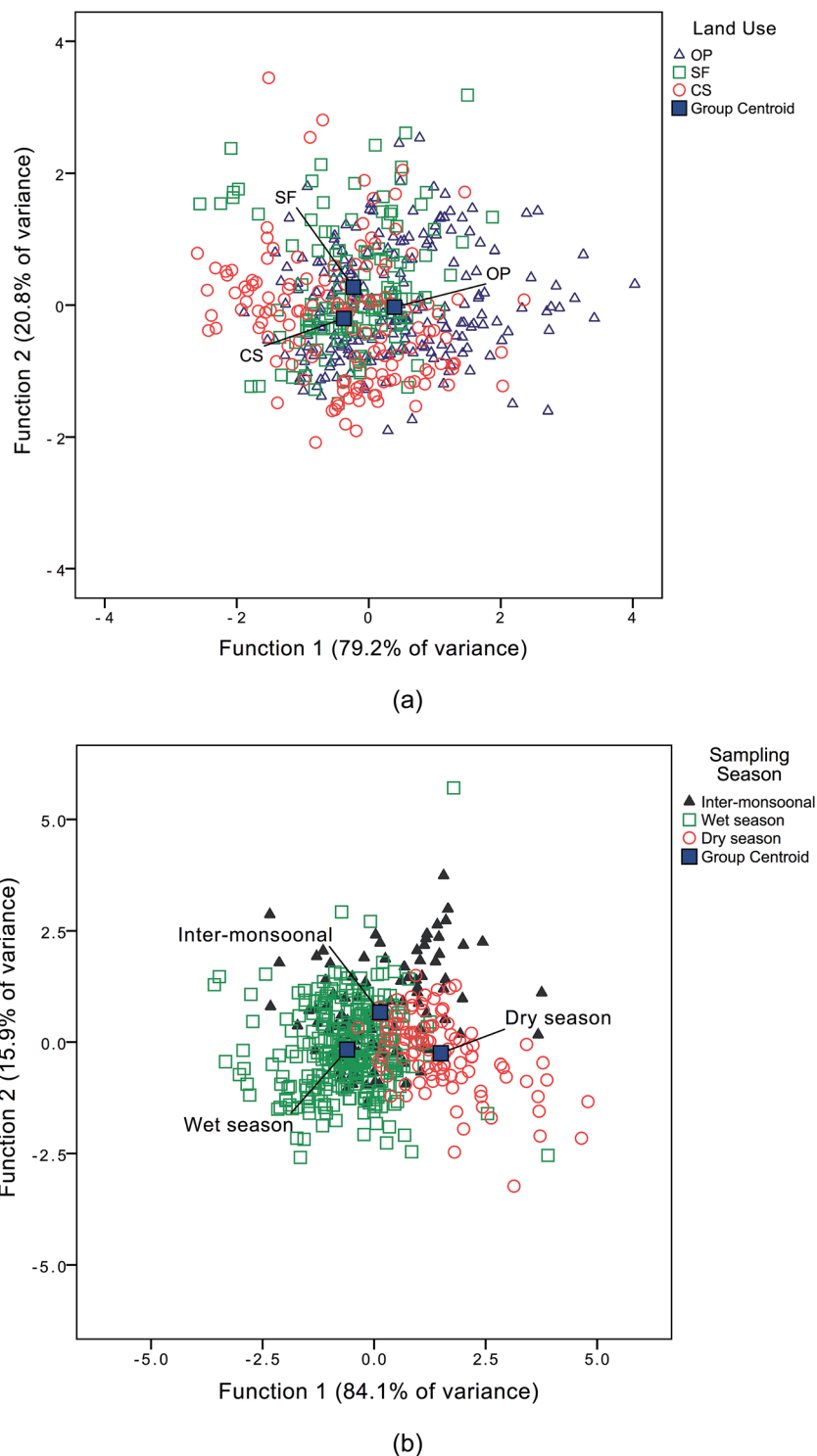


Fig. 4 Group separation from the discriminant analysis according to: (a) types of land use; (b) seasonal variations.

from coastal swamps (CS) were found to comprise DOM which was less processed (*i.e.* the DOM was fresher or younger), while DOM in waters sampled from the oil palm plantations (OP) showed evidence of greater processing, particularly in those samples collected from canals with stagnant water.

Seasonal trends in DOM characteristics were also evident in the discriminant analysis: DF1 suggests that the ratio of IC5/IC4 correlated positively with IC2/IC4 and explained 84.1% of the variance (Table 4). IC4/ a_{340} was dominant in water sampled during the wet season and (Fig. 4), suggesting that DOM was fresher during the wet season (WS) compared with the dry season (DS) when DOM was more processed. While no seasonal variations in EEMs were observed by Baker & Spencer⁶⁴ in their study in a temperate maritime catchment with anthropogenic DOM inputs in the Tyne, UK, other studies highlighted seasonal variability in EEMs. For example, Zhao *et al.*⁶⁵ observed seasonal variations in EEMs from semi-arid lakes in NE China. Seasonal patterns of DOM distribution also have been found in subtropical Florida Bay, USA where relative abundance of humic-like (Ex/Em = <260, 345/462) and protein-like component (Ex/Em = 275/326) was higher during the early wet season (June to August).⁶⁶

The ratios IC2/IC4 and IC5/IC4 were high in samples from the oil palm plantations (OP) during the dry season, suggesting that the DOM was more processed in the OP samples and could have been affected by microbial activities and/or photo-degradation during this period. Preliminary $\delta^{13}\text{C}$ and molar C : N values of both DOM and particulate organic matter (POM) in an Australian tropical rainforest catchment suggested that exports of microbially processed organic matter were higher from upper soil horizons during the dry season.⁶⁷ Subsequently, Lee-Cruz *et al.*⁶⁸ investigated soil bacterial communities in logged forest and oil palm plantations in Sabah and found a high abundance of *Actinomycetales*, which are dominant in cultivated areas.⁶⁹ Their study indicated that oil palm plantation soils have a higher bacterial diversity and turnover and are more heterogeneous. A study in Jambi, Indonesia revealed a high abundance of the genus *Burkholderia*, *Cupriavidus* and *Acinetobacter* in bacteria isolates from oil palm plantation aquatic sediments.⁷⁰ *Burkholderia* and *Cupriavidus* are nitrogen-fixing^{71,72} plant growth promoting bacteria⁷² while *Acinetobacter*, which has been reported ubiquitous in soil and surface waters,⁷³ is a nonmotile, agent for biodegradation, leaching and removal of organic and inorganic waste.⁷⁴ An earlier water quality study in the Sukau area of the Kinabatangan catchment (Fig. 1) during a weak La Niña event (2005 to 2006) indicated that the Biochemical Oxygen Demand (BOD) of a stream in an oil palm plantation ranged from 1.3 to 2.1 mg l⁻¹.⁴⁴ Dry season water samples from downstream reaching Sg. Langat in Selangor, Malaysia, which was also located within oil palm plantations, had mean BOD values ranging from 2.1 to 2.6 mg l⁻¹.⁷⁵ Therefore, we hypothesize that peak M we found in the Lower Kinabatangan River catchment, which varied seasonally and according to land use, could be derived from microbial and/or photo-degradation processes.

The variation in DOM according to the season and land cover is illustrated in Fig. 5 by plotting DOC against PARAFAC

component IC4 for each land use type. Tabulated DOC concentrations varied from 9.88 to 12.85 mg l⁻¹ (Table 1). Samples from secondary forests (SF) and coastal swamps (CS) showed a strong positive correlation between DOC and PARAFAC component C4 (r^2 of 0.6 and 0.7 respectively). It also showed that DOM composition in both SF and CS was moderately constrained by monsoon and flow, compared to samples from the oil palm plantations (OP), which were highly constrained in particular during the inter-monsoonal period and wet season. This is consistent with the discriminant analysis (Fig. 4), which indicated that the ratio of IC4 to a_{340} was dominant in samples collected in SF during the wet season,

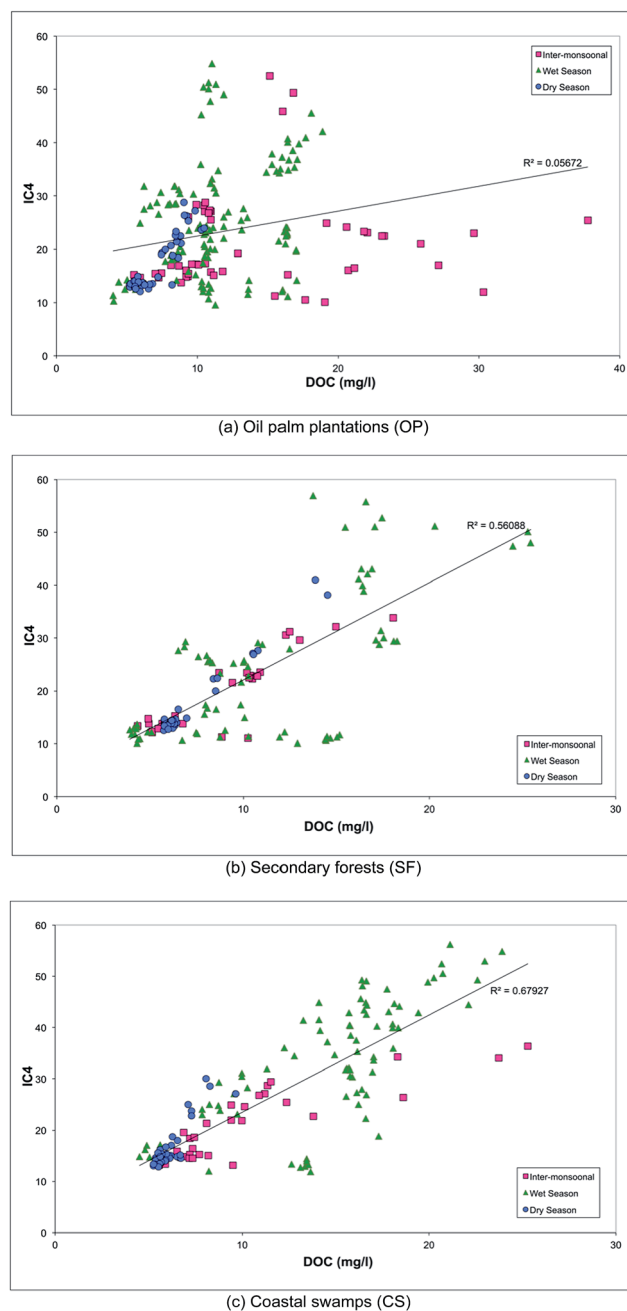


Fig. 5 DOC against PARAFAC component C4 according to different types of land use.

while the spectral slope (275–295 nm) was found to be dominant in CS during the inter-monsoonal period (October 2009). There were positive correlations between UV absorbance a_{340} nm and PARAFAC component C4 (peak A) with a regression value of 0.5 for all types of land cover (Fig. 6). UV absorbance at ~340 nm and spectral slope have been showed to be indicative of DOM molecular weight,^{48,76} and to correlate positively with

the lignin concentration.²⁹ The lignin concentration in aquatic ecosystems was strongly influenced by seasonal hydrology, river catchment discharge, flooding events and types of vegetation and land use.⁷⁷ A quantitative aquatic carbon budget for the Langat River in Malaysia indicated that although C3 plant-derived matter was the primary source of carbon in wetland areas, sewage treatment and landfill sites in the lower catchment provided significant additional inputs of organic carbon.⁷⁸ Nedwell *et al.*⁷⁹ demonstrated that carbon mineralisation in a subtropical mangrove swamp in Jamaica was higher compared to other areas, indicating abundant OM availability. Mangrove forests also typically have rich tannins, which is likely to be the main source of protein-like fluorescence.⁸⁰ They are also associated with decreasing bacterial counts⁸¹ and hydrophobic acids,⁸² which could explain observations of low molecular weight DOM in CS samples in the Lower Kinabatangan River catchment during the inter-monsoonal period.

Our results indicated that the ratio IC4 (peak A) to a_{340} was high and the spectral slope ($S_{275-295}$) was low in waters sampled from secondary forests during the wet season. This could be associated with DOM inputs that were fresher and of higher molecular weight. There was also evidence of DOM degradation (bio- and photo-degradation) in river reaches downstream, including the estuary. The consistent high DOC concentrations that we observed in our study are indicative of high concentrations of humic materials in the waters sampled. Previous work has demonstrated that secondary forests have the potential to absorb and store a large proportion of carbon and nutrients lost as a result of changes in land use and particularly deforestation.⁸³⁻⁸⁵ Secondary forests can be effective nutrient sinks enabling the rapid accumulation of nutrients over time. With respect to organic matter production, secondary forests can return significant OM in litter fall although they store fewer nutrients in their litter.^{86,87} This results in high nutrient cycling rates but may also potentially contribute to nutrient loss.⁸⁶

Conclusion

We conclude that the characteristics of DOM in the Lower Kinabatangan River, Malaysia are dominated by the fluorescence peaks A (IC4) and M (IC2, IC3 and IC5). These peaks indicate the importance of microbial and photo-degradation processes, particularly during the dry season, which break down the aromatic carbon molecules that account for DOM fluorescence. Discriminant analysis of the PARAFAC dataset indicated that OP samples could be distinguished by plotting peak M (IC2, IC3 and IC5) against a_{340} , confirming the importance of microbial activity and photo-degradation processes in streams associated with oil palm plantations. The ratio IC4/ a_{340} and spectral slope successfully distinguished secondary forests, followed by oil palm plantations and coastal swamps, suggesting that DOM with a higher MW is found in SF. This also suggests variations in the quality of DOC production in different land use types, modified by the monsoonal cycle. This is supported by the PARAFAC model presented here which yielded three peak M components. Hence the paper suggests that analysis of EEMs, supported by PARAFAC, is a useful tool to

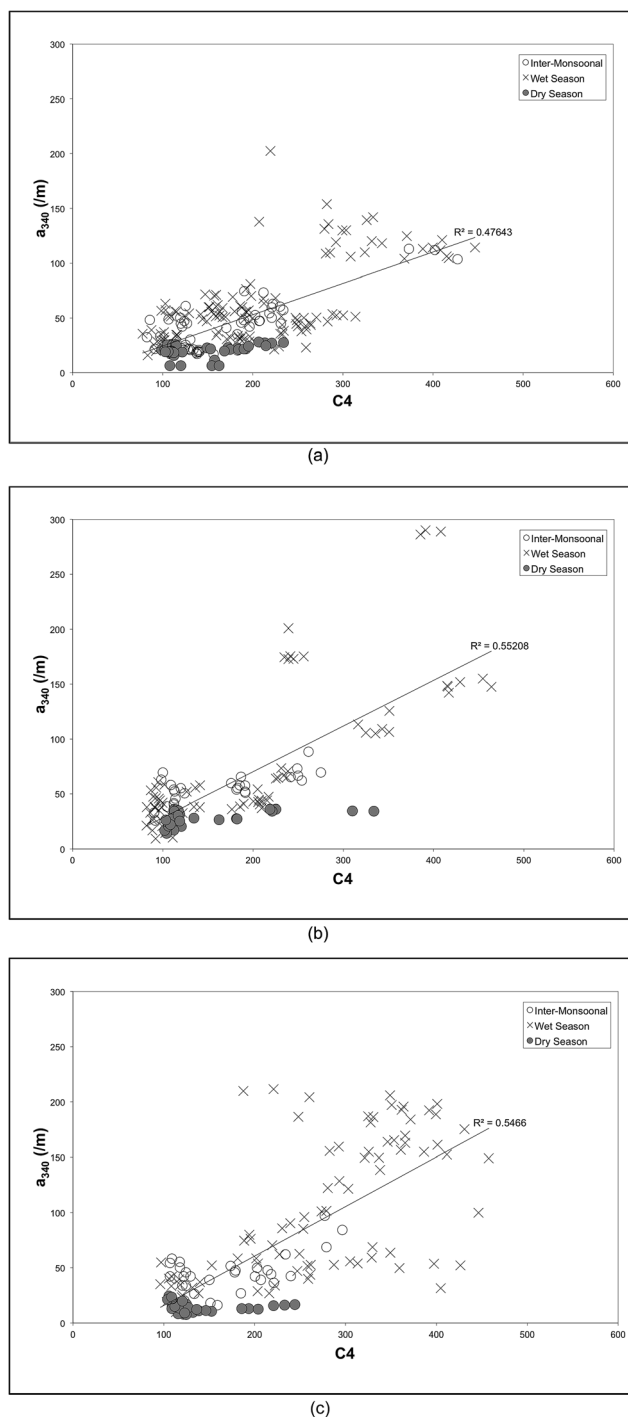


Fig. 6 Correlation between PARAFAC component C4 and UV absorbance at 340 nm according to the sampling period: (a) oil palm plantations (OP); (b) secondary forests (SF); (c) coastal swamps (CS).

determine and characterise the humic and fulvic substances in aquatic ecosystems, which correlate strongly with DOC.

Acknowledgements

We thank the Malaysia Ministry of Higher Education (MoHE), Universiti Malaysia Sabah, Department of Irrigation and Drainage (DID) Sabah, Malaysian Meteorological Department for providing fund, hydrological and meteorological data for this study. Thanks are also extended to Sabah Forestry Department and Sabah Wildlife Department for permitting this research to be undertaken in Kinabatangan, Sabah, Malaysia. We are grateful to: Ms Anne Ankcorn for drawing Fig. 1; Mr Zainal Abidin Jaafar, Mr Budin Ransangan and Ms Asnih Etin, for their great help with the field sampling. Finally, we are thankful to the editor and two anonymous reviewers for their valuable comments and suggestions.

References

- 1 G. Abril, J. M. Martinez, L. F. Artigas, P. Moreira-Turcq, M. F. Benedetti, L. Vidal, T. Meziane, J. H. Kim, M. C. Bernardes, N. Savoye, J. Deborde, E. L. Souza, P. Alberic, M. F. L. de Souza and F. Roland, *Nature*, 2015, **505**(7483), 395–398.
- 2 T. H. Huang, Y. H. Fu, P. Y. Pan and C. C. T. Arthur, *Current Opinion in Environmental Sustainability*, 2012, **4**(2), 162–169.
- 3 J. J. Cole, Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegel, C. M. Duarte, P. Kortelainen, J. A. Downing, J. J. Middelburg and J. Melack, *Ecosystems*, 2007, **10**, 171–184.
- 4 J. E. Richey, J. M. Melack, A. K. Aufdenkampe, V. M. Ballester and L. L. Hess, *Nature*, 2002, **416**, 617–620.
- 5 E. Mayorga, A. K. Aufdenkampe, C. A. Masiello, A. V. Krusche, J. I. Hedges, P. D. Quay, J. E. Richey and T. A. Brown, *Nature*, 2005, **436**, 538–541.
- 6 W. J. Mitsch, B. Bernal, A. M. Nahlik, Ü. Mander, L. Zhang, C. J. Anderson, S. E. Jorgensen and H. Brix, *Landscape Ecology*, 2013, **28**(4), 583–597.
- 7 I. Aselmann and P. J. Crutzen, *J. Atmos. Chem.*, 1989, **8**, 307–358.
- 8 D. C. Donato, J. B. Kauffman, D. Murdiyarso, S. Kurnianto, M. Stidham and M. Kanninen, *Nat. Geosci.*, 2011, **4**, 293–297.
- 9 G. Mayora, M. Devercelli and F. Giri, *Hydrobiologia*, 2013, **717**(1), 51–63.
- 10 N. Saigusa, S. Yamamoto, R. Hirata, Y. Ohtani, R. Ide, J. Asanuma, M. Gamoto, T. Hirano, H. Kondo and Y. Kosugi, *Agr. Forest Meteorol.*, 2008, **148**, 700–713.
- 11 Y. Ogata, T. Ishigaki, Y. Ebie, N. Sutthasil, C. Chiemchaisri and M. Yamada, *Waste Manage.*, 2015, **44**(C), 164–171.
- 12 M. Alkhatib, T. C. Jennerjahn and J. Samiaji, *Limnol. Oceanogr.*, 2007, **52**, 2410–2417.
- 13 S. Atapattu and D. Kodituwakku, *Agr. Forest Meteorol.*, 2009, **96**(3), 361–373.
- 14 B. Mattsson, C. Cederberg and L. Blix, *J. Cleaner Prod.*, 2000, **8**, 283–292.
- 15 R. Sidle, M. Tani and A. Ziegler, *For. Ecol. Manage.*, 2006, **224**(1–2), 1–4.
- 16 C. M. Ji, P. P. Eong, T. B. Ti, C. E. Seng and C. K. Ling, *Renewable Sustainable Energy Rev.*, 2013, **26**(C), 717–726.
- 17 E. B. Fitzherbert, M. J. Stuebig, A. Morel, F. Danielsen, C. A. Bruhl, P. F. Donald and B. Phalan, *Trends in Ecology and Evolution*, 2008, **23**(10), 538–545.
- 18 L. P. Koh and D. S. Wilcove, *Trends in Ecology and Evolution*, 2008, **24**(2), 67–68.
- 19 D. Graeber, G. Goyenola, M. Meerhoff, E. Zwirnmann, N. B. Ovesen, M. Glendell, J. Gelbrecht, F. Teixeira de Mello, I. González-Bergonzoni, E. Jeppesen and B. Kronvang, *Hydrol. Earth Syst. Sci.*, 2015, **19**, 2377–2394.
- 20 Y. H. Lu, J. E. Bauer, E. A. Canuel, R. M. Chambers, Y. Yamahita, R. Jaffé and A. Barrett, *Biogeochemistry*, 2014, **119**, 275–292.
- 21 J. B. Fellman, M. P. Miller, R. M. Cory, D. V. D'Amore and D. White, *Environ. Sci. Technol.*, 2009, **43**(16), 6228–6234.
- 22 M. Fuentes, G. Gonzalezgaitano and J. Garchiamina, *Org. Geochem.*, 2006, **37**(12), 1949–1959.
- 23 U. K. Ahmad, Z. Ujang, Z. Yusop and T. L. Fong, *Water Sci. Technol.*, 2002, **46**, 117–125.
- 24 C. J. Williams, Y. Yamashita, H. F. Wilson, R. Jaffé and M. A. Xenopoulos, *Limnol. Oceanogr.*, 2010, **55**(3), 1159–1171.
- 25 M. Miller, D. McKnight, S. Charpra and M. Williams, *Limnol. Oceanogr.*, 2009, **54**, 2213–2227.
- 26 C. Stedmon and S. Markager, *Limnol. Oceanogr.*, 2005, **50**(2), 686–697.
- 27 Y. Yamashita, R. Jaffé, R. Maie and E. Tanque, *Limnol. Oceanogr.*, 2008, **53**, 1900–1908.
- 28 R. M. Cory and D. M. McKnight, *Environ. Sci. Technol.*, 2005, **39**(21), 8142–8149.
- 29 R. Spencer, P. Hernes, R. Rug, A. Baker, R. Dyda, A. Stubbins and J. Six, *J. Geophys. Res.*, 2010, **115**, G03013.
- 30 H. Hong, L. Yang, W. Guo, F. Wang and X. Yu, *Biogeochemistry*, 2012, **109**, 163–174.
- 31 S. Harun, A. Baker, C. Bradley, G. Pinay, I. Boomer and R. L. Hamilton, *Hydrol. Res.*, 2015, **46**(3), 411–428.
- 32 W. J. Junk, *Environ. Conserv.*, 2002, **29**(4), 414–435.
- 33 R. Bro, *Chemom. Intell. Lab. Syst.*, 1997, **38**, 149–171.
- 34 C. A. Stedmon and S. Markager, *Estuarine, Coastal Shelf Sci.*, 2003, **57**(5–6), 973–979.
- 35 R. Josephine, R. J. Alfred and I. Rajah, *Presented in Part at World Water Day*, 2004, pp. 1–10.
- 36 F. Tongkul, *J. Southeast Asian Earth Sci.*, 1991, **6**, 395–405.
- 37 B. D. Acres and C. J. Folland, *The Soils of Sabah. Vol. 2*, Land Resources Division, Ministry of Overseas Development, Sandakan and Kinabatangan Districts, England, 1975.
- 38 Town and Regional Planning Department Sabah, in *Sabah Coastal Zone Profile*, The Integrated Coastal Zone Management Unit, Kota Kinabalu, Sabah, 1998.
- 39 R. Boonratana, *Int. J. Primatol.*, 2000, **21**, 497–517.
- 40 N. M. Gazzaz, M. K. Yusoff, M. F. Ramli, A. Z. Aris and H. Juahir, *Mar. Pollut. Bull.*, 2012, **64**(4), 688–698.
- 41 R. Dambul and P. Jones, *Geografia*, 2008, **5**(1), 1–25.
- 42 J. Suhaila, S. M. Deni, W. W. Wan Zin and A. A. Jemain, *Sains Malays.*, 2010, **39**, 533–542.

- 43 Department of Environment Malaysia, Study on pollution and water quality improvement for Sg. Kinabatangan Basin. Final Report Volume II: Main Report (Part I). Unpublished Report, Ministry of Natural Resources and Environment Malaysia, 2009.
- 44 S. Harun, S. Al-Shami, R. Dambul, M. Mohamed and M. H. Abdullah, *Sains Malays.*, 2015, **44**(4), 545–558.
- 45 N. K. Abram, P. Xofis, J. Tzanopoulos, D. C. MacMillan, M. Ancrenaz, R. Chung, L. Peter, R. Ong, I. Lackman, B. Goossens, L. Ambu and A. T. Knight, *PLoS One*, 2014, **9**(6), e95388.
- 46 L. Yang and J. Hur, *Water Res.*, 2014, **59**, 80–89.
- 47 T. Ohno, *Environ. Sci. Technol.*, 2002, **36**(4), 742–746.
- 48 J. R. Helms, A. Stubbins, J. Ritchie, E. Minor, D. Kieber and K. Mopper, *Limnol. Oceanogr.*, 2008, **3**, 955–969.
- 49 P. Kowalczyk, M. J. Durako, H. Young, A. E. Kahn, W. J. Cooper and M. Gonsior, *Mar. Chem.*, 2009, **113**(3–4), 182–196.
- 50 X. Luciani, S. Mounier, H. Paraquetti, R. Redon, Y. Lucas, A. Bois, L. Lacerda, M. Raynaud and M. Ripert, *Mar. Environ. Res.*, 2008, **65**(2), 148–157.
- 51 C. Stedmon and S. Markager, *Limnol. Oceanogr.*, 2005, **50**, 1415–1426.
- 52 Y. Yamashita, L. J. Scinto, N. Maie and R. Jaffé, *Ecosystems*, 2010, **13**, 1006–1019.
- 53 X. Yao, Y. Zhang, G. Zhu, B. Qin, L. Feng, L. Cai and G. Gao, *Chemosphere*, 2011, **82**(2), 145–155.
- 54 P. Coble, *Mar. Chem.*, 1996, **51**(4), 325–346.
- 55 E. Parlanti, K. Wörz, L. Geoffroy and M. Lamotte, *Org. Geochem.*, 2000, **31**, 1765–1781.
- 56 C. A. Stedmon, S. Markager and R. Bro, *Mar. Chem.*, 2003, **82**, 239–254.
- 57 J. B. Fellman, E. Hood and R. G. M. Spencer, *Limnol. Oceanogr.*, 2010, **55**(6), 2452–2462.
- 58 J. R. Helms, J. Mao, A. Stubbins, K. Schmidt-Rohr, R. G. M. Spencer, P. J. Hernes and K. Mopper, *Aquat. Sci.*, 2014, **76**(3), 353–373.
- 59 K. R. Murphy, C. A. Stedmon, T. D. Waite and G. M. Ruiz, *Mar. Chem.*, 2008, **108**(1–2), 40–58.
- 60 Y. Zhang, M. A. van Dijk, M. Liu, G. Zhu and B. Qin, *Water Res.*, 2009, **43**(18), 4685–4697.
- 61 C. M. Sharpless and N. V. Blough, *Environ. Sci.: Processes Impacts*, 2014, **16**, 656–671.
- 62 J. Payne, *Sabah Biodiversity Conservation Project, Malaysia: Kinabatangan Multi Disciplinary Study*, Ministry of Tourism and Environmental Development, Sabah & Danish Co-operation for Environment and Development (DANCED), 1996.
- 63 R. Jaffe, K. M. Cawley and Y. Yamashita, Applications of Excitation Emission Matrix Fluorescence with Parallel Factor Analysis (EEM-PARAFAC) in Assessing Environmental Dynamics of Natural Dissolved Organic Matter (DOM) in Aquatic Environments: A Review, in *Advances in the Physicochemical Characterization of Dissolved Organic Matter: Impact on Natural and Engineered Systems*, ed. F. Rosario-Ortiz, Washington, DC, American Chemical Society, 2014, vol. 1160, pp. 27–73.
- 64 A. Baker and R. G. M. Spencer, *Sci. Total Environ.*, 2004, **333**, 217–232.
- 65 Y. Zhao, K. Song, Z. Wen, L. Li, S. Zang, T. Shao, S. Li and J. Du, *Biogeosciences Discuss*, 2015, **12**, 5725–5756.
- 66 N. Maie, Y. Yamashita, R. M. Cory, J. N. Boyer and R. Jaffe, *Appl. Geochem.*, 2012, **27**, 917–929.
- 67 A. M. Bass, M. I. Bird, M. J. Liddell and P. N. Nelson, *Limnol. Oceanogr.*, 2011, **11**, 399–405.
- 68 L. Lee-Cruz, D. P. Edwards, B. M. Tripathi and J. M. Adams, *Appl. Environ. Microbiol.*, 2013, **79**, 7290–7297.
- 69 P. Hill, V. Kristufek, L. Dijkhuizen, C. Boddy, D. Kroetsch and J. D. van Elsas, *Microb. Ecol.*, 2011, **61**, 286–302.
- 70 M. Wijayanti, A. Meryandini, A. T. Wahyudi and M. Yuhana, *Makara Journal of Science*, 2014, **18**, 71–78.
- 71 A. M. Hirsch and N. A. Fujishige, Molecular Signals and Receptors: Communication between Nitrogen-fixing Bacteria and their Plant Hosts, in *Biocommunication of Plants: Signaling and Communication in Plants*, ed. Witzany G. and Baluska F., Springer-Verlag Berlin, Heidelberg, 2012, vol. 14, pp. 255–280.
- 72 P. Paganin, S. Tabacchioni and L. Chiarini, *Cent. Eur. J. Biol.*, 2011, **6**, 997–1005.
- 73 A. Howard, M. O'Donoghue, A. Feeney and R. D. Sleator, *Virulence*, 2012, **3**, 243–250.
- 74 D. Abdel-El-Haleem, *Afr. J. Biotechnol.*, 2003, **2**(4), 71–74.
- 75 M. Z. Azrina, C. K. Yap, A. Rahim Ismail, A. Ismil and S. G. Tan, *Ecotoxicol. Environ. Saf.*, 2006, **64**(3), 337–347.
- 76 A. Baker, E. Tipping, S. Thacker and D. Gondar, *Chemosphere*, 2008, **73**(11), 1765–1772.
- 77 C. N. Jex, G. H. Pate, A. J. Blyth, R. G. M. Spencer, P. J. Hernes, S. J. Khan and A. Baker, *Quat. Sci. Rev.*, 2014, **87**, 46–59.
- 78 K. Y. Lee, M. I. Syakir, I. D. Clark and J. Veizer, *Aquat. Geochem.*, 2013, **19**(5–6), 443–475.
- 79 D. B. Nedwell, T. H. Blackburn and W. J. Wiebe, *Mar. Ecol.: Prog. Ser.*, 1994, **110**, 223–231.
- 80 N. Maie, N. M. Scully, O. Pisani and R. Jaffe, *Water Res.*, 2007, **41**, 563–570.
- 81 K. Sahoo and N. K. Dhal, *Indian J. Mar. Sci.*, 2009, **38**, 249–256.
- 82 J. A. Aitkenhead-Peterson, W. H. McDowell and J. C. Neff, Sources, production, and regulation of allochthonous DOM inputs to surface waters, in *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, ed. S. E. G. Findlay and R. L. Sinsabaugh, Elsevier, New York, 2003, pp. 25–70.
- 83 R. F. Hughes, J. B. Kauffman and V. J. Jaramillo, *Ecology*, 1999, **80**, 1892–1907.
- 84 J. L. Schedlbauer and K. L. Kavanagh, *For. Ecol. Manage.*, 2008, **255**, 1326–1335.
- 85 M. van Breugel, J. Ransijn, D. Craven, F. Bongers and J. S. Hall, *For. Ecol. Manage.*, 2011, **262**(8), 1648–1657.
- 86 S. Brown and A. E. Lugo, *J. Trop. Ecol.*, 1990, **6**, 1–32.
- 87 C. E. M. Silva, J. F. C. Goncalves and E. G. Alves, *Photosynthetica*, 2011, **49**(2), 246–252.