STABLE ISOTOPES ANALYSES OF CARBON-13 AND NITROGEN-15 IN KELANTAN RIVER SEDIMENTS

NUR ZAFIRAH BINTI ZULKIFLI

UNIVERSITI SAINS MALAYSIA

2019

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by

NUR ZAFIRAH BINTI ZULKIFLI

Thesis submitted is fulfillment of the requirements

for the degree of

Master of Science

March 2019

ACKNOWLEDGEMENT

Alhamdulillah, thanks to the grace of Allah, the Most Compassionate and Merciful because His consent gives me the guidance to complete this thesis.

A very invaluable appreciation and thanks to my supervisor, Dr. Muhammad Izzuddin Syakir Bin Ishak for giving me much support and guidance throughout my research project. His guidance had helped me from the research stage until the phase of writing this thesis. I felt very overwhelmed by having a very good supervisor and mentor who gave a lot of inspiration in this research.

In addition, I would like to thank Dr. Syahidah Akmal Binti Mohammad for helping me analysed the isotope data. Next, I would also like to thank the laboratory assistants in the Industrial Technology School, who taught me ways to use the equipment and machines in the lab because without their help I might fail to carry out this experiment.

I am also grateful for having friends who were always on my side during the up and down times in completing this thesis. Many thanks to all of them and may God reward all of their good deeds. Finally, my endless gratitude is extended to my parents and lovely family for all the supports and prayers throughout my study period. Thanks to all of your prayers, this thesis is perfectly completed. Thank you.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

%	Percentage
δ	Delta
$\pm$	Plus minus
$\approx$	Approximately
$\delta^{13}C$	Delta carbon 13
$\delta^{15}N$	Delta nitrogen 15
<	Less than
>	Greater than
‰	Parts per mill
ANOVA	Analysis of variance
BOD	Biochemical oxygen demand
C/N ratio	Ratio of the mass of carbon to the mass of nitrogen in a substance
C_3	The plants exhibiting C_3 pathway
C_4	The plants exhibiting C_4 pathway
CAM	Crassulacean acid metabolism
CHN	Used to measure Carbon (C), Hydrogen (H) and Nitrogen (N)
COD	Chemical oxygen demand
DID	Department of Irrigation and Drainage
DO	Dissolved oxygen
DOE	Department of Environment
IRMS	Isotopic Ratio Mass Spectrometer
MEA	Millennium ecosystem assessment
mg/l	Milligram per liter
N	Nitrogen
NH3-N	Ammoniacal nitrogen
NH_4^+	Ammonium
NO_3^-	Ammonia
PCA	Principal component analysis

pH	pH meter
POM	Particulate organic matter
SPSS	Statistical Package for the Social Sciences
SS	Suspended solid

ANALISIS ISOTOP STABIL KARBON-13 DAN NITROGEN-15 DALAM SEDIMEN DI SUNGAI KELANTAN

ABSTRAK

Peningkatan proses pemendapan telah meningkatkan ancaman bencana alam di Sungai Kelantan (cth: banjir). Memandangkan kesan hakisan tanah kepada pemendapan, pengenalpastian sumber hakisan adalah penting bagi pengurusan tadahan air di Kelantan. Isotop stabil karbon dan nitrogen, bersama-sama dengan analisis nisbah C/N telah dijalankan untuk mengenal pasti sumber pendapan di sungai Kelantan. Pensampelan telah dilakukan pada bulan Julai 2015 (Monsun Barat Daya, SWM) yang mewakili musim kering dan Januari 2016 untuk musim hujan (Northeast Monsun, NEM). Sampel dianalisis dengan menggunakan *Spectrometer Mass Ratio Isotopic Analysis Elementary* (EA-IRMS) dan *Perkin Elmer 2400 Series II CHN Elemental Analyzer*. Isotop stabil $\delta^{13}C$ menunjukkan bahawa tumbuhan jenis C_3 dominan di tadahan air Sungai Kelantan dengan tidak mempunyai perbezaan statistik yang ketara antara bulan Julai dan Januari. Ini menunjukkan sumber hakisan yang sama terutamanya dari pokok yang berkayu seperti pokok hutan, getah dan kelapa sawit. Nilai $\delta^{15}N$ yang berbeza dapat diperhatikan pada bahan organic tanah pada bulan Januari (NEM) yang menunjukkan pembersihan yang berlebihan (hakisan), natijah dari peranan iklim terhadap peningkatan pemendapan. Permerhatian terhadap nisbah C/N yang dicirikan oleh sedimen di Sungai Kelantan adalah *autochthonous*, menunjukkan perolehan dari sumber akuatik. BOD, COD dan SS adalah parameter utama yang menentukan kualiti air Sungai Kelantan. Pemendapan diperhatikan berlaku sepanjang tahun terutamanya semasa NEM. Penemuan ini mengenalpasti bahawa aktiviti penggunaan tanah adalah aktiviti utama dalam tadahan itu, yang memerlukan

usaha pengawalan bagi menguruskan magnitud hakisan tanah ke tahap yang lebih kelestarian.

STABLE ISOTOPES ANALYSES OF CARBON-13 AND NITROGEN-15 IN KELANTAN RIVER SEDIMENTS

ABSTRACT

Intensification of sedimentation process has increased the vulnerability of Kelantan River to natural hazards (i.e., climate change and floods). Considering the impact of soil erosion to sedimentation, identification of source of erosion is important to Kelantan watershed management. Stable isotope of carbon and nitrogen, along with C/N ratio analysis were carried out to identify the potential source of sedimentation in Kelantan watershed. Samples were collected in July 2015 (Southwest Monsoon, SWM) representing dry season and January 2016 for the wet season (Northeast Monsoon, NEM). The samples were analyzed using Elementary Analysis Isotopic Ratio Mass Spectrometer (EA-IRMS) and Perkin Elmer 2400 Series II CHN Elemental Analyzer. The stable isotope of $\delta^{13}C$ suggested that C_3 type plants are dominant in Kelantan watershed with statistically no significant difference between July and January. This indicates similar source of erosion mainly from woody plant such as forest trees, rubber and oil palm. Distinct $\delta^{15}N$ signature of soil organic matter is observed during January (NEM) indicates extra washout (erosion), suggesting the role of climate in intensifying sedimentation. Note the C/N ratio characterized by the sediments in the Kelantan River is autochthonous, exhibits an aquatic derived. BOD, COD and SS are the major parameters that determined the water quality of Kelantan River. Sedimentation is observed to occur in all year round particularly during the NEM. These findings provide a first-order identification of major land use activities in the catchment thus, assist the mitigation effort in managing the magnitude of soil losses to a level that more sustainably sounds.

CHAPTER 1

INTRODUCTION

1.1 Background of study

This study focuses on the off-site effect of erosion, the sediment loading in river networks of Kelantan Watershed. Consequent intensifications of the sediment in the river from upstream of the watershed often reduces the capacity of river to deliver high-quality water to downstream users, and eventually increases the risk of flooding in the river basins (Ibrahim et al., 2012; Qi et al., 2012; Saviour & Stalin 2012; Zhang et al., 2016).

The 2014 Kelantan flood disaster is a classic example where studies agreed that extensive soil erosion at the upstream areas with subsequent sedimentation on riverbed due to rampant land clearing activities is one of the main factors other than extremely heavy rainfall (Nurul Akma et al., 2015). Changing of land use for agriculture in the watershed has been reported to reach for almost 400% in 12 years period from 1988-2000 (Adnan & Atkinson, 2011). Come as no surprise, the flood disaster was called ‘Bah Kuning’ (yellow-coloured flood) due to its high mud content transported along with the voluminous water (Baharuddin et al., 2015)

In addition, increased soil erosion and sedimentation rates can expose the array of ecosystem services provided by the watersheds to the environmental risk (i.e. ineffective nutrient cycling and degradation of water quality) (MEA 2005). Such impact on ecosystem services may demand more chemical supply to maintain the agriculture industry, thus, more pollution generated from the washout (Mahabalaleshwara & Nagabhushan, 2014; Kuehn, 2015) (Giliba et al., 2011; Chakravarty et al., 2012).

Fundamentally, climate, topography, geology, soils, vegetation and land-use activities are among the main factors that determine the sediment supply in the watershed (Rosgen 2006, Brooks et al. 2013). Excessive sediment can adversely affect the water quality of Kelantan River. To determine what constitutes excess sediment in a stream, it is necessary to recognize that soil erosion and the sedimentation processes occur naturally and, therefore, that the elemental signatures of sediment loads in the streamflow can be identified by elemental tracing techniques.

Several techniques can be utilized to trace the elemental signatures that exist in the sediments. Heavy metals analysis technique can be employed for the impact assessment of industry in the watershed. Nonetheless, if the rate of soil losses is of the research interest, radionuclide technique may be the best. In the context of this thesis, stable isotope technique is applied to characterize the isotopic variations of $\delta^{13}C$ and $\delta^{15}N$ in the sediments. Such approach allow to first-order identification of possible major source of sedimentation in Kelantan watershed. In addition, C/N ratio of the river sediment is used to elucidate the source between terrestrial and aquatic particulates.

As mentioned, carbon and nitrogen isotope has been used to determine the source of organic matter to trace the source of sedimentation in Kelantan River (Zhang et al., 2007; Mukundan et al., 2010; Liu et al., 2017; Koszelnik et al., 2017; Derrien et al., 2018). The discrimination of $\delta^{13}C$ sources is derived primarily from photosynthetic pathways which results in distinct $\delta^{13}C$ values from fractionation processes (Boutton, 1991; Coleman & Fry, 1991 Fry, 2006; Schimel, 1993; Werth & Kuzyakov, 2010).

Considering the nitrogen cycle the isotopic value of atmospheric nitrogen is about 0‰ (Peterson & Fry, 1987) and fractionates to a range between −10‰ and +10‰

depending on the processes within the nitrogen cycle. In general, $\delta^{15}N$ fractionation is complex, with a multitude of nitrogen sources and internal changes potentially altering nitrogen isotopic ratios (Shearer and Kohl, 1993; Evans, 2007; Finlay & Kendall, 2007; Garzon-Garcia et al., 2017).

It is imperative, that, efforts are made by watershed scientist to manage the basin by conducting a reconnaissance study in identifying major land use activities in their respected watershed. The information of isotopic variations in the river sediments will provide a snapshot of major land use activities in the watershed thus, assist the watershed management to control the magnitude of soil losses to a level that more sustainably sounds.

1.2 Problem statement

Considering the impact of erosion and sedimentation in Kelantan river, characterization of $\delta^{13}C$ and $\delta^{15}N$ in rivers sediments is critical to Kelantan watershed management. The sediment samples from seven tributaries of Kelantan river were collected for characterization of $\delta^{13}C$ and $\delta^{15}N$. Unique characteristic of stable isotopes variation, provides first order identification of isotopic composition which can be used to describe the source of sedimentation in Kelantan River.

1.3 Objectives of the study

The purpose of this study is to utilize the $\delta^{13}C$ and $\delta^{15}N$ to identify the source of sedimentation in Kelantan river networks. Stable isotope technique is a cost-effective approach to characterize the isotopic composition in sediments which lead to first-order identification of major sources of sedimentation issues (Smith & Blake, 2014; Collins et al., 2016; Owens et al., 2016; Jalowska et al., 2017). As well, this study is complemented by other supplementary data like water quality and sediment yield for the purpose of discussion. The study was conducted at Kelantan watershed comprises seven main rivers. This work is a reconnaissance study on the impact of land use to the watershed and further clarifies the relations among anthropogenic activities and its impact to sediments accumulation in the Kelantan watershed.

In summary, the aim of this study is to obtain a “snapshot” of the impact of land use activities on Kelantan Watershed through specific objectives below;

1. To characterise the stable isotopic composition of $\delta^{13}C$ and $\delta^{15}N$ in Kelantan river sediments,
2. To determine the C/N ratio of sediments in the rivers, and
3. To establish a first-order identification of major anthropogenic sources contributed to sedimentation.

1.4 Hypothesis

Hypothetically, the river sediment is transported by erosion process from terrestrial part wash out down to the river during rainfall event. Climate, topography, geology, soil weathering and anthropogenic activities such as land clearing, agriculture, mining and urbanization are the factors that triggers massive erosion process (Figure 1.1). In order to ensure the source of sediment, stable isotope analysis were conducted to identify the carbon and nitrogen isotopic composition (‰). The anthropogenic and natural signatures can be determined from the unique individual isotopic value that varies within the systematic process of carbon and nitrogen cycle (Deines, 1980; O'Leary, 1988; Kendall & McDonnell, 1998; Kohn, 2010).

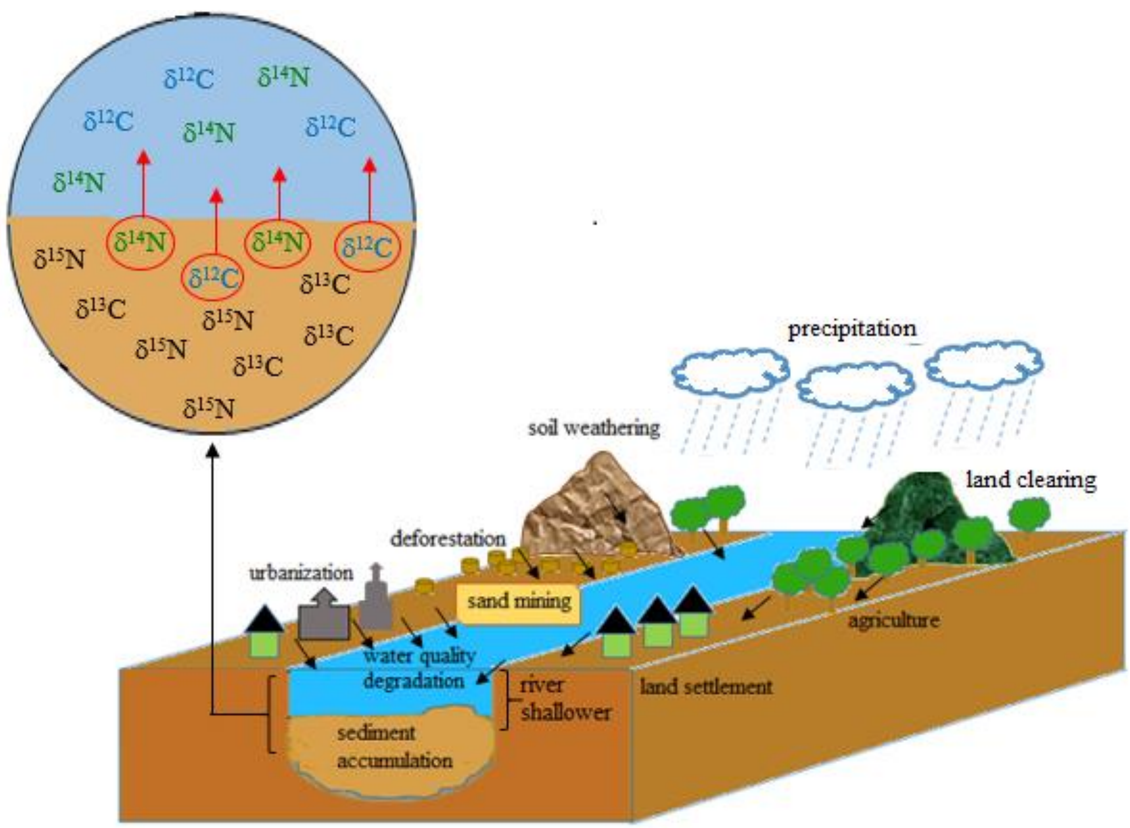

Figure 1.1: The cross section of sediment mechanism (in terms of isotope perspective) in a river

1.5 Scope of study

This thesis discuss a reconnaissance study of the land use impact on the Kelantan watershed using the stable isotopic technique. The result will serve as a baseline data of $\delta^{13}C$ and $\delta^{15}N$ in tropical watershed. Such information is useful for further understanding of complex and dynamic carbon and nitrogen cycle in a developing watershed.

CHAPTER 2

LITERATURE REVIEW

2.1 Challenges faced by Kelantan watersheds

Kelantan is located at the Northeast of Peninsular Malaysia and the state is prone to flooding due northeast monsoon setting started from November to March (MatAmin et al., 2012). Rampant land clearing has led to land degradation and soil erosion (Qi et al., 2012; Zhang et al., 2016) where the implication is on water quality and sediment accumulation in the river networks (Ibrahim et al, 2012; Saviour & Stalin 2012).

For record, Kelantan receives about 2433 mm of rainfall per year (MNA, 2016). The climate setting itself has led to progressive sedimentation all year round (Ansah-Asare, 1995; Ansari et al., 2000). In fact, this has been worsen by illegal logging and agriculture activities at upstream of Kelantan watershed, accelerating the rate of erosion, in turn, results in massive sedimentation, water quality degradation and shallower river (Ambak & Zakaria, 2010; Ibrahim et al., 2012). In the case of Kelantan catchment, the highest suspended solids were recorded at Galas, followed by Nenggiri, Lebir, Kelantan, and Pergau Rivers (Ambak & Zakaria, 2010). Shallower river due to massive sedimentation was identified as one of the risk factors which contribute to flood disaster in Kelantan watershed (Zhang et al., 2005; Robins et al., 2016; Hadi et al., 2017).

2.2 Soil erosion and sedimentation

Soil erosion can be defined as a process of material detachment from the soil surface by the act of water and/or wind (Sparovek & Jong van Lier, 1997; McConkey et al., 2012) through geological time and crucial for soil formation under natural situation (Grimm et al., 2003; Thiemann et al., 2005). Sediment refers to the soil or mineral particles transported from land by soil erosion, surface runoff, raindrop impact or stream flow, and deposited in a river channel (Chang, 2003; Peter et al., 2013; Zhang (b) et al., 2013). Results from progressive erosion process will lead to sediment accumulation in river.

2.2.1 The processes of erosion and sedimentation

Erosion process is influenced by natural and anthropogenic factors. There are several types of erosion agents which are water, wind, ice (glacier), and gravity (Zachar, 1982, Wang et al., 2014). This study focuses on water erosion due to geological & geographical settings of Peninsular Malaysia (Ibrahim et al., 2012; Taha & Kaniraj, 2013; Labrière et al., 2015; Holz et al., 2015). Nonetheless, human-induced factor such as poor management in development has accelerated the process. Basically, erosion consists of four main steps; rainfall, detachment, transportation, and deposition, (Figure 2.1). Detachment is the disintegration of loose soil particles when rain drop makes the first touch with the soil. The soil particles were transported by floating, splashing, rolling and dragging and the translocation to another site (Ellison, 1948; Broz et al., 2003; Shi et al., 2012). The soil particles were then finally deposited at some other lower slopes (Holz et al., 2015) as the soil particles were transported and deposited at the bottom of river, which is known as a sedimentation process. High accumulation of sediments in river water body can result in water deterioration, aquatic habitat damages, shallower river, and consequently an increase in flooding risk caused by the decrease in water storage capacity within the catchment area (Ling et al., 2016; Ahilan et al., 2016).

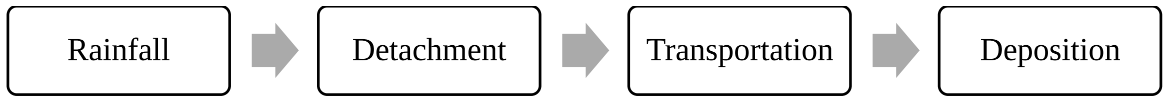

Figure 2.1: The erosion process is driven by water (rain) agents. Water droplets will cause detachment, transport and translocation of soil particles thus deposition of sediment (Hairsine & Rose, 1991).

Erosion process requires potential and kinetic energy as a triggering factor. Potential energy (PE) is an energy stored in an object. It results from mass (m), height difference (h) and acceleration due to gravity (g). The potential energy is defined using the following Equation (1) (Morgan, 1996),

$$PE = mhg \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation (1)}$$

The potential energy is converted into kinetic energy (KE), which is energy of motion. This energy involved mass (m) and velocity (v) of the agent in soil erosion. The kinetic energy formula is defined using the following Equation (2) (Morgan, 1996),

$$KE = \frac{1}{2}mv^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation (2)}$$

The degree of erosion also depends on erosivity (the energy of erosion) and friction of soil erosion (Thiemann et al., 2005). Water erosion resulting from rainfall, can be divided into four main erosion stages; splash, rill, sheet, and gully erosions (Gray & Sotir, 1996; Fang et al., 2015). Splash erosion is the earliest to occur when rain falls on the soil and also the least severe stage. Absence of vegetation will increase the rate of splash erosion compared to undisturbed area (Thomaz & Luiz, 2012; Moghadam et al., 2015). Interestingly, according to Ryżak et al., 2015, the impact of raindrops is significantly different between the first and subsequent drops of rainfall. Moreover, the detachment of soil particles due to splash erosion is strongly influenced by the surface area of the soils.

Removal process of soil surface particles due to rain drop impact and runoff is known as sheet erosion, where rill erosion occurs as the formation of the small channel cuts by the soil as the sheet erosion progresses. At this stage, it has greater impact on upland with the gravitational water flow. Absence in mitigation will result in gully erosion which potentially caused significant soils losses to adjacent water bodies (Ionita et al., 2015).

Both erosion and sedimentation processes modify the landscape and as the processes move towards equilibrium, there may be a tendency to increase the risk of natural hazards particularly in the catchment where its population is high (Wright & Schoellhamer, 2004). Besides flood risk, erosion and sedimentation processes may deteriorate water quality, disturb the aquatic habitat and decrease the light penetration for aquatic plant growth (Fred & Judith, 1995).

2.3 The implication of anthropogenic activities on watersheds

Land degradation occurs due to various factors, either natural or man-made factors (Table 2.1). Rampant land clearing has had an impact on watersheds, especially erosions and deposits.

Table 2.1: The consequences within watershed caused by natural processes and anthropogenic activities.

CAUSE →		EFFECT
Weathering Water Wind	Natural process	Soil degradation Soil erosion Soil runoff Landslides Sedimentation Deterioration water quality Shallower river Increase flood risk
Anthropogenic activities Land clearing/ deforestation Agriculture activities Land settlement & development Mining activities Timber production	Human-induced	

Deforestation, agriculture, mining, and development within the catchment are the major anthropogenic activities as reported by Wright & Schoellhamer 2004. If this is so, how to trace the sources and understand the priority solutions in addressing the problem? To date, there is no stable isotope studies of $\delta^{13}C$ and $\delta^{15}N$ in Kelantan river sediment. This study will serve as a baseline data of $\delta^{13}C$ and $\delta^{15}N$ variations in tropical river sediments.

2.4 Hydrology and environment impact studies of Kelantan watershed

There are several studies done by researchers in Kelantan watershed. One of the studies done by Anees et al., (2018) to find the soil erosion probability zones & accordingly prioritize watersheds using remote sensing and Geographic Information System (GIS) techniques. From the study, it point that high rainfall and agricultural activities enhanced soil erosion rate on steep slopes in the catchment. Pixel-based soil erosion analysis method through remote sensing and GIS was a very effective technique in finding accurate causes of soil erosion.

Besides that, in 2017, Jamaludin has develop a functional framework for hydrological applications using stream flow as the functional data. The results indicated that two stations which were Galas River and the Kelantan River (Guillemard Bridge), have a distinct flow pattern from the other stream flow stations. The flow curves of these two rivers are considered as the extreme curves because of their different shape and magnitude.

In the same of 2017, a study done in Kelantan river estuary to understand the source of pollutants. From the study it demonstrated that heavy metals mainly originated from natural weathering, erosion of rocks, soils in the catchment and enriched near the river mouth and total organic carbon can promote the enrichment of heavy metals in sediments (Wang et al. 2017).

Based on the findings of Aini et al., (2016), the result showed that factors influence the channel morphology alterations in different season was significant due to the discharge, erosion, sedimentation and enlargement in Galas River Kelantan. Almost similar to previous study, Saadatkhah et al., (2016) done a study to assess the impact of land cover changes in the study area focused on the surface water, soil moisture and loss water from different land use classes and the possible impact of land cover alterations on the ecosystem of Kelantan river basin. The results indicated the direct increased in surface water from development area, grassland regions and agriculture areas compared with surface water from other land covered areas in the study area. The urban areas and less vegetation density areas have a possibility to increase for surface water during the monsoon seasons, whereas the inter flow from forested and secondary jungle areas gives to the normal surface water.

In 2014, Basarusin et al., (2014) investigate the influence of rainfall during extreme rainfall events on the hydrological model in the Kelantan River catchment. The study managed to identify that rainfall change has a major impact to determine the runoff depth and peak discharge for the study area.

Along Kelantan watershed also have a lot of mining activities. A study done by Yen & Rohasliney, (2013) to describe the effects of sand mining on the Kelantan River with respect to physical & chemical parameter analyses. The Kelantan River case study discovered that TSS, turbidity & nitrate contents exceed the Malaysian Interim National Water Quality Standard (INWQS). High value of TDS, TSS, turbidity & nitrogen nutrients is caused by sand mining & upstream logging activities.

Apart from that, a finding from Dasar et al., (2009) showed heavy metals Pb, Zn, Cu and Cd was identified at low concentration in sediment samples, except for Fe and Mn. The presence of Fe and Mn in sediment samples likely from natural origin. Anthropogenic metal concentrations in sediment were low, demonstrating that Sungai Kelantan has not experienced extreme pollution.

2.5 Sediment tracing within watersheds

Tracing means finding or discovering something and can get a verdict by an investigation. Tracing sediment technique offers a practical approach to identify sources and sinks of sediments. As well, it tracks sediment movements and estimates spatial distribution of erosion and sediments rates (Kimoto et al., 2008). Sediment tracer has been used effectively on various scales from constant slope in the laboratory to large complex catchments (Kimoto et al., 2008). Sediment tracing techniques allow tracking the pathway of non-point sources pollutants from dry land and in water bodies (Kimoto et al., 2008; Koiter et al., 2013; Walling, 2013; Mabit et al., 2014). Such techniques provides essential information of the sediments within the watershed (Belmont et al., 2014), hence, leading to better understanding on the dynamic processes occur within the watershed (i.e. alteration of earth landscape) due to anthropogenic factors (Koltun et al., 1997; Owen et al, 2005; Evans et al., 2006; Gellis & Walling, 2011; Mukundan et al., 2012; Gellis & Mukundan, 2013; Owen et al., 2016).

Anthropogenic activities such as industrialisation, agriculture and deforestation play significant role in accelerating erosion which leads to massive sedimentation in water bodies. Industrialization signatures can be characterised from the elements in sediments which are set as possible proxies to factories, urbanization and mining processes. Such activities release pollutants from manufacturing, processing, effluent, and waste treatment plants that finally deposited in the riverbed (Soliman, 1974; Wolfe et al., 2001; O'Driscoll et al., 2010; Wantzen & Mol, 2013). Changes in land-cover related with urbanization may alter surface flow path which determine the load of runoff to stream channels, thus, in turn modify the geomorphology of channels (Wolman, 1967; O'Driscoll et al., 2010; Wantzen

& Mol, 2013). Agriculture activity is one of the main factors contributing to sediment and nutrient pollutions in rivers (Ulen et al., 2007, Wood et al., 2005; Gebreyesus & Kirubel, 2009). Intensive agriculture has led to soil degradation and erosion, hence, deteriorates the water quality of rivers (Ockenden et al., 2014). Most of the signatures in river sediments which potentially can be traced from sediments are pesticides, fertilisers, nutrients, and soils which have been washed out from agriculture land surface through generated runoff (Wolfe et al., 2001; MEA, 2005; Restrepo et al., 2015). The tracing techniques used together with information of sediment yield data can provide an overview about the geomorphological process, essential for watershed management (Owen et al., 2016).

Current development has seen those techniques evolve to advanced applications in defining historical changes in sediment sources using the floodplain, dam, lake and watersheds (Collins et al., 1997; Owens & Walling, 2002a; Walling et al., 2003; Slimane et al., 2013; Pulley et al., 2015; Chen et al., 2016). The tracing technique comprises several approaches like properties study, statistical properties, analyses and the application of numerical mixing model (Owen et al., 2016). This study focuses on characterization of stable isotopic Carbon-13 and Nitrogen-15 in the river sediments. However, other techniques will be discuss as in Section 2.4.

2.6 The source of tracing techniques in sediments

There are several methods applicable to discriminate the potential sources of erosion from sediments within a catchment. This section provides a brief outline of the current tracing techniques. The main tracing technique for sediment includes; i) stables isotopes, ii) C/N ratio, iii) radionuclides iv) heavy metal and v) magnetic properties (Othman et al., 2003; Othman & Ismail, 2012; Owens et al., 2016; Guan et al., 2017).

2.6.1 Tracing techniques in sediments

Each approach demonstrates individual uniqueness in tracing the source of pollution in sediments. However it is up to researchers to pick the most appropriate technique that match their research interest (Table 2.2). Given the stable isotope has unique composite signatures due to its stability, low sampling requirement and ability to distinguish source of sediments, therefore, the technique is employed to this study.

Table 2.2: Summaries of different sediment tracing techniques according to their timeframe, scales, advantages and limitations.

Tracing technique	Applicable timeframe	Applicable special scale	Advantage	Limitation	References
Isotopes	Since 1954, Runoff event; centuries	Plot to catchment	Able to distinguish different type of land uses; estimate runoff event based and seasonal erosion	The chronology of sedimentation is crude, which is separated by a turning year of 1963 (main peak); not for serious erosion; able to distinguish cultivated and uncultivated soils, Not standalone	(Wallbrink & Murray 1993; Wallbrink 1998; Zhang et al., 2007; Fox & Papanicolaou 2007; Walling, 2013).

C/N ratio	Man-made, natural	Plot to catchment	Able to identify source found in sediment originate from allochthonous or autochthonous	Not applicable	(Jennerjahn et al., 2004; Waterson, 2005; Spano et al., 2014).
Radionuclide	Man-made, natural cosmogenic, natural geogenic	Plot to catchment	Able to distinguish cultivated, uncultivated lands, estimate runoff events	Need long term study, required skill and staff	(Wallbrink & Murray 1993; Zhang et al., 2007; Walling, 2013).
Heavy metals	Rain event based; seasonal; decades	Catchment	Able to reconstruct sedimentation rates in floodplains and catchments having historic river pollution	Limits by mixed or unknown sources of each metal	(Chillrud et al., 2003; Franz et al., 2013).
Mineral magnetic	Runoff event; decades	Plot to catchment	Able to reconstruct history of sediment sources and discriminate soil burned at different severities	Possibilities of changes in oxidation or reduction conditions	(Yu & Oldfield 1989; Walden et al., 1997; Ven Der Waal et al., 2015).

Essentially, stable isotopes carbon and nitrogen as well as C/N ratio provide the information about the source of organic matter in the river sediment. For the effective management practices, we require the identification of actual sediment source to understand the possible erosion process, thus, plan for mitigation strategies in watershed management.

The combination of both methods (stable isotope carbon and nitrogen and C/N ratio) give a good compliment to each other. Through this study, stable isotope reveals the type of plant (carbon isotope) and possible land use (nitrogen isotope) sources. While, C/N ratio helps in ensuring the sources of the sediments i.e; allochthonous or autochthonous.

Another reason for stable isotope techniques and C/N ratio analysis is resource availability. Stable isotope of carbon and nitrogen analysis can be performed in Analytical Biochemistry Research Centre (ABrC), Universiti Sains Malaysia using isotope ratio mass spectrometer (IRMS). While, C/N ratio analysis CHN Elemental Analyzer is available in School Biology.

In brief, stable isotope carbon and nitrogen have shown a great potential sensitivity in tracing sediment sources, hence serve as the most appropriate method for identifying sediment origin in context of this study (Fox & Papanicolaou et al. 2008; Haddachi et al., 2013).

2.6.2 Stable isotopes

Environmental isotope is a useful tool to help infer in geochemical processes (Kendall & McDonnell, 1998). Application of tracer is very helpful in providing new insight of hydrological processes in a catchment as it gives variant of small-scale indication of catchment-scale processes (Kendall & McDonnell, 1998). Unique isotopic characteristic of individual element allow us to study their isotopically distinct ratios depending on their sources such as atmospheric, geogenic and biology. Biogeochemical cycle in particular system may determine the isotopic ratios of the sediments thus, such predictable pattern can be reconstructed (Kendall & McDonnell, 1998).

Stable isotopes provides composite signature due to its stability, low sampling requirements, and unique ability to distinguish soils produced from different land-uses (Vaalgamaa et al., 2013). The advantage can be effectively used in large-scale watersheds to characterize the source of sediment movement in short time scale (Papanicolaou & Fox, 2004; Laceby et al., 2015). In most hydrological studies, common stable isotope elements are hydrogen, oxygen, nitrogen and carbon.

Stable isotope carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) are useful to determine source of sediments (Fox & Papanicolaou 2007; Tumbull et al., 2008; Alewell et al, 2009; Papanicolaou et al, 2013). Stable isotope of $\delta^{13}C$ can be used for first-order identification of sediment source whether from forest cropland or grassland (C_3, C_4 or CAM type plants) (Balesdent et al, 1998).

In tracing source of agriculture sediment, stable isotope of carbon (C) and nitrogen (N) are used to infer sources of sediment (McConnachie and Petticrew, 2006; Fox and Papanicolaou, 2007; Schindler Wildhaber et al., 2012; Laceby et al., 2015a). Stable isotopes of carbon and nitrogen fractionation within soil, are dependent upon a number of processes, such as, vegetation decomposition, fertilizer sorption, and denitrification. These processes are altered due to soil-environmental factors, such as, vegetation type, soil moisture and temperature, concentration of soil gases, and land/crop management.

Assimilation, mineralization, volatilization, denitrification, and decomposition processes may determine the isotopic pattern of $\delta^{13}C$ and $\delta^{15}N$ whether enrich or deplete. These processes are accompanied by fractionations, whereby plants or soil discriminate between nitrogen isotopes, tending to favour the incorporation of 14N over 15N or vice versa. $\delta^{15}N$ values are typically enrich for agriculture soils as compared to forest soils under similar environments (Papanicolaou, & Fox, 2004).

The $\delta^{13}C$ value of soil reflects types of vegetation with only involve small enrichment during decomposition. The difference in $\delta^{13}C$ values for C_3 and C_4 plants induced by the unique photosynthetic pathway of each plant type results in the average plant tissue of $\delta^{13}C$ for C_4 plant, –12‰ and C_3 plants, –26‰ (Papanicolaou, & Fox, 2004).

2.6.2(a) Case studies

A previous study was conducted by Xiao & Liu, (2010) using stable isotope to identify the origin of sediment in an urban river. From the study, it demonstrated that stable isotope nitrogen value which is +8.5‰ comes from the industrial effluent. While, stable isotope carbon showed value with -27.7‰ indicating the source of C_3 type plants, contributed by the growing vegetation along the river bank (Xiao & Liu, 2010).

Besides the river sediment, the $\delta^{13}C$ and $\delta^{15}N$ too, can be traced from suspended matter in water bodies in the Godavari studies, which reported transformation mechanism of organic matter in the system (Sarma et al., 2012). Significant variability of isotopic distribution was observed over the entire length of the Godavari estuary representing multiple sources of organic matter. The mean isotopic ratios for stable carbon and nitrogen are -25.1‰ and 8.0‰ respectively. Significant enrichment in isotopic ratios of stable isotope carbon in sediment profile (upper, -26.2 and lower, -24.9 ‰) indicates less influence of terrigeneous material towards mouth of the estuary (Sarma et al., 2012).

In Northeast China, carbon and nitrogen isotope were used to identify the source of organic matter sources in the watershed due to intensive agricultural activities. Based on the results, it demonstrated that isotopic of $\delta^{13}C$ ranged from −28.22‰ to −23.98‰ and $\delta^{15}N$ slightly lower +3.7 ± 2.42% in sediment, reflecting the dominance of anthropogenic C and N input within the area (Lu et al., 2010). Overall, the source of sediment can be identified based on the isotopic signatures measured in the sediment samples.

2.6.2(b) Limitation

Stable carbon and nitrogen isotope techniques involve with continuous biochemical processes such as carbon and nutrient cycling through the processes of immobilization and mineralization. Organic matter is usually categorized into three classes; active, slow and passive which are related to their stability over time. The active class signifies the pool of organic matter that is the most susceptible to microbial decomposition (<2 yr), the slow class is moderately susceptible, and the passive class is the most resistant to microbial decomposition (500 – 5000 yr) (Brady & Weil, 2001). This becomes important as the conveyance time of sediment through a river basin can vary widely from days to decades and up to centuries. Note, some of the organic matter can be lost through decomposition. As well, organic matter is composed of many different organic compounds including carbohydrates, amino acids, lignin and polyphenols, which decompose at different rates (Brady and Weil, 2001). Decompositional processes can result not only the changes in the quantity of organic matter but also in the composition which can be difficult to characterize. However, stable isotopes techniques, can be improved as researchers are looking for compound-specific stable isotope signatures that target compounds which are more resistant to decay and that bind strongly to soil and sediment particles, thereby providing a more robust fingerprint analysis (Gibbs, 2008; Blake et al., 2012; Hancock and Revill, 2013).

2.6.3 C/N ratio

The C/N ratio is defined as the ratio of total atomic carbon to total atomic nitrogen (Papanicolaou et al., 2003) and represented by the following equation (Rogers, 2013):

$$\mathbf{C/N = (\%C/\%N)/\ (14/12)}$$

C/N can be described as a tool to test the ecosystem health and soil fertility. The soil in C/N ratio reflects the plant and microorganism composition, present in the soil. Different sources of sample give different values of C/N ratio. It has been largely used as a proxy to explain the source and fate of organic matter in the environment of waters (e.g., Gordon and Goni, 2003; Wu et al., 2007; Zhang et al., 2007; Ramaswamy et al., 2008), and it enables to discriminate pollutant origins related with sediment organic matter (Nasir et al., 2015). In aquatic ecosystem, there exist two main sources, which are autochthonous and allochthonous. Autochthonous is an organic matter derived from aquatic parts such as phytoplankton and algae. While allochthonous is an organic matter derived from terrestrial washed out. By using C/N ratio, the source of aquatic parts can be identified between anthropogenic or natural sources (Rostad et al., 1997; Rogers, 2013).

Terrestrial plant has a wide range of C/N ratio ranging between 10 and 40 such as gymnosperms 16.4; pteridophytes-ferns and spore plants 25.6 (Papanicolaou et al., 2003), whereas, the lower C/N ratio for most microorganisms ranging between 4 and 9 (Papanicolaou et al., 2003). As the decomposition process occurs, carbon will be released due to microbial oxidation and respiration of carbon dioxide as well sequestering of nitrogen. As a result, a decrease in C/N ratio is relative to plant (Papanicolaou et al., 2003). Terrestrial plants have higher C/N ratio compared to aquatic plants as they have an abundant carbon ring structure such as cellulose and lignin and resin give strength to the plant, while aquatic plants have lower C/N as they have less carbon ring structure thus making them more fragile (Rogers, 2013).

Potentially, C/N is a powerful tool for identifying the source of soil in a catchment (Papanicolaou et al., 2003). It gives a new understanding about the source of organic carbon and nitrogen in the catchment. In the case of Godavari catchment, the study discovered that the major source of organic matter in the high (August) season is from the soil, whereas the other season is the autochthonous, river derived where phytoplankton is the dominant source (Balakrishna & Probst, 2005). Besides, this study revealed that the amount of organic material transported from downstream to the oceans during the high (August) season are 3 to 91 times higher than the low (March) and moderate (November) seasons (Balakrishna & Probst, 2005).

2.6.3(a) Case studies

A study was conducted at Kuala Sungai Baru in order to identify the organic matter in the sediment by using C/N ratios. According to the result, higher C/N ratio is contributed by industrial activities where climate plays significant role in intensifying the allocthonous source i.e. agriculture wastes especially palm oil, rubber and paddy field as well pig farm effluent. Such intensification has led to increase in C/N ratio to 68.04 (Hamad & Omran, 2016).

In other cases, the application of C/N ratios in this study serves as indicators to know the source of organic carbon of the mangrove ecosystem in Ba Lat Estuary. Based on the results, C/N ratios from the bottom to the surface of sediments marked the changes of the organic matter with the C/N ratios values >12 indicated terrestrial source (e.g; mangrove litter) and <12 derived from marine phytoplankton source (Tue at el., 2011). C/N ratios is therefore an effective indicator that can be used to identify the source of organic matter in catchment sediments (Yu et al., 2010).

2.6.3(b) Limitation

The identification of organic matter originally using the composition of the C/N element is constrained by the measured ratio capability to accurately represent the source characteristics. Although the relative C/N ratio varies, the material from all sources is subject to the decomposition process which results in the absolute reduction of mass and the selective destruction of the biochemical fraction of the constituent. This effect on the C/N ratio associated with degradation of detritus and susceptibility to bacterial decomposition. Organic matter degradation causes the alteration of C/N ratios value; the C/N ratio value increases when sinking the algae particulate organic matter into the water body (Twichell et al., 2002), on the contrary, humification and mineralization process in terrestrial will significantly lower the C/N ratio (Sorensen, 1981; Schmidt et al., 2000; Nasir et al., 2016).