

ISOTOPIC ($\delta^{13}\text{C}$ AND $\delta^{15}\text{N}$) VARIATIONS IN TROPICAL RIVER SEDIMENTS OF KELANTAN, MALAYSIA: A RECONNAISSANCE STUDY OF LAND USE IMPACT TO THE WATERSHED

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Abstract. Intensification of sedimentation process has resulted in shallower river, thus increasing their vulnerability to natural hazards (i.e. climate change, floods). Considering the impact of soil erosion to the sedimentation, identification of the main source of erosion is critical to watershed management. Stable isotope of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) were carried out in Kelantan catchment. Results from $\delta^{13}\text{C}$ showed that C_3 type plant represents as major plant (-29.10‰ to -23.60‰) in the river. While for $\delta^{15}\text{N}$, the isotopic variations demonstrate distinct pattern of dry (Southwest Monsoon, SWM) and wet (Northeast Monsoon, NEM) seasons, suggesting significant pollutants washout from terrestrial (due to agricultural activities) to the water bodies. In addition, the Kelantan river system is an autochthonous as determined by carbon to nitrogen (C:N) ratio. Essentially, this study will serve as a precursor of future study to understand the impact of anthropogenic activities on carbon and nitrogen cycles in tropical catchment.

Keywords: *erosion, sedimentation, carbon, nitrogen, cycle, tropical, deforestation, stable isotopes, agriculture, land use, C_3 plants, C:N ratio, water quality, sediment yield*

Introduction

Kelantan basin is located in northeast of Peninsular Malaysia. The main river is known as Kelantan river with the total length of 248 km, with draining that flows northwards in the direction of the South China Sea. The catchment area is approximately 11,900 km² (Yen and Rohasliney, 2013) occupying more than 85% of Kelantan state. Along the river, the topography is comprised of rain forested hills, lowland forests and limestone caves. Currently, the type of activities that occur around the area include deforestation, vegetation and urbanization (Basarudin et al., 2014).

Land use activities that degrade natural landscape through clearing of tropical rainforests, unsustainable agriculture and rapid urban expansion have had significant impacts to hydrological conditions and ecological processes (Adnan et al., 2014; Hadi et

al., 2017) in the Kelantan watershed. It is also vulnerable to climate change (Huang and Lo, 2015; Zafirah et al., 2017). Changes in geographical area leads to alteration of hydrological process. Impact of various land use activities include flowing of fine sediment into the river, due to soil surface erosion (Chen et al., 2015). Soil erosion is the result of overland flow as rainfall occurs, which in turn results in serious environmental problem if not properly controlled (Mahabaleshwara and Nagabhushan, 2014). Increasing sedimentation in the river can cause extensive catchment flooding due to overflow at the river, water pollution and poor drainage system (Kithiia, 2012; Zafirah et al., 2017). Mitigation process is often delayed due to lack of capability to identify the cause and source of erosion. This paper will discuss the application of environmental isotopes technique to identify the source of erosion in Kelantan catchment. Sediments in the Kelantan rivers were collected and analyzed by using Isotopic Ratio Mass Spectrometer (IRMS) to measure the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and Perkin Elmer 2400 Series II CHN Elemental Analyzer for C:N analysis in the sample.

Soil erosion and sedimentation mechanism

Soil erosion requires three steps to trigger the process: (i) detachment, (ii) transport and (iii) deposition (Pidwirny, 2008; Zafirah et al., 2017). Detachment process is defined as a particle that is disengaged from the main subject. It requires the procedure of breaking the bond that binds the particle together. Factors of weathering in physical, chemical and biological state causes the bond particle in the subject to weaken and detach.

It is then followed by transportation process, whereby the particle moves with the presence of the medium or agent at high velocity. This step depends on mass of particle, size, shape, surface configuration and medium type to undergo the process (Pidwirny, 2008; Safaei et al., 2014). Finally, it ends with deposition process, whereby the velocity of the medium reduces or increases in particle resistance (Stephen, 2016).

Sedimentation is a result of erosion process where it refers to the accumulation of particle that is carried out by a medium such as water, wind or ice for transportation. Sedimentation process is a natural process, although it may be influenced by anthropogenic factors. Transported sediments can be chemical, organic material or inorganic, mineral matter and pollutants. Increase in sediments and siltation have threatened the surrounding ecology, irrigation of river and aquatic habitat (Huggins et al., 2007; Kjelland et al., 2015). It also makes the river to become more shallow and easier to overflow.

Stable isotope as tool in fingerprint detection

Stable isotope analysis is one of the potential tool to detect and trace the fingerprint of organic matter in the environment (Liu et al., 2017) such as aquatic, water and sediment, terrestrial, soil, plant and others. The stable isotope carbon and nitrogen were used to analyze the values, therefore determining the categories and understanding the process of sedimentation in the catchment (Tue et al., 2011). Carbon isotope were used to differentiate the type of plants present in the selected area. $\delta^{13}\text{C}$ have been used to determine the C_3 and C_4 plants, which indicates the photosynthesis process that plants undergo (Boullion et al., 2003a; Tue et al., 2011).

The ranges of C_3 plants are from -32 to -22‰ and -16 to -9 for C_4 (Medina et al., 1999; Kendall et al., 2001; Schaal et al., 2008; Kohn, 2010), hence it is useful as an

ecosystem components tracer (Bouillon and Boschker 2006; Werner and Máguas, 2010; Gilbert et al., 2012). Variations of $\delta^{13}\text{C}$ provide clues for further investigation on environmental condition and land use activities in the watershed (Cravotta, 2001; Fushan et al., 2014).

Stable nitrogen isotope is commonly used to detect the sources of pollution, and it is made up of several of classes such as soil organics, fertilizers, animal or sewage waste and precipitation (Heaton, 1986; Lim et al., 2010; Zhao et al., 2016). Different of $\delta^{15}\text{N}$ is determined by fractionation process, which consist of four types, including equilibrium, kinetic, mass independent or transient kinetic isotope fractionation (Heaton, 1986; Dähnke and Thamdrup, 2013; Ryabenko, 2013). From different values, it will then be used to classify the possible sources based on the fingerprint, as well as the activities nearby the sampling location. Therefore, this approach is used to identify the possible sources of sedimentation in Kelantan catchments.

Material and Methods

Study area

Malaysia is located near the equator and is one of the tropical countries that is hot and humid all year round. The average temperature is about 27°C and receives rainfall on average 2500 mm annually. Peninsular climate differs from Malaysian Borneo as the peninsular is directly affected by wind and is exposed to the El Niño effect. The phenomena cause dry season as it reduces the amount of rainfall. Climate change has a significant impact on Malaysia as it is crucial in determining the sea level as well as amount of precipitation, which results either in drought or extensive rainfall, which increases the flood risks. In addition, Malaysia also experiences monsoon seasons, Northeast Monsoon (NEM) from November to March and Southeast Monsoon (SEM) from May to September. Monsoon occurs due to atmospheric pressure patterns in Southeast Asia that results from different pressure between Asia continent and land mass in Australia, known as Inter-Tropical Convergence Zone (ITCZ). NEM hit Peninsular Malaysia during northern hemisphere during winter seasons, together with high pressure from China and low pressure in Australia thus combination of forces the ITCZ in south areas. Opposite circulation occurs when northern hemisphere experience summer seasons, low pressure in Asia and high pressure in Australia forcing the ITCZ in northwards resulting SWM in Peninsular Malaysia. Both seasons, NEM and SWM play the main factors in determining the amount of precipitation in Malaysia (Loo et al., 2015). However, between these two monsoons, NEM give extra rainfall events compared to SWM (Suhaila et al., 2010).

This study focuses in Kelantan catchment area, located at east coast of Peninsular Malaysia (*Figure 1*). The Peninsular Malaysia lies between 1° and 7° North and 99° to 105° East, extending 748 km SSE-NNW and 322 km ENE-WSW. The landscapes of peninsular at inland areas are mainly from denudation terrains of bedrocks, resulting from weathering and erosion process. The range of Titiwangsa (highland) located somewhat at the middle of Peninsular region, separates the eastern and western part of the region. In addition, it is composed mainly of granite with some regions of metasedimentary rocks (Ishak, 2014). These series of mountain ranges play a crucial role in creating the streams and rivers network pattern (Hutchison and Tan, 2009).

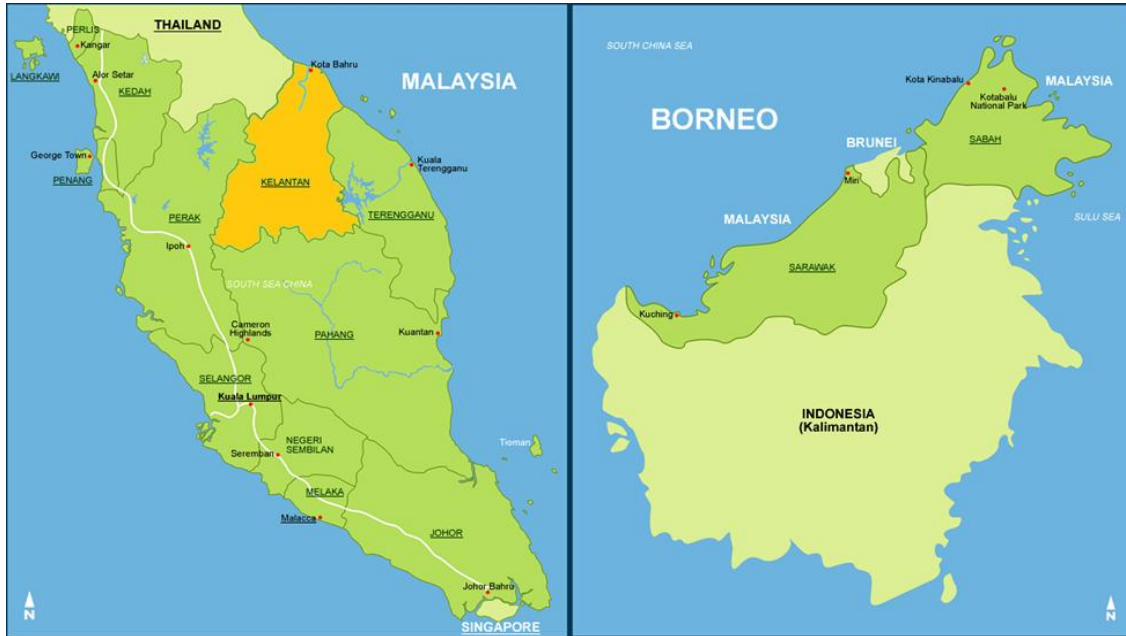


Figure 1. Malaysia map (World Map, 2017)

Kelantan Basin

The study area covers the catchment around Kelantan state which is located in the northeast of Peninsular Malaysia lies between $4^{\circ} 40'$ and $6^{\circ} 12'$ North and $101^{\circ} 20'$ and $102^{\circ} 20'$ East (*Figure 2*). Kelantan catchment comprises an area about $11,900 \text{ km}^2$, (Yen and Rohasline, 2013). Three main rivers at Gua Musang District which are Nenggiri River, Betis River and Broke River were selected. The dominant land use of this area is agriculture, native forest and countryside native. The next river is Lebir River located at Kuala Krai district. Pergau River which is located in Jeli district, has one of the highest waterfalls in Southeast Asia. The river merges with Galas River. The land use of this area comprises of croplands and new settlements. Kelantan river, which is the third longest river in Peninsular Malaysia, is also included in this study.

Climate and hydrology of Kelantan Basin

The regional climate of Kelantan state has temperatures ranging between 21 to 32°C and recurrent rain throughout the year. However, it is exposed with extra rainfall in Northeast Monsoon from November to March every year. The average rainfall is about 2062 to 2543 mm per year and humidity is constantly high on the lowlands ranging between 82% and 86% annually (Irwan et al., 2013).

Vegetation and land use in Kelantan watershed

Majority of Kelantan's land cover consist of forest. Its economy constitutes mainly from agriculture industries dominated by oil palm plantation, rubber, paddy and other cash crops.

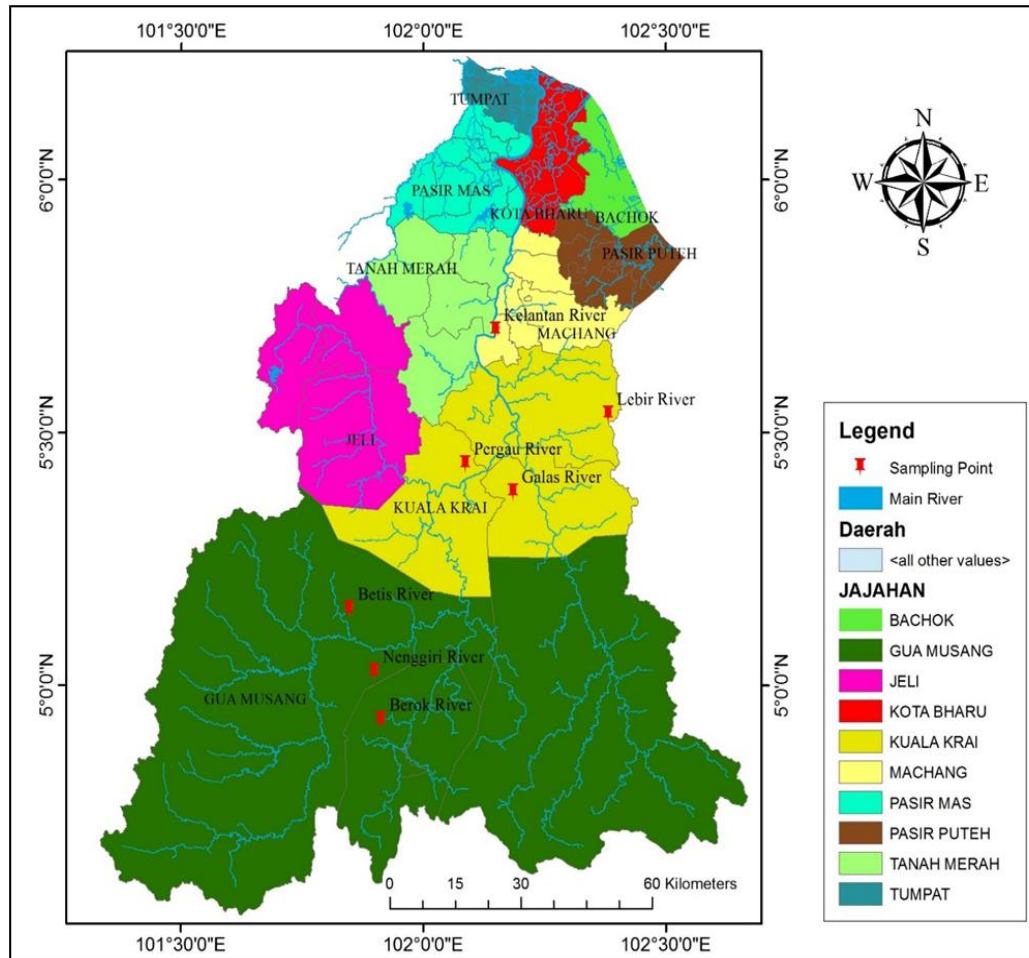


Figure 2. Map of the Kelantan river and study sites

Sample collection and analytical procedures

Sediment sample collection was carried out in July 2015 and January 2016. The sediments were sampled at seven selected stations; Broke, Betis, Nenggiri, Lebir, Galas, Pergau and Kelantan river. The sediment was sampled at 10” of top sediment, with approximately 100 g per sediment sample by using grab sampler and subsequently packed into zipper bag, and is preserved in a cold storage box. Samples were stored in the laboratory accordingly (Shanbehzadeh et al., 2014).

Sample preparation

In the laboratory, 50 g of sediment samples were washed by using 10% of hydrochloric acid prior to remove carbonates (Kennedy et al., 2005) and rinsed with distilled water for three times. The samples were then dried at 80 to 90 °C to remove moisture. The subsample was then grounded into powder form. Grinding was performed using a mortar and pestle. The sample were finally sieved through a 425 μm sieve and stored in glass jars.

Stable isotope analysis

Each sediment sample was weighed into small tin capsule (8 x 5 mm) for 12mg in triplicates. The sample was folded and compressed into a tight ball before being loaded into an auto-sampler. All the replicated samples were analysed for stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic composition using Flash EA 2000 elemental analyser (ThermoScientific, Waltham, MA) coupled to a Delta V Advantage isotope ratio mass spectrometer (Thermo, Milan, Italy).

Raw isotope ratios from the analysis were normalized to the international scales using USGS-40 and USGS-41 reference materials (~0.5 mg, respectively) assayed with the unknown samples. For quality control material, Urea (IVA-Analysentechnik GmbH & Co., Germany) was used to correct for drift. It was measured for every 12 samples with known values of $\delta^{13}\text{C} = -40.81\text{‰}$ and $\delta^{15}\text{N} = -0.49\text{‰}$. Variations in stable isotope ratios were reported as parts per thousand (‰) deviations from internationally accepted standards which are Vienna Pee Dee Belemnite (VPDB) for carbon, atmospheric nitrogen (AIR) for nitrogen, in the delta (δ) notation.

The δ notation is defined using the following Equation (1):

$$\delta (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \quad (\text{Eq.1})$$

where R_{sample} is the isotope ratio ($^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) of the sample, and R_{standard} is the isotopic ratio of the international reference materials.

Carbon Nitrogen Ratio (C:N Ratio) Analysis

Same as isotope analysis, each sediment sample was weighed into small tin capsule (8 x 5 mm) for 2 mg in triplicates. The sample was folded and compressed into a tight ball before being loaded into an auto-sampler. All the replicated samples were analyzed for carbon and nitrogen composition using Perkin Elmer 2400 Series II CHN Elemental Analyzer (Perkin Elmer).

Samples were introduced from an autosampler into a combustion furnace with a temperature of 925°C. The resulting gases (CO_2 , NO_x , and H_2O) were passed through combustion and reduction columns, mixed, and separated through thermal conductivity detector (TCD) gas chromatography column (Stephen et al., 2011). Acetanilide standards were run every triplicates samples to ensure proper instrument operation.

The C:N ratios is defined using the following Equation (2):

$$\frac{C}{N} \text{ ratio} = \left(\frac{\%C/\%N}{(14/12)} \right) \quad (\text{Eq.2})$$

Water quality and sediment yields data

Water quality data (2004 - 2014) were provided by Department of Environment (DOE). The parameters include chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), pH, dissolved oxygen (DO), and Ammoniacal nitrogen ($\text{NH}_3\text{-N}$). Besides, data of sediment yields in Kelantan were also retrieved from Department of Irrigation and Drainage (DID) Kelantan. The data is a 30-year dataset that ranges from 1980 to 2009. Both secondary data were analyzed using Principal Component Analysis (PCA).

Results and Discussion

Stable isotopes analysis of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediment at different catchment area in Kelantan

Plant types can be divided into three categories; C_3 , C_4 and Crassulacean acid metabolism (CAM) based on carbon fixation of carbon dioxide during photosynthesis process. Every plant group will produce different $\delta^{13}\text{C}$ signatures of the organic carbon. C_3 plant is ranged from approximately -34‰ to -23‰, C_4 -18‰ to -12‰ and CAM -32‰ to -12‰, (Brand, 1996; Faure and Mensing, 2005). In Malaysia, there are less number of CAM plants, as it is usually found in dry or arid condition (Masrahi et al., 2012), which allows stomata to remain shut during the day.

A distinct inclination of $\delta^{13}\text{C}$ sediment values emerged in all seven studied locations were plotted in *Figure 3*. In overall, the mean value for $\delta^{13}\text{C}$ for July was $-27.05 \pm 1.02\text{‰}$ followed by January, $-26.80 \pm 1.76\text{‰}$ (*Table 1*). The results from both dry and wet seasons in Kelantan catchment showed that the value ranged from -29.10‰ to -23.60‰, which represent C_3 type plants suggested that terrestrial plants (allochthonous) were the main source of sediment contribution in all seven rivers.

The mean of $\delta^{13}\text{C}$ at Brok samples is $-26.81 \pm 1.46\text{‰}$ and Betis is $-24.90 \pm 0.98\text{‰}$ (*Table 1*). Both are located at Gua Musang district. The major type of vegetation here is rubber (*Hevea brasiliensis*) (Da Matta et al., 2001), tapioca (*Manihot esculenta*) (Calatayud et al., 2002) and banana (*Musa spp.*) (Janssens et al., 2009), all representing C_3 type plants. Nenggiri is the main river of Betis and Brok tributaries and average of the $\delta^{13}\text{C}$ in sediments is $-26.08 \pm 1.28\text{‰}$ (*Table 1*). Galas and Pergau have almost the same average of $\delta^{13}\text{C}$ in sediments, $-27.36 \pm 0.60\text{‰}$ and $-27.12 \pm 0.84\text{‰}$ (*Table 1*) respectively. The rivers are located in Dabong, south of Kelantan. Rubber estate appears as the main land use activity, followed by small farming of banana and tapioca.

Lebir River which is located in Kuala Krai district, with average of $\delta^{13}\text{C}$ is $-27.99 \pm 0.88\text{‰}$ (*Table 1*), of which palm oil plantation is the main land use activity representing approximately 80% of the catchment area. According to Lamade et al., (2009), $\delta^{13}\text{C}$ of oil palm (*Elaeis guineensis*) leaves is around $\approx -27\text{‰}$, which is also categorized as a C_3 plant type. For Kelantan river sediments located at the downstream catchment, the mean value of $\delta^{13}\text{C}$ is $-28.22 \pm 0.82\text{‰}$ (*Table 1*). Small farming activities like banana, cocoa, tapioca and rubber estate are present around the catchment area.

Table 1. *Isotopic composition of stable isotope $\delta^{13}\text{C}$ in sediment*

Stable Isotope $\delta^{13}\text{C}$ [‰]								
Season	Rivers							Average season
	Broke	Betis	Nenggiri	Galas	Pergau	Lebir	Kelantan	
Jul (SEM)	-25.85	-25.71	-27.19	-28.31	-28.21	-26.48	-27.42	-27.05 ± 1.02
	-26.79	-24.15	-26.43	-27.07	-27.53	-27.51	-27.51	
	-28.07	-25.81	-27.84	-26.94	-27.79	-27.96	-27.48	
Jan (NEM)	-25.55	-23.60	-24.88	-27.75	-26.10	-28.68	-28.88	-26.80 ± 1.76
	-25.56	-25.78	-24.74	-26.65	-26.72	-28.65	-28.90	
	-29.05	-24.34	-25.42	-27.42	-26.40	-28.66	-29.10	
Average	-26.81 ± 1.46	-24.90 ± 0.98	-26.08 ± 1.28	-27.36 ± 0.60	-27.12 ± 0.84	-27.99 ± 0.88	-28.22 ± 0.82	

Cocoa (*Theobroma cacao*) (Gattward et al., 2012) also represents the C_3 type plant range. However, the result is still tentative, thus, require further investigation using advance technique such as compound specific isotope analysis (CSIA).

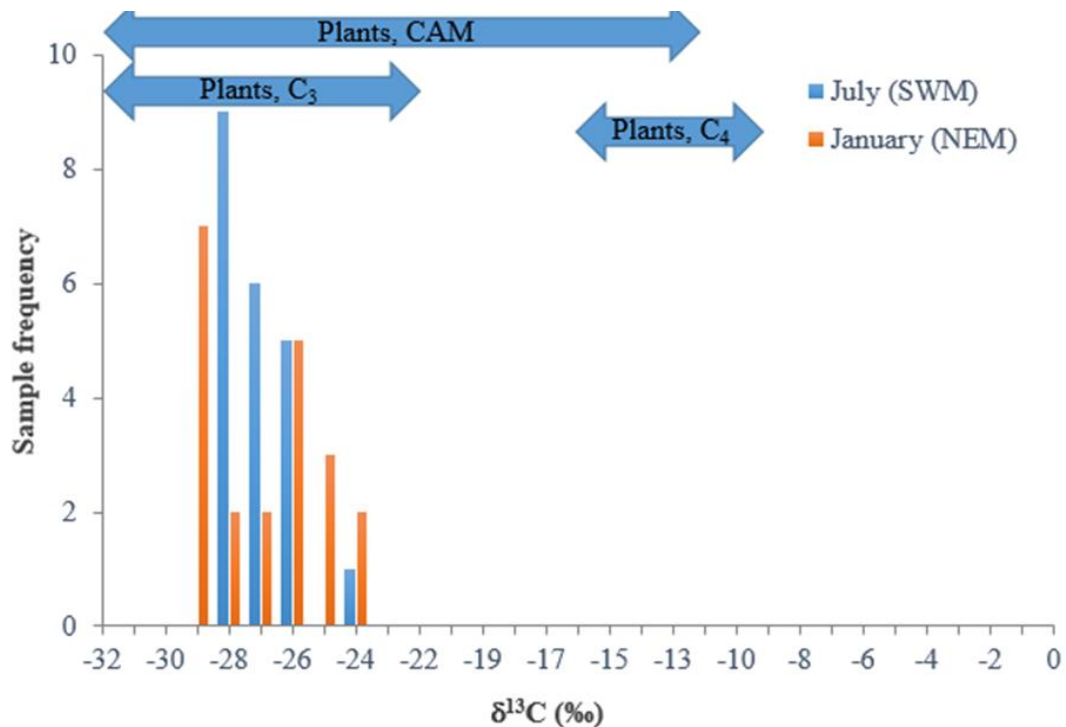


Figure 3. Bar frequency plot $\delta^{13}\text{C}$ [‰] sediments in two different seasons

The range of $\delta^{13}\text{C}$ could reflect sources of sedimentation, where most of the terrestrial plant that are present along the studied locations, are mainly from C_3 type plant. Theoretically, variations of C_3 values were due to kinetic isotope fractionation process, which includes microbial respiration of organic carbon, assimilation process of residual materials (Thornton and McManus, 1994; Teranes and Bernasconi, 2005) and changes in global carbon cycle (Oehlert and Swart, 2014), thus deposited in the water bodies.

The $\delta^{15}\text{N}$ sediment values at different study areas were presented in Figure 4, with information on organic content resulted from decomposition process. In general, the average value for $\delta^{15}\text{N}$ in July (SWM) and January (NEM) were $+0.65 \pm 2.44\text{‰}$ and $+3.35 \pm 1.02\text{‰}$ (Table 2) respectively. Both results of the two different seasons showed that $\delta^{15}\text{N}$ were ranged from -3.98‰ to $+5.25\text{‰}$ (Table 2), which demonstrated the dynamic of N cycle.

The average values of $\delta^{15}\text{N}$ for Brok, Betis, Nenggiri are $1.48 \pm 2.48\text{‰}$, $2.26 \pm 1.82\text{‰}$ and $0.70 \pm 2.74\text{‰}$ (Table 2), respectively, enriched in $\delta^{15}\text{N}$. The upstream of Betis River is flowing from Lojing and merges with Brok River at the confluence of Nenggiri River. Richness of $\delta^{15}\text{N}$ indicates more nitrogen source mainly from anthropogenic activities (Dolenec et al., 2006; Brahney et al., 2014). The average values of $\delta^{15}\text{N}$ for Galas River, Pergau River and Lebir River are $1.51 \pm 2.63\text{‰}$, $2.50 \pm 0.90\text{‰}$ and $3.45 \pm 2.63\text{‰}$ (Table 3) respectively. Matured oil palm and rubber plantations are the major land use activities around the catchment areas.

Table 2. Isotopic composition of stable isotope $\delta^{15}\text{N}$ in sediment

Stable Isotope $\delta^{15}\text{N}$ [‰]								
Season	Rivers							Average season
	Broke	Betis	Nenggiri	Galas	Pergau	Lebir	Kelantan	
Jul (SEM)	1.41	1.82	-1.27	1.25	3.71	-1.45	-1.98	$+0.65 \pm 2.44$
	-2.73	5.25	-3.98	-2.94	1.90	2.33	0.67	
	0.09	-0.29	1.92	0.37	1.19	4.82	1.62	
Jan (NEM)	3.31	2.42	2.89	3.47	3.21	4.87	4.17	$+3.35 \pm 1.02$
	2.96	2.82	2.47	4.48	2.62	5.03	4.31	
	3.82	1.54	2.19	2.42	2.40	5.14	3.81	
Average	1.48 ± 2.48	2.26 ± 1.82	0.70 ± 2.74	1.51 ± 2.63	2.50 ± 0.90	3.45 ± 2.63	2.10 ± 2.49	

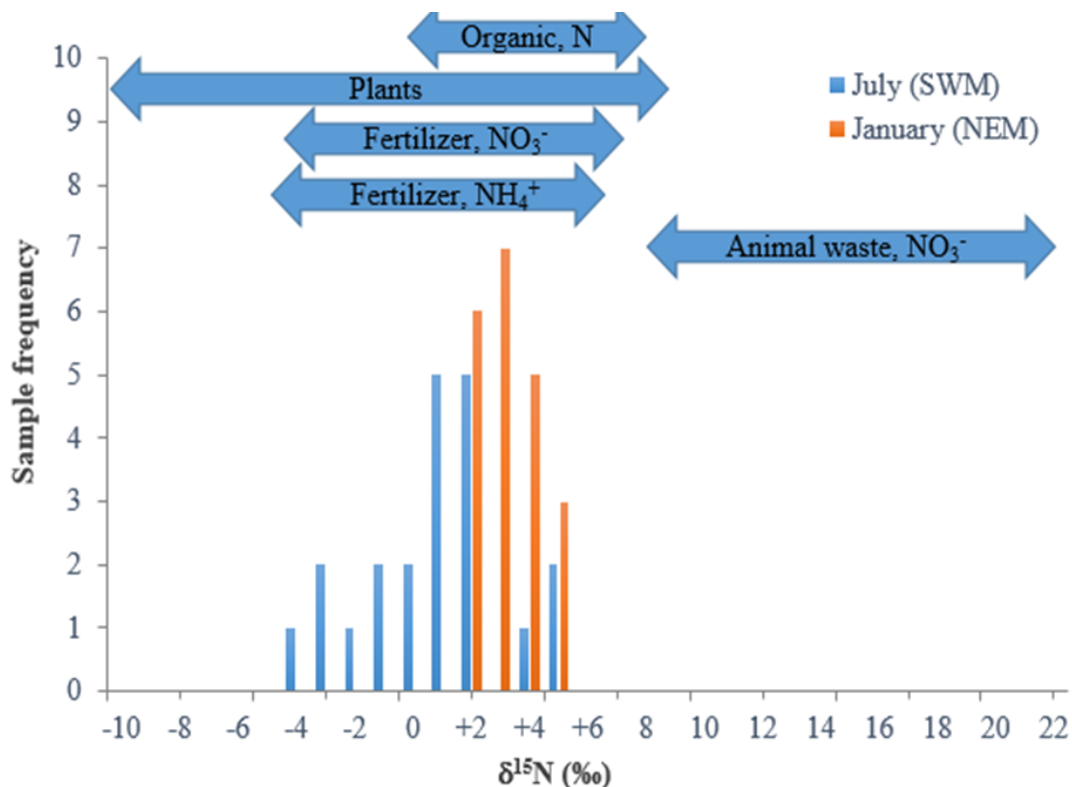


Figure 4. Bar frequency $\delta^{15}\text{N}$ [‰] sediments at two different seasons, Southwest Monsoon (July) and Northeast Monsoon (January)

Kelantan river, which is situated at the downstream area, have average values of $\delta^{15}\text{N}$ $2.10 \pm 2.49\text{‰}$ (Table 2). The villages around the catchment may affect the nitrogen concentration in the sediments due to all the wash out from upstream river. Kelantan river exposed by many land use activities such as mining activity and development around the river area for new residential and towns, thus, posing significant impact on river sedimentation.

Distinct of $\delta^{15}\text{N}$ values are due to kinetic isotopic reaction and together with unidirectional reaction in hydrosphere cycle perform by bacteria activities (Heaton, 1986). The overlapping of $\delta^{15}\text{N}$ values reflect complex fractionation caused by multiple

processes (mineralization, nitrification, plant uptake and denitrification) in nitrogen cycle (Lajtha and Schlesinger, 1986; Ryabenko, 2013).

Fertilizer appears as one of the main “fingerprints” in sediment samples. Both nitrate (NO_3^-) and ammonia (NH_4^+) are common results from industrial fixation of atmospheric nitrogen via measurable process of isotopic fractionation, whereby $\delta^{15}\text{N}$ depletes (Gunter, 1986). Meanwhile, organic nitrogen in soil undergo mineralization process that causes it to fractionate. It involves steps that can fractionate it and change $\delta^{15}\text{N}$ values in favorable condition with the aid of bacteria activities (Heaton, 1986).

The isotopic fingerprints of $\delta^{15}\text{N}$ (*Figure 4*) in sediments (+0 to +9) represent the Soil Organic Matter (SOM), suggesting significant erosion (due to land clearing) during the NEM (An et al., 2008; Chakravarty et al., 2012; Ickowitz et al., 2015).

C:N ratios in sediments

C:N ratio in sediments was analyzed to complement the terrestrial and organic matter sources characterized by $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Finlay and Kendall, 2007; Sanderman et al., 2015). *Figure 5* shows a biplot $\delta^{13}\text{C}$ and C:N ratio presenting various types of terrestrial and aquatic organic matter overlapping from sediment collections in Kelantan. There is absence of C_3 type plant from terrestrial source, which constitutes a ratio of more than 15. However, although the “fingerprint” of terrestrial plants might be present, in our case, the allochthonous component was not clearly identified, perhaps, due to the catchment settings (climate, hydrology, etc) that may speed up the rate of decomposition process in water body (McGill and Cole, 1981). Besides, the C:N ratio too can be changed due to degradation of organic matter during sediment diagenesis (Gao et al., 2012).

In overall, about 95% of C:N ratio were determined <12 (*Figure 5*), indicating the source of sedimentation particularly from aquatic part which is autochthonous (Tue et al., 2011). Even though it is believed that high turbidity and sedimentation in Kelantan catchment causes absence of aquatic macrophytes and seagrass, microalgae were present as autochthonous input. Besides that, it is evident that there are terrestrial, allochthonous input from the river being transported, which is phytoplankton (Tue et al., 2011). The C:N ratios value tend to decrease over time as degradation process release carbon dioxide (CO_2) or methane (CH_4), ammonia and other microbially-associated nitrogen (Gao et al., 2012). Additionally, low of C:N ratio is caused by abundance of ammonium ions is absorbed into clay minerals (Rumolo et al., 2011).

C:N ratio shows higher in Nenggiri and Kelantan river with a slightly change in $\delta^{13}\text{C}$ range suggest that post depositional decay in organic sedimentary, might be due to rapid sedimentation process (Sanderman et al., 2015). From this biplot, it shows that the source of sediments was from a mixture of C_3 from terrestrial part, phytoplankton and algae. The input from outside is seemed superimpose to the large river, where it does not give such a vast impact to the ecosystem.

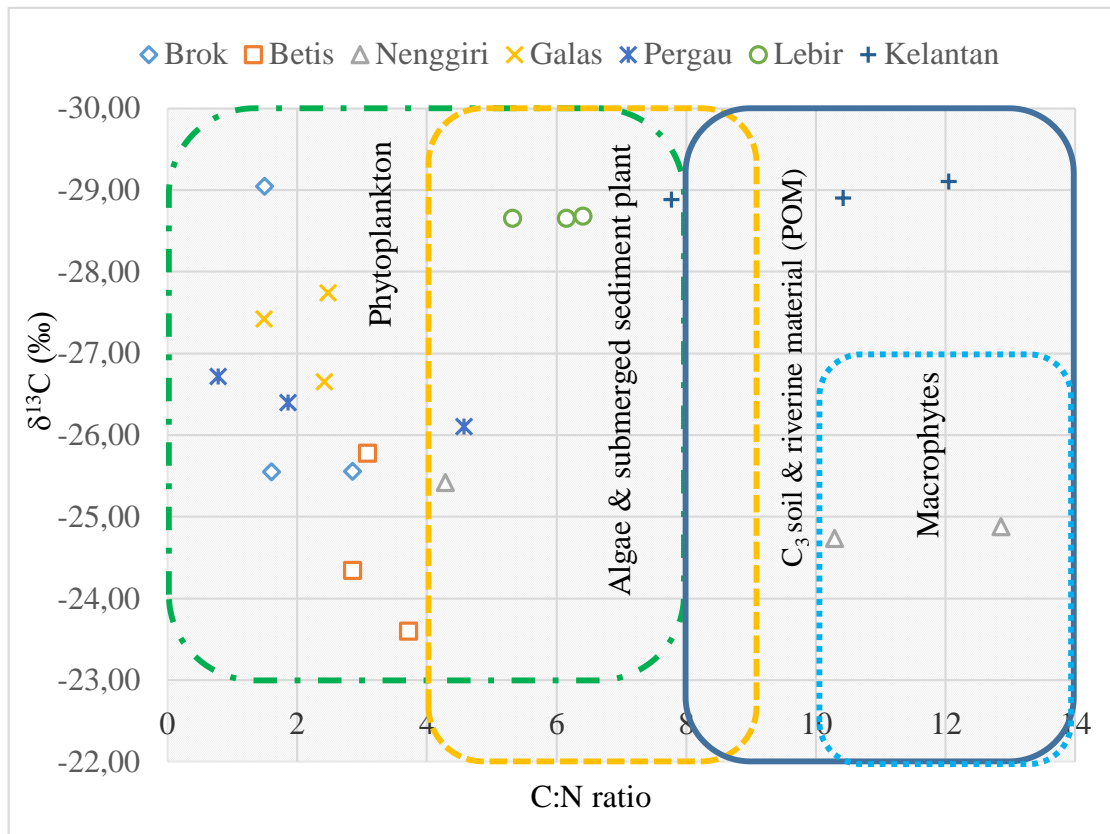


Figure 5. The $\delta^{13}\text{C}$ and C:N ratio of various types of terrestrial and aquatic organic matter overlap by the sediment range from Kelantan catchments

Sediment accumulation in Kelantan river networks

Sedimentation in river is one of major flood factors in Kelantan's watershed. As mentioned in methodology, the sediment yield data were analyzed using multivariate principal component analysis (PCA) to determine major factors that are responsible for the sediment accumulation in water bodies. PCA is a technique to reduce large data into small variable number to summarize the data analysis (Pallant, 2001; Wuttichaikitcharoen and Babel, 2014).

Table 3. Proposed factor of sediment yields in Kelantan watershed

Sediment yield	Kelantan catchment	F1	F2
	Component	All	Oct, Nov, Dec
	Eigenvalue	9.66	2.31
	Variability (%)	80.54	19.24
	Cumulative (%)	80.54	99.77
	Factor	Climate	Northeast Monsoon

PCA for sediment yields datasets (Table 3) shows that the main component for factor loading (Table 4) are characterized by two components with Eigenvalue > 1, which consist of all months throughout the year and component two only on October, November and December. This explains 99% (Figure 6) of cumulative variability respectively, reflecting seasonal factor whereby Northeast Monsoon in component

factor two in agreement with Butt et al. (2011) and Hua (2014). The reason is because during this period, east coast states such as Kelantan receives extra rainfall, thus triggering erosion process, which results in sediments transport into the water.

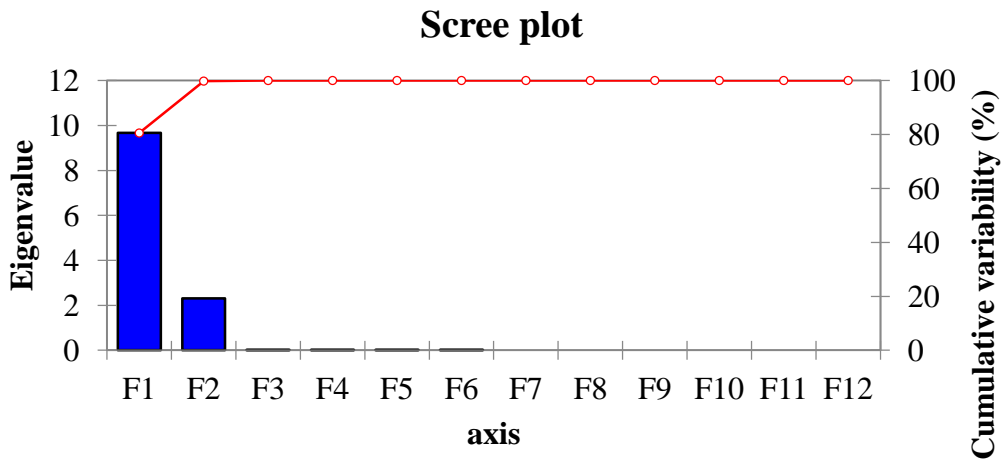


Figure 6. Scree plot Eigenvalue for sediment yield in Kelantan catchment

Table 4. Factor loadings of sediment yields over two principal component

Months	F1	F
Jan	0.96	-0.27
Feb	0.96	-0.27
Mar	0.96	-0.26
Apr	0.96	-0.27
May	0.97	-0.25
Jun	0.96	-0.26
Jul	0.97	-0.25
Aug	0.99	-0.13
Sep	0.89	0.46
Oct	0.67	0.74
Nov	0.72	0.70
Dec	0.66	0.75

Moreover, sediments yield show significant results in Nenggiri Rivers, suggesting rampant land use activities which degrades the soil along the river banks. Logging and deforestation activities at upstream of Gua Musang is one of the evidences showing unsustainable land use activities that destroys the ecosystem services (Adnan and Atkinson, 2011). Anthropogenic activities such as deforestation and agriculture are the main factors of erosion process that contributes to sedimentation. Sand mining is also identified as one of the reasons that intensifies sedimentation in Kelantan river (Syahreza, 2012).

Water quality data (Principal Component Analysis, PCA)

Sediment transport have had tremendous impact on water quality of Kelantan river. A water quality set of data provided by Department of Environment (DOE) since 2004 to 2014 was analyzed by using PCA to determine major factors that responsible for the

degradation of river networks in Kelantan catchment (Berok, Betis, Galas, Kelantan, Lebir, Nenggiri, Pergau).

PCA for water quality parameters datasets (*Table 5*) shows the main factor that plays a crucial role in determining the quality data of Kelantan catchment, which are characterized by two factor components with Eigenvalue > 1 . According to Chatfield and Collin (1980) assumption, stated that components with eigenvalue less than 1 should be eliminated. This explains 51% (*Figure 7*) of total variance, due to anthropogenic factor, contributed by urbanization along the river (Ishak, 2014) with superimpose of natural factor.

Principal component analysis results show factor loadings in *Table 6*. Based on these parameters loading, the variables are grouped accordingly with their factors group. Factor loading with value more or equal than 0.60 were bold in the table below. Factor loading 1 consists of three parameters, which are Chemical oxygen demand (COD), Biochemical oxygen demand (BOD) and Suspended solid (SS). While Factor loading 2 are dissolved oxygen (DO) and pH unit followed by Factor loading 3 Ammoniacal nitrogen ($\text{NH}_3\text{-N}$), Factor loading 4 dissolved oxygen (DO) and Factor loading 5 Suspended solid (SS).

Results showed that chemical oxygen demand (COD) is the most significant parameter in determining water quality of Kelantan river, which reflects the parameters to measure oxygen required to oxidize chemical substance through chemical process (Talib and Amat, 2012). According to Northeast Georgia Regional Development Center, (2001) COD values always have high value compared to BOD. This is because COD measurement only requires a few hours while BOD measurement can lead up to five days. Both COD and BOD are correlated process to each other as oxidation process that occurs during organic matter break down to a more stable form (Talib and Amat, 2012).

The second factor that contributes to COD value is phosphate concentration, as they are directly proportional to each other (Talib and Amat, 2012). The COD value will be high as phosphate concentration increases. The main source of phosphorus is mainly from agriculture fertilizer, manure industrial effluent and sewage. The major factor that causes high concentration of phosphorus in the river is soil erosion especially during flooding event (USGS, 2016).

Furthermore, as BOD is correlated with COD, it suggests that the other factor that influence BOD value is organic waste and detritus from terrestrial part, agriculture and also urban runoff, (Northeast Georgia Regional Development Center, 2001). These are also the same contributing factors of COD. Both COD and BOD play a major role in the deterioration of Kelantan's water quality.

Table 5. Proposed factor of water parameter in Kelantan catchment

Water quality	Kelantan catchment	F1	F2
	Component	COD, BOD, SS	pH, DO
	Eigenvalue	1.90	1.17
	Variability (%)	31.68	19.48
	Cumulative (%)	31.68	51.17
	Factor	Anthropogenic	Anthropogenic

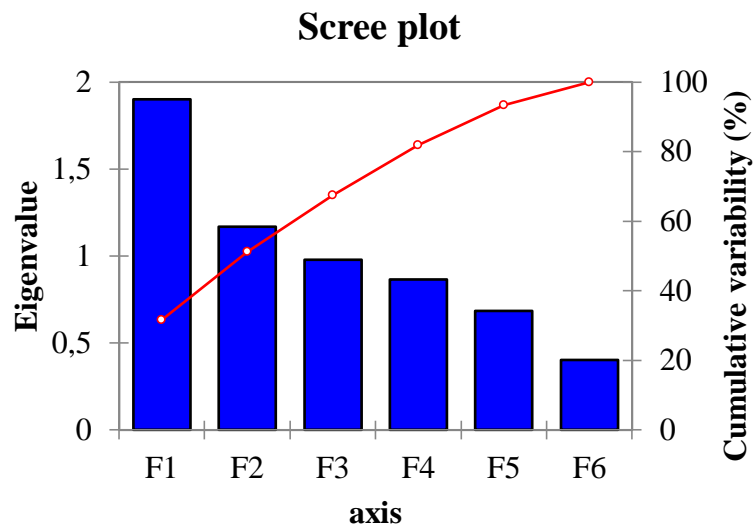


Figure 7. Scree plot eigenvalue for water quality parameter

Table 6. Factor loading of river parameters over two principal component

Parameter	F1	F2
DO mg/l	-0.32	-0.61
BOD mg/l	0.74	-0.39
COD mg/l	0.84	0.09
SS mg/l	0.70	0.07
pH Unit	-0.11	0.76
NH3-NL mg/l	0.20	0.24

Besides COD and BOD, suspended solids (SS) too, pronounces significantly, in agreement with stable isotopes results. This factor supports the sediment yield data, which was discussed earlier in the erosion mechanism. The other two parameters, which are dissolved oxygen and ammonical nitrogen are not the factors in determining the water quality of Kelantan river. Theoretically, DO depends on the water temperature (temperature depend on COD and BOD), sediment quantity in water flow and aeration. (Northeast Georgia Regional Development Center, 2001)

Conclusions

Stable isotope of $\delta^{13}\text{C}$ suggested that C_3 type plant are the dominant plants in Kelantan river with an autochthonous system as depicted in C:N ratio. However, it was evidenced through isotopic fingerprint of $\delta^{15}\text{N}$ and multivariate analyses of Water Quality and Sediment Yield datasets, anthropogenic factors have had significant impact on water quality and sedimentation of Kelantan river. Essentially, this research will help stakeholders to develop better strategies in restoring ecosystem services of Kelantan watershed. Balanced ecosystem, therefore, plays significant role in servicing the humanity, makes the ecosystem more resilience to natural disasters.

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