PHYSICO-CHEMICAL CHARACTERISTICS OF PINANG RIVER ESTUARY, BALIK PULAU, PENANG

NURUL RUHAYU MOHD ROSLI

UNIVERSITI SAINS MALAYSIA

2018

PHYSICO-CHEMICAL CHARACTERISTICS OF PINANG RIVER ESTUARY, BALIK PULAU, PENANG

by

NURUL RUHAYU MOHD ROSLI

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

August 2018

ACKNOWLEDGEMENT

Alhamdulillah. All praises to Allah Azza wa Jalla for blessing me with optimum physical and mental strength to conduct the research and PhD thesis writing successfully.

I would like to express my deepest appreciation to my main supervisors Associate Professor Dr. Khairun Yahya and Dr. Anita Talib, co-supervisor Associate Professor Dr. Ross Vennell, parents Pn. Murni Mohamed Yahya and En. Mohd Rosli Abdul Hamid, siblings, beloved kids Nur Aina Syazrina and Muhammad Azuan Safri for their courage, attention, understanding, patient and du'a throughout my study.

I am very lucky to have very helpful, kind and supportive lab mates, friends, the field and administration staffs of Centre for Marine and Coastal Studies and School of Biological Sciences, Universiti Sains Malaysia to carry out this research efficiently. Thank you so much for everything, truly grateful.

I express my sincere gratitude to the Research University (RU) Grant (1001/PPANTAI/811210) for funding to run this research, also to the World Federation of Scientists (WFS) for awarding partial scholarship and to the MyBrain15, Ministry of Higher Education, Malaysia for awarding the full scholarship.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS, SYMBOLS AND UNITS

%	percentage
<	less than
>	more than
±	Plus-Minus
°C	degree Celcius
µg/L	micrograms per liter
µm	micron or micrometer
µS/cm	microsiemens per centimeter
2-D	two-dimensional
ADCP	Acoustic Doppler Current Profiler
APHA	American Public Health Association
BOD	biological oxygen demand
C	carbon
$C_6H_{12}O_6$	glucose
cm	centimeter
CO_2	carbon dioxide
CR	community respiration (*r*)
DB	dark bottle
DO	dissolved oxygen
DOE	Department of Environment
EC	electrical conductivity
ft/s	feet per second
g	gram
GPP	gross primary productivity (*p*)
GPS	global positioning system
H_2O	water

i.e.	that is
IB	initial bottle
K	potassium
km	kilometer
LB	light bottle
LiDAR	Light Detection and Ranging
m	meter
mg/L	miligrams per liter
mg/m^3	miligrams per cubic meter
mL	mililiter
mm	milimeter
MMD	Malaysian Meteorological Department
mS/cm	milisiemens per centimeter
N	nitrogen
NEM	net ecosystem metabolism
nm	nanometer
NPP	net primary productivity
O_2	oxygen
OD	optical density
P	phosphorus
PBAPP	Perbadanan Bekalan Air Pulau Pinang Sdn. Bhd.
pH	hydrogen ion concentration
PKBD	Pejabat Kesihatan Barat Daya
PPDM	Pejabat Pertanian Daerah Manjung
ppt	part per thousand
ROMS	Regional Ocean Modeling System
rpm	revolutions per minute
s	second

SAM	Sahabat Alam Malaysia
SONAR	Sound Navigation and Ranging
sp.	species
SWOT	Surface Water and Ocean Topography
TSS	total suspended solids; the TSS loading term used in this thesis also known as sediment loading
TDS	total dissolved solids
VBES	Vertical Beam Echosounder

GLOSSARY

allochthonous	originates from other places
anthropogenic	influenced by human beings on nature
autochthonous	originates in its place
autotrophic	the system produces more organic matter than it consumes
bathymetry	underwater topography of oceans and rivers
concentration	the mass of solute per unit river volume
epilithic	growing on the surface of rocks or stones
fjord	a silled basin with great freshwater inflow, which mixes with brackish water exports it to the surface of water
flushing time	the time required for amount of freshwater inflow to equal the amount of freshwater originally present in the estuary or the ability an estuary can flush its existing water out to the open sea (per unit hour)
heterotrophic	the system consumes more organic matter than it produces
hyper-tidal	tidal range more than 6 m
loading	the discharge of solute concentration in flowing waters per unit time
macro-tidal	tidal range from 4 until 6 m
meso-tidal	tidal range from 2 until 4 m
micro-tidal	tidal range less than 2 m
non-point source	pollution resulting from many diffuse sources
partially stratified	stratification of salinity is increased smoothly from surface to bottom
polarographic	a method using a special electrode and a range of applied voltages
residence time	the time required for particle to spend in an estuarine system
salt-wedge	a very sharp boundary interface, which the freshwater pushes back into the seawater
stratification	salinity or temperature on estuaries occurs as freshwater and colder water buoyant over saline and warmer water
tidal period	the different hours of two high tides

tidal prism	volume of water leaving the estuary during low tide
tidal range	the different height between high tide and low tide
vertically well-mixed	similar salinity or temperature on both surface and bottom of water columns

CIRI-CIRI FIZIKO-KIMIA DI MUARA SUNGAI PINANG, BALIK PULAU, PULAU PINANG

ABSTRAK

Sungai Pinang terletak di barat laut Pulau Pinang. Panjangnya adalah kira-kira 6.5 km, dengan hulu yang sempit dan cetek di hulu tetapi lebih lebar dan dalam di hilir. Sungai ini membekalkan air tawar kepada hampir satu pertiga penduduk Balik Pulau. Malangnya, efluen antropogen dari pertanian, domestik dan akuakultur mengalir terus ke dalam sungai sehingga, menjejaskan kualiti air. Oleh itu, kajian ini dijalankan untuk menentukan proses muara di Sungai Pinang yang melibatkan pencampuran air tawar dan air laut yang boleh mempengaruhi aspek hidrodinamik, biologi, fizikal dan kimia sungai. Ciri-ciri ini mungkin memberi kesan kepada peredaran air muara, skala masa pengangkutan sungai (iaitu masa mastautin dan masa luahan) dan bahan pencemar (iaitu kepekatan nutrien dan sedimen; dan bebanannya). Status metabolisme ekosistem bersih (MEB) di Sungai Pinang juga dinilai daripada segi nisbah antara fotosintesis dan respirasi. Kajian diurnal dijalankan selama 24 jam di dua stesen semasa dua kitaran pasang surut ketika pasang perbani dan pasang anak dan musim hujan dan kering. Data sekunder (dari Oktober 2007 hingga Oktober 2008) bagi luahan, saliniti dan isipadu sungai sepanjang Sungai Pinang digunakan untuk menentukan masa mastautin dan masa luahan. Sistem muara Sungai Pinang dianggap sebagai pasang surut mikro dan muara yang separa berstrata. Masa luahan tidak mempengaruhi masa mastautin (R^2=0.028) di Sungai Pinang. Muara sungai ini mengalami masa mastautin (pasang perbani, kering: 17.77 – 42.86 jam; pasang perbani, lembap: 16.29 – 23.91 jam; pasang anak, kering: 25.47 – 186.69 jam; pasang anak, lembap: 23.44 – 89.88 jam) dan masa luahan (pasang perbani, kering: 12.68 –

75.08 jam; pasang perbani, lembap: 44.05 – 186.79 jam; pasang anak, kering: 15.69 – 107.75 jam; pasang anak, lembap: 9.90 – 222.73 jam) yang lebih panjang semasa kedua-dua keadaan pasang surut. Namun semasa pasang anak, keputusan signifikan lebih tinggi daripada pasang perbani ($p<0.05$). Hanya masa luahan menunjukkan peningkatan yang signifikan dalam musim hujan di bahagian hilir muara sungai ($p <0.05$). Beban nitrit (3.35 kg/j), ortofosfat (maksimum 18.85 kg/j) dan sedimen (86,837.86 kg/j) signifikan lebih tinggi semasa pasang anak dalam musim hujan ($p<0.05$). Sementara itu, beban ammonia (maksimum 44.32 kg/j) dan nitrat (maksima 15.96 kg/j) adalah tinggi sepanjang kajian ini. Di samping pasang surut dan masalah sedimentasi, bahan buangan yang tidak dirawat daripada aktiviti antropogen di sepanjang sungai boleh menyebabkan kekeruhan sungai dan peningkatan keperluan oksigen biologi ('biological oxygen demand', BOD_5) (maksimum 11.23 mg/L) yang mana mendorong sistem muara Sungai Pinang berada dalam keadaan heterotrofik.

PHYSICO-CHEMICAL CHARACTERISTICS OF PINANG RIVER ESTUARY, BALIK PULAU, PENANG

ABSTRACT

The Pinang River is located at the north-western of Penang Island. Its length is approximately 6.5 km, with narrow and shallow upstream, but wider and deeper downstream. This river supplies freshwater to nearly one-third of Balik Pulau population. Unfortunately, anthropogenic effluent from agriculture, domestic and aquaculture are being directly discharge into the river thus, deteriorating the water quality. Therefore, this study was undertaken to determine the Pinang River estuarine processes which involve the mixing of freshwater and seawater that may influence the river hydrodynamic, biological, physical and chemical aspects. These characteristics would possibly affect the estuarine water circulation, river transport time scales (i.e. residence time and flushing time) and pollutants (i.e. nutrient and sediment concentrations; and its loadings). Net ecosystem metabolism (NEM) status in Pinang River was also evaluated in terms of ratio between photosynthesis and respiration. Diurnal studies were carried out for 24 hours at two stations during two tidal cycles at spring and neap tides and wet and dry season. A secondary data (from October 2007 until October 2008) on river discharge, salinity and volume along Pinang River were utilised to determine the residence time and flushing time. Pinang River estuarine system was considered as micro-tidal and partially stratified estuary. The flushing time did not influence the residence time (R^2=0.028) in Pinang River. This river estuary experienced longer residence time (spring, dry: 17.77 – 42.86 hours; spring, wet: 16.29 – 23.91 hours; neap, dry: 25.47 – 186.69 hours; neap, wet: 23.44 – 89.88 hours) and flushing time (spring, dry: 12.68 – 75.08 hours; spring, wet: 44.05 –

186.79 hours; neap, dry: 15.69 – 107.75 hours; neap, wet: 9.90 – 222.73 hours) during both tidal events. However during neap tide, the results were significantly higher than spring tide ($p<0.05$). Only the flushing time showed significantly higher in wet season at lower part of the river estuary ($p<0.05$). The nitrite (maximum 3.35 kg/h), orthophosphate (maximum 18.85 kg/h) and sediment (86,837.86 kg/h) loadings were significantly higher during neap tide in wet season ($p<0.05$). Meanwhile, the ammonia (maximum 44.32 kg/h) and nitrate (maximum 15.96 kg/h) loadings were high throughout the study. Besides tidal event and sedimentation problem, untreated discharged from anthropogenic activities along the river may affect the river turbidity and increase in biological oxygen demand (BOD_5) (maximum 11.23 mg/L) which leads the Pinang River estuarine system to be in heterotrophic condition.

1.0 INTRODUCTION

1.1 Water Catchment Area

Water catchment area generally originates from the springs that form the streams and creeks on the hilltop. Any changes that occur in the watershed by anthropogenic activities or natural phenomena are closely related to environmental conditions and could potentially lead indirectly to changes in estuarine ecosystems (Richards & Host, 1994; Dauer et al., 2000; Peters & Meybeck, 2000; Anderson, 2001; Merseburger et al., 2005; Yan et al., 2005; Lehrter, 2006; DOE, 2007; Das et al., 2011; Nyamangara et al., 2013). Modification of landforms and the changes associated with vegetation not only change the balance of water flow, but also affect the overall process of water quality of aquatic system (Peters & Meybeck, 2000). Factors such as water drainage pattern from the upstream, unpredictable weather patterns, seasonality and tides can cause changes in the river processes such as the salinity, temperature, nutrients and total suspended solids (TSS) from time to time (Levinton, 1994).

Estuaries are a semi-enclosed system, which are highly productive, very complex and dynamic systems (Heip et al., 1995; Wolanski, 2007) with seasonal factors and topography of biogeochemical compounds and processes (Heip et al., 1995). Estuarine ecosystem have a variety of primary producers such as phytoplankton, phytobenthos, benthic microalgae, epiphytic algae, macrophytes (swamp marsh plants, mangrove), macrophytes (seaweed) and macroalgae. Most of the estuarine species consists of various types of euryhaline organisms (Lokman, 1992; Calder & Maÿal, 1998; Brauner et al., 2013) that can tolerate wide range in salinity.

1.2 River Bathymetry and Classification of Estuarine Circulation

Bathymetry is the study of the underwater topography of oceans and rivers. Generally, the river bathymetry studied in conjunction with global positioning system (GPS) is used to set the coordinates while mapping a river model. As the development of technology in bathymetry measurement progresses, techniques used in this measurement are varied such as boat-mounted Sound Navigation and Ranging (SONAR) (Merwade, 2009), Acoustic Doppler Current Profiler (ADCP) (Farina et al., 2015), Surface Water and Ocean Topography (SWOT) (Yoon et al., 2012), airborne Light Detection and Ranging (LiDAR), Vertical Beam Echosounder (VBES), gvSIG UK algorithm (Sánchez-Carnero et al., 2012) and remote sensing coupled with ancillary datasets (Adnan & Atkinson, 2012). Although the modern techniques were considered better, but the conventional way of measuring depth by cross-sectional and at discrete points along the river are still conveniently to carry out (Merwade, 2009). Even though these modern tools would not be able to replace ground truthing data collection, these tools can provide improvement and enhance the quality of available data (Jordan & Fonstad, 2005). Moreover, most of the equipment (except SONAR) used for bathymetry technology are costly and could measure a depth of 1 km and more. As this river is a shallow river, therefore it is more practical, realistic and inexpensive to practice the conventional way in Pinang River.

Pinang River bathymetry was mapped by using Surfer 13 software to provide a better two-dimensional (2-D) model from surface area. The Surfer 13 is a grid-based mapping tool that offers a better and accurate interpolation and interpretation of unmeasured data locations into measured discrete data. The contours produced give an almost precise data prediction of areas around the points taken. The inaccessible specific locations due to river depth and topography may give minimal impact on the bathymetry as a whole (Glenn et al., 2016). Surfer is widely used in research such as bathymetric modelling (Pye & Simon, 2015), three-dimensional (3-D) surface mapping (Koehler, 2004), water quality modelling (Anh et al., 2014; Rajesh et al., 2015), terrain modelling (Litwin et al., 2013) and groundwater modelling (Kumari et al., 2013). The study of bathymetry is essential to get a clearer picture of the Pinang River topography. Later on in this study, it will be used to obtain the river volume in order to determine the residence time, flushing time and the loadings.

Generally, freshwater and seawater creates different circulation in an estuary. On the other hand, the tides, rainfall, wind, evaporation, upwelling, an oceanic eddy and storms (Wolanski, 2007) produce the estuary circulation. In addition, vertical mixing change the salinity and temperature from surface to bottom part of water and vice versa (Wolanski, 2007). Stratification of salinity or temperature in estuaries occurs as freshwater and colder water buoyant over saline and warmer water (Wolanski, 2007). Turbulence generated from the right and left of the estuary banks could affect the water circulation (Fischer et al., 1979).

Determination of estuary type depends on the tidal range between the highest and the lowest tidal heights i.e. micro-tidal (tidal range less than 2 m), meso-tidal (tidal range from 2 – 4 m), macro-tidal (tidal range from 4 – 6 m) and hyper-tidal (tidal range more than 6 m) (Wolanski, 2007). In Malaysian scenario that experiences semi-diurnal tide, the Pinang River is classified as micro-tidal river (Nurul Ruhayu & Khairun, 2013).

The salt contribution in the estuaries is associated with the tidal mixing, vertical and lateral salinity variations and shear (Ketchum, 1983; Dyer, 1997). The estuary circulations are divided into four types i.e. vertically well-mixed, partially stratified, salt-wedge and fjord (Figure 1.1). A vertically well-mixed estuary has similar salinity or temperature on both surface and bottom of water columns. A partially stratified estuary shows the stratification of salinity from surface to bottom is smoothly increased. A salt-wedge is defined by a very sharp boundaries interface where the freshwater pushes back the seawater. A fjord is a silled basin with abundant freshwater inflow and at the same time the mixing brackish water exported in the surface of water. The circulation of estuary for the Pinang River has not been studied to date.

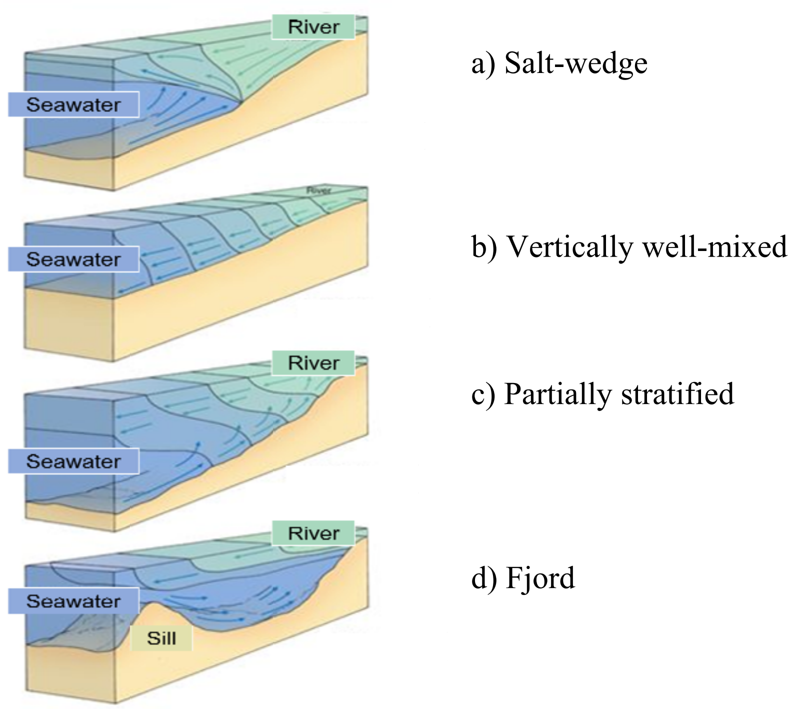

Figure 1.1 Four types estuary circulation that influenced by water density through salinity stratification and velocity (Source: Slideplayer.com).
a) Salt-wedge
b) Vertically well-mixed
c) Partially stratified
d) Fjord

1.3 Residence Time and Flushing Time in River

River estuaries are very complex and productive systems (Wolanski, 2007). However due to many developments near estuaries, these system become more eutrophic as anthropogenic inputs of nutrients increases (Nixon, 1995; Carpenter et al., 1998; Kemp et al., 2005) and causes deterioration to its ecological health (Wolanski, 2007). The residence time, flushing time and water circulation are the key physical factors to determine the health of a particular estuary, which is affected by human-induced stresses (Wolanski, 2007).

The nutrient enriched in the freshwater input may deteriorate the river water quality if the seawater exchange is low. Estuarine residence time and flushing time has been used to assess the possible effects of changes on nutrient enrichment (Kelly, 1997; Sheldon & Alber, 2006) primary productivity (Jorgensen and Richardson, 1996) and in estimating chlorophyll concentration (Monbet, 1992). Generally, a healthy and stable river system has shorter residence time as well as the flushing time. These water circulations are important physical factors to determine the health of a particular estuary, which is impacted by anthropogenic activities (Wolanski, 2007).

Some estuarine circulation is swift and flushes immediately pollutants to the open sea while others are poorly flushed and retain the pollutants at long period. Different characteristics of estuaries have various flushing rate and associated with nutrients and sediments (Sheldon & Alber, 2006).

There are many ways to estimate residence time such as by using basis data and numerical model (Choi & Lee, 2004; Cucco & Umgiesser, 2006; Cucco et al., 2009; Ascione Kenove et al., 2012) and also using hydrodynamic calculation (Gómez-

Gesteira et al., 2003). The most recommended method for estimation the residence time is using tidal prism model created by Ketchum in 1951 (Luketina, 1998) and later modified by Dyer (1973) (Sheldon & Alber, 2006).

The freshwater fraction method by Dyer (1973; 1997) has been used widely to quantify the flushing time for the estuarine segments (Chandra Shaha et al., 2012) and individual segment (Sheldon & Alber, 2002). The freshwater fraction models were the most suitable method to estimate estuarine flushing time, as detailed freshwater flow and salinity were collected (Guo et al., 2000; Sheldon & Alber, 2002; Chandra Shaha et al., 2012). The flushing time is commonly used to determine the ability of an estuary to flush its existing water out to the open sea.

It is obvious that the residence time of an estuary will increase or decrease with its flushing time. The longer it takes to flush an estuary, the longer its residence time will be. It can be emphasized that, estimation of residence time and flushing time using basis calculation of data i.e the classical simple tidal prism and freshwater fraction models by Dyer (1973; 1997) were applied to this study.

1.4 Nutrient and Total Suspended Solids (TSS) Loadings in the River System

Nutrient and TSS loadings and organic matter enrichment are identified as a serious threat in many estuaries due to anthropogenic activities (Smith, 2003; Chaudhuri et al., 2012; Wan Ruslan et al., 2017). In estuaries, nutrient enrichment has increased dramatically due to the inclusion of organic matter from mangroves as rubbish, inorganic nitrogen and phosphorus from domestic and agricultural waste as well as the inclusion of organic carbon from sewage into streams (Wösten et al., 2003). The balance between organic matter and nutrient loading is very critical and play a major role in determining the balance between autotrophy and heterotrophy in a river ecosystem (Eyre & Mckee, 2002). The rate of absorption of these nutrients determines whether mangrove estuary is a source or sink of nutrients (Wösten et al., 2003; Chaudhuri et al., 2012). The most important role of mangrove ecosystem is in the carbon sequestration, which is controlled on the global carbon cycle (Twilley et al., 1992), besides, as a net source of carbon dioxide (CO_2) to the atmosphere if the mangrove area been disturbed (Eyre & Mckee, 2002; Cloern et al., 2014).

The nutrient and TSS loadings refer to the total amount of nitrogen or phosphorus and suspended solids entering the water during a given time (Amon-Armah et al., 2013; Defne & Ganju, 2014). The impact of nutrient and TSS loadings would depend on how quickly the inputs are carried through the river estuary. If the loading of nutrient and TSS from the sources of pollution were higher than the river flows, it would demonstrate to river pollution and vice versa.

Nevertheless, no study has been done on the loading and movement of nutrient and TSS in Pinang River. Being a small and shallow river system, any anthropogenic activities along the river with low flushing will alter the ecosystem health and thus would eventually lead to the deterioration in the river system.

The previous spatial studies by Nurul Ruhayu (2011) investigated that the existing of anthropogenic activities in Pinang River increased nitrate concentration at the upstream due agricultural activities, and the increased of orthophosphate, TSS and biological oxygen demand (BOD_5) concentrations at the middle-stream were probably due to domestic and aquaculture effluents. The study of diurnal distribution of nutrient and TSS concentrations and the loadings was conducted to observe any variation or trends between spring and neap tides in the dry and wet seasons in 24 hours.

Loading involves the discharge of solute concentration in flowing waters per unit time (Pinckney et al., 2001). The river bathymetry, stratification, volume, residence time and flushing time are among the factors that are associated with nutrient transportations (Pinckney et al., 2001). Generally, higher nutrient concentration leads to greater nutrient loading in stream because of higher river discharge and vice versa (Ansa-Asare & Asante, 2000; Sigleo & Frick, 2007). The river discharge is the volume of water flowing through a river channel (Meals et al., 2013).

Anthropogenic activities located along the river influences the system in term of nutrient concentration (Scharler & Baird, 2005; Akalu et al., 2011), TSS concentration (Yap et al., 2006; Gong et al., 2014), nutrient loading (Ansa-Asare & Asante, 2000; Das et al., 2011; Nyamangara et al., 2013; Lemley et al., 2014), TSS loading (Ansa-Asare & Asante, 2000; McKee et al., 2006; Das et al., 2011; Barnard et al., 2013; Hasan et al., 2015; Wan Ruslan et al., 2017); and these flocculation of pollution may compiled until estuarine waters (Akoma, 2008; Athuman & Nkotagu, 2013; Tening et al., 2013). Different types of anthropogenic activities, river flow and precipitation leads to variations of nutrient or TSS concentrations in the ecosystem (Pinckney et al., 2001; Gao et al., 2008; Das et al., 2011).

Although the concentration of nutrient and TSS might be low due to dilution by large volume of seawater, the loading may increase because of the total volume of seawater velocity that enters the estuary (Pinckney et al., 2001). Precipitation has minimal influences on sediment discharge even though, rationally the sediment production would increase due to precipitation and anthropogenic activities as been studied in other disturbed river ecosystems (Wan Ruslan & Mohmadisa, 2014).

1.5 Net Ecosystem Metabolism (NEM) in River

The photosynthesis (*p*) is a process carried out by primary producer in an aquatic ecosystem. The equation involved upon photosynthesis is as follows:

$$6CO_2 + 6H_2O \xrightarrow[\text{light} \nearrow \ \searrow \text{fluorescence}]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2 \qquad (1)$$

By referring to the photosynthesis equation, theoretically, the primary productivity can be measured using; i) the decrease in CO_2 (carbon dioxide) or water (H_2O), ii) the increase in glucose ($C_6H_{12}O_6$) or dissolved oxygen (DO), iii) the amount of chlorophyll-*a*, iv) the quantity of fluorescence produced, and iv) the quantity of light absorbed (Ong et al., 1985).

As the photosynthesis occurs in aquatic ecosystem by primary producers, life organisms such as zooplankton, bacteria and other aquatic organisms living in the ecosystem also perform respiration (*r*) process at the same time. The equation involved during respiration is as follows:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O \qquad (2)$$

According to the respiration equation, the organisms would consume $C_6H_{12}O_6$ to obtain energy and DO to produce CO_2 and H_2O.

The metabolic activity of the river during lighted period, which performs photosynthesis, is known as autotrophic, meanwhile, during dark period when respiration is conducted is known as heterotrophic (Dodds, 2006).

Primary productivity is a rate of photosynthetic organisms that produce organic compound in an aquatic ecosystem. Organic matter which contains carbon compounds formed by living things is strongly influenced by the anthropogenic activities of the water catchment, hydrology and climatology (Paerl, 1997). Organic compound produced during the photosynthesis process is $C_6H_{12}O_6$ and DO. Meanwhile, CO_2 and H_2O are generated during respiration process. In estuarine waters, the dominant primary producers that undertake the photosynthesis process are phytoplankton, seagrasses, benthic microalgae, epiphytes and submerged aquatic vegetation (Pinckney et al., 2001).

The concentration of DO was commonly measured by titration using Winkler method (Strickland & Parsons, 1972; Ong et al., 1985). This classical Winkler titration method with the highest accuracy has been widely used (Furuya & Harada, 1995). Most of the study recorded the accuracy of DO was 0.1 mg/L (Carpenter, 1965), 0.15 mg/L (Hall & Moll, 1975) and 0.02 mg/L (Strickland & Parsons, 1972). However, the Winkler method is not suitable for ecosystem with lower primary productivity i.e. seawater, open sea, polluted waters and also for ecosystem with higher eutrophication especially in polluted river with high bacteria population (Khairun, 2004). A study by Gnaiger and Forstner (2012) and Noor Ashikin (2014) showed that there was no significant difference ($p>0.05$) between classical Winkler titration method and polarographic method in order to estimate primary productivity. The polarographic method has been used widely, and calibration is needed to acquire more precise results (Langdon, 2010). The advantage of using this method over Winkler method is that the interference encountered during chemical preparation can be evaded (Ong et al., 1985) and the DO measurement could be done *in-situ* during field activities, besides, enabling the continuous DO monitoring during the sampling day. The disadvantage of using Winkler method was the discontinuous oxygen monitoring (Thottathil et al., 2008), and the presence of constituents may reflect the reagent; as well as the end point indicator (i.e during titration) that is not clear would at the same time affect the reading (Khairun, 2004).

The net ecosystem metabolism (NEM) is a measure of trophic conditions of an ecosystem that depends on the balance between photosynthesis and respiration. A river ecosystem is considered autotrophic when $p/r > 1$, while heterotrophic occurs when $p/r < 1$. An autotrophic system occurs when the system produces more organic matter than it consumes by autotrophy organisms, and on the other hand, a heterotrophic system consumes more organic matter than it produces by heterotrophy organisms (Gazeau et al., 2005; Colangelo, 2007). Autotrophic systems react as basins for CO_2 and source of oxygen meanwhile, heterotrophic systems as a CO_2 source and import oxygen from the atmosphere (Garnier & Billen, 2007). Therefore, NEM is an estuary indicator of the trophic condition whether the source of organic matter is autochthonous (originates in its place) or allochthonous (originates from other places) (Caffrey, 2003). Caffrey (2003) described that if the NEM is more than 1, it indicates that the river system is autotrophic (autochthonous organic matter dominates); meanwhile, if the NEM is less than 1, indicating the river system is heterotrophic (allochthonous organic matter dominates). During heterotrophy condition, oxygen used up for bacterial degradation of organic matter is greater than generated by primary productivity (Abhilash et al., 2012). An increased nutrient level also increases the bacteria heterotrophic activity, subsequently lead to CO_2 supersaturation, and followed by oxygen undersaturation (Gupta et al., 2009).

Some studies have indicated that NEM is an easily quantifiable and integrative approach for assessing the trophic response of an entire system to nutrient eutrophication (Kemp & Boynton, 1980; D'Avanzo et al., 1996; Kemp et al., 1997). NEM provides a measure of how a system processes nutrients and organic material (Smith & Hollibaugh, 1997) thus, can be used as an indicator of ecosystem function whether it is an autotrophy ($p>r$) or heterotrophy ($p<r$). NEM also has been found to respond predictably to nitrogen load in shallow systems (Nixon et al., 1986; Borum & Sand-Jensen, 1996; Nixon et al., 2001) if light and other required nutrients are not limiting (Nixon et al., 1986; Nixon et al., 2001).

The level of primary productivity is also assessed by the concentration of chlorophyll-*a* in the river. Chlorophyll-*a* is a major photosynthetic pigment that exists on primary producer as compared to other pigments such as chlorophyll-*b*, chlorophyll-*c*, chlorophyll-*d*, chlorophyll-*e*, xanthophylls, phycobilins and carotenes (APHA, 2012). Furthermore, chlorophyll-*a* is the most important pigment present in salt waters.

The chlorophyll-*a* was used to measure the biomass of phytoplankton population. The chlorophyll-*a* is a biochemical component which is dominant in all eukaryotes and prokaryotes that is responsible for photosynthesis in an aquatic ecosystem. There are positive relationships between primary productivity and chlorophyll-*a* (Bot & Colijn, 1996; Wang & Wang, 2011). The phytoplankton and phytobenthos biomass were reported significantly difference with primary productivity in shallow coastal waters (Westlake, 1963).

1.6 Background of Pinang River in Balik Pulau, Penang

Pinang River supplies freshwater sources to nearly one third of Penang population by the Penang Water Authority (Perbadanan Bekalan Air Pulau Pinang Sdn. Bhd., PBAPP). The upper part of the river originates from the hilly slopes of Laksamana Hill and Tiger Hill forest reserve in Balik Pulau district. However, the hilly topography of the upstream area is surrounded with durian orchards since 1959 (www.sinarharian.com.my, dated 1st June 2013). The durian plantation consists of about 3,000 trees surrounding the hilly area (Suhaimy, A., personal communication, 4 October 2007).

Pinang River is one of such example of a river that is being heavily influenced with anthropogenic activities. Many residential houses are concentrated near the river corridors and some of these houses are without sewerage systems. Besides, the development of aquaculture ponds has cleared part of the mangrove area situated at the middle of the river. Direct discharges from these anthropogenic activities have deteriorated the Pinang River water quality (Nurul Ruhayu, 2011; Khairun et al. 2012; Nurul Ruhayu & Khairun, 2017).

In addition, Pinang River has economic and strategic importance as it serves as a second entrance to visit Penang National Park. This protected area was legally gazetted under Malaysia's National Park Act in year 1980. Scientists, researchers, nature lovers and tourists have always explored the national park. Therefore, it is important to keep this river system clean in order to promote tourism as well as preserve our natural heritage.

1.7 Rational of the Study

In order to determine the estuarine processes (i.e. river bathymetry, residence time, flushing time, nutrient and TSS loadings, and NEM) of the Pinang River, diurnal studies were carried out at two stations during two tidal cycles at different tidal event and seasonality.

In addition, to evaluate the trends and variation of residence time and flushing time for a year period (October 2007 – October 2008), secondary data on river discharge, salinity and volume were analysed as explained in Section 1.6.

Therefore, the ultimate goal of this study was to determine which factors (residence time, flushing time and loading) might affect the NEM in Pinang River.

The outcome of this study, can be used in mitigation measures by the stakeholders in decision making to minimize any impact in order to sustain a healthy ecosystem.

1.8 Objectives

1. To determine the estuarine circulation type and investigate the residence time and flushing time of Pinang River during different tidal event and season.

2. To determine the nutrient and TSS loadings and net ecosystem metabolism in the Pinang River during different tidal event and season.

3. To verify the relationships of the net ecosystem metabolism with the transport time scales (residence time and flushing time), and the nutrient and TSS loadings in Pinang River estuarine system.

1.9 Structure of Thesis

The thesis is organized into ten chapters. Chapter 1.0 is an overview of the research and the background study of Pinang River in Balik Pulau, Penang. Chapter 2.0 reviews previous studies related to river bathymetry, transport time scales i.e. residence time and flushing time, nutrient and TSS loadings, primary productivity, respiration and NEM. Chapter 3.0 illustrates the background of the study sites. Chapter 4.0 illustrates the material and methodology used in this study. Chapter 5.0 estimates the Pinang River bathymetry and evaluation of estuarine circulation type. Chapter 6.0 evaluates the transport time scales i.e. the residence time and the flushing time of Pinang River during different tidal event and season. In this chapter, a secondary data on river discharge, salinity and volume (spatial studies) for a year (October 2007 – October 2008) with one tidal cycle has been used to perceive the trends and variation of residence time and flushing time between spring and neap tides during both dry and wet season. In this 24 hours study (diurnal studies), two tidal cycles were analysed to relate the trends of residence time and flushing time with the nutrient and TSS loadings and the NEM in the next chapters. Chapter 7.0 determines the nutrient and TSS loadings in the Pinang River during different tidal event and season. Chapter 8.0 identifies the NEM status in Pinang River. Chapter 9.0 studies the relationships of the NEM with the transport time scales (residence time and flushing time) and the nutrient and TSS loadings in Pinang River estuarine system. Finally, Chapter 10.0 concludes the findings of this research. References and appendices are listed at the end of the thesis.

2.0 LITERATURE REVIEW

2.1 Characteristics of Estuarine System

Estuarine system generates a unique, very complex and productive ecosystem. A precise definition of an estuary is a seawater body that undergoes dilution process with freshwater flowing from the upper and middle-stream (Wolanski, 2007) beside, the mixing of nutrients from land and sea. This condition could effect the salinity and temperature stratifications as the tidal event occurred. Estuaries near mangroves area, are rich with food sources, provide shelter and habitat for fish and shrimp juveniles and also for shellfish organisms (Wolanski, 2007). The organisms in the sediment and river itself are subjected to these changes and have to adapt to these conditions. The estuarine floor has covered by muddy and many organisms lives in while, seaweed, algae and phytoplankton are the major primary producers. Estuaries are among the environment most affected by anthropogenic activities such as development, aquaculture, agriculture and industry sectors.

2.2 Bathymetry and Type of Estuary

The river bathymetry study is essential to determine the type of estuary, whether it is a vertically well-mixed, partially stratified, salt-wedge or fjord (Wolanski, 2007) (refer to Figure 1.1 in Section 1.2). The estuary type was determined by studying the salinity stratification between the levels of water column and the distribution along the river (Wolanski, 2007).

Generally, the river bathymetry study in conjunction with global positioning system (GPS) is used to set the coordinates and to obtain the length of river while mapping a river profile. Although the modern techniques like Sound Navigation and Ranging

(SONAR), Acoustic Doppler Current Profiler (ADCP), Surface Water and Ocean Topography (SWOT), Light Detection and Ranging (LiDAR), Vertical Beam Echosounder (VBES) and remote sensing were considered better, but the conventional way of measuring depth by cross-sectional and collecting at particular locations along the river depending on the river morphology are still conveniently carried out (Merwade, 2009). A conventional and manual techniques require basic instrument i.e. depth finder to detect the river depth. The ground truthing data collection then is used to model a two-dimensional (2-D) model from surface area using colourmap (Golden Software, 2014). The river bathymetry and morphology are associated with river flow, tidal event, estuarine flushing and wind (Defne & Ganju, 2014).

2.3 Residence Time and Flushing Time

The investigation of transport time scales of aquatic system started since 1950s'. Based on the aforementioned literature, there are many misunderstandings, misleading and confusions in the past studies with mixing time scales, equations and overlapping terminology of residence time and flushing time (Monsen et al., 2002; Sheldon & Alber, 2002).

Residence time is defined as the amount of time taken for particle to spend in an estuarine system (Zimmerman, 1976; Zimmerman, 1988; Dyer, 1997; Gómez-Gesteira et al., 2003 and Ascione Kenov et al., 2012). Another definition of residence time is a starting point for a particle that will be remaining in the river at desired location (Sheldon & Alber, 2002). Wang et al. (2004) in their study interpreted the residence time as the average of time the water parcel is in the estuarine system before been flushed out of the river. In another study by Monsen et al. (2002) and Delhez and Deleersnijder (2006), residence time is defined as exposure time i.e. the total time spent for a water parcel before it leaves the estuary.

Occasionally in literature, the flushing time is wrongly referred to as residence time (Sheldon & Alber, 2002). Dyer (1973; 1997) defined flushing time is the time required for the amount of freshwater inflow to equal the amount of freshwater originally present in the estuary. Zimmerman (1976) interpreted that flushing time is average transit time of freshwater from upper part to the mouth of estuary. Officer (1976) defined the flushing time as the time needed to displace the existing water in an estuary at an equal rate to the comparable outflow. Guo et al. (2000) described flushing time as the time interval in which the total amount of the existing water will be restored by new water entering the estuary. Flushing time is also known as freshwater transit time (Zimmerman, 1976) and freshwater residence time (Hilton et al., 1998; Hagy et al., 2000).

Sheldon and Alber (2002) in their study clarified the residence time and flushing time concept and compared the methods to calculate estuarine transport time scales that are commonly used in literature. Sheldon and Alber (2006) reported that, those simple models were perceived to be still useful as primary approaches for scaling a larger ecosystem as easily accessible and widely applicable models. They also added that tidal prism and freshwater fraction models were right to evaluate estuarine transport time scales if they are applied appropriately (Sheldon & Alber, 2006).

Researchers often use the residence time term while referring to freshwater transit time by using freshwater fraction method (Sheldon & Alber, 2002). A study done by Ascione Kenov et al. (2012) discovered that the residence time resulted from freshwater fraction model by Dyer (1973) and Lagrangian models are comparable.

In another study, box model was used to calculate residence time which was suitable for a constant flow rate of larger scale of estuary (Officer, 1980 referred by Sheldon & Alber, 2002). Jay et al. (1997) noted that calculation of transport time scales were similar for estuarine waters except for fjords.

Nowadays, after the findings of the meaning of residence time and flushing time were revealed and proved, the proposed classical model of tidal prism and freshwater fraction model was applied to obtain residence time and flushing time respectively, by using Dyer (1973; 1997) concept (Guo et al., 2002; Sheldon & Alber, 2002; Wang et al., 2004; Ascione Kenov et al., 2012; Shaha et al., 2012). In order to calculate the residence time and flushing time of a river, the study on the bathymetry, hydrodynamic, tidal prism and salinity distribution of the river should be taken into account (Sheldon & Alber, 2002; Sheldon & Alber, 2006). These measurements are very useful and meaningful to be in the formulated calculation by Dyer (1973; 1997).

Theoretically, short residence time and short flushing time during spring tide are contrary to during neap tide. This condition is related to the tidal prism, which is closely associated with the volume of river estuary. The larger tidal prism during spring tide contributes to fast flowing water that results into shorter residence time and faster flushing time and vice versa. There are several assumptions in the simple tidal prism model i.e. the estuary is well mixed at high tide (Dyer, 1973; Luketina, 1998; Sheldon & Alber, 2002) and it is suitable for very short estuaries (Dyer, 1973; Sheldon & Alber, 2002). Monsen et al. (2002) added that in order to apply the simple tidal prism model, the river flow should be smaller than tidal flow and the system must be at a steady state. However, Herman et al. (2007) revealed that the assumption of an estuary should be well-mixed condition not always valid and could be applied to any rivers.

The residence time recorded shorter at estuaries experience less water quality crisis because the substances would remain shorter time in the river system before it is discharged out to the sea (Ascione Kenov et al., 2012). Chances for contaminants deposited on the riverbed were lesser when the residence time was shorter due to high river flow (Ascione Kenov et al., 2012). Ascione Kenov et al. (2012) denoted that high depletion of oxygen in estuaries is associated with long residence time in previous studies.

As the residence time was defined as the time taken before its being flushed out from the system, the residence time could be unreasonably long in estuaries with intertidal areas (Ascione Kenov et al., 2012). Howarth et al. (2000) reported that longer residence time increased the primary productivity and decreased river flow in the Hudson River. Short residence time was limiting factors that reduce the phytoplankton biomass and could cause pollution as a result of high nutrient concentration (Wang et al., 2004). Shorter residence time during neap tide in wet season compared to spring tide was due to higher freshwater discharge transported pollutants seaward against weak neap current in Amba estuary, India (Velamala et al., 2016). Velamala et al. (2016) also verified that the estuary residence time were longer at neap tide during dry season compared to spring tide. A study in Musa estuary, Persian Gulf, showed that a constant current was an indicator of accumulation area of pollutant. Two factors that influence the residence time were river discharge and seawater inflow (Gómez-Gesteira et al., 2003; Shen & Haas, 2004). The residence time decreased with the increase of seawater inflow or river discharge (Gómez-Gesteira et al., 2003). Shen and Haas (2004) reported that the residence time decreased as flows from the tributaries to the river mouth during high flow and mean flow at York River estuary. The differences of the residence time for the tributaries station were longer between high flow and mean flow compared to the stations along the estuary mainstream under the same river flow circumstances (Shen & Haas, 2004).

Reduced residence time due to well-flushed estuary leads to alleviate nutrient loading (Defne & Ganju, 2014). The relationship of residence time and biomass in the estuaries were positively correlated in the ratio of 1:1 (Josefson & Rasmussen, 2000). The short residence time may alter and could diminish effects on the river estuary eutrophication (Josefson & Rasmussen, 2000). Faster residence time was characterised by low ratio of river flow and tidal current (Shen & Haas, 2004).

Any anthropogenic disturbances adjacent to the river estuary such as construction, reclamation and flood control measures would decrease the estuarine volume and increase the residence time (Velamala et al., 2016). High human population due to anthropogenic activities at the upstream contributes to longer residence time as well (Gong et al., 2008). Residence time is important to enhance and support the understanding of aquatic systems (Ascione Kenoc et al., 2012).

The residence time and flushing time would not be similar if the mixing of incoming and existing waters in an estuarine system for each tidal cycle was not completed (Wang et al., 2004). Both the residence time and flushing time controls the estuarine internal process until the nutrient input is modified (Balls, 1994). Nutrient could be flushed out of a river when shorter residence time and flushing time. Whereas, the nutrient would be remain longer in the river as longer residence time and flushing time.

Flushing time is an important indicator to assess the water quality of estuarine ecosystem (Huang, 2007). The flushing time was related to the tidal exchange between the river estuary and the adjacent ocean that involved the freshwater and seawater intrusions, stratification, wind and bathymetry (Ji et al., 2007). A long of flushing time indicated that longer time would be taken to flush out the pollutants from an estuary (Bricelj & Lonsdale, 1997 as referred to Shaha et al., 2012). Shorter flushing time near the mouth of estuary during spring tide compared to neap tide is due to larger tidal amplitude as spring tide took place (Shaha et al., 2012). In the Sumjin River estuary, the flushing time was short during neap tide than spring tide due to an increase in gravitational circulation as tidal amplitude reduced (Shaha et al., 2012). High flushing rate can minimize the eutrophication level in estuarine system (Josefson & Rasmussen, 2000) as the nutrient concentrations were brought to the seaward and diluted by the seawater.

2.4 Nutrient and Total Suspended Solids (TSS) Loadings

The existence of anthropogenic activities such as agriculture, domestic and aquaculture concentrated along the river corridor will result in the deterioration of water quality of the river system and contribute to the destruction on the river ecosystem and estuary edges as well. Any anthropogenic activities located along the river will give serious impact on the river system in term of nutrient (Nyamangara et al., 2013) and TSS loadings (Wang et al., 2009; Wan Ruslan et al., 2017), thus, flocculation of pollutants may be ended up into estuarine waters (Athuman & Nkotagu, 2013; Tening et al., 2013). Many estuaries were affected by excessive nutrient and TSS loadings of non-point source pollution from different anthropogenic activities (Das et al., 2011). Different anthropogenic activities such as agriculture, aquaculture, domestic and industry lead to different effect on water quality and pollutant concentrations (Schaffelke et al., 2005; Das et al., 2011). The effect of this development may also led to unstable soil structure and loss of major habitat in marine coastal areas (Schaffelke et al., 2005).

The widespread existence of agricultural activity at the upstream is the main cause of river pollution (Piscart et al., 2009; Wan Ruslan & Mohd Nazrul, 2015). A study in Pinang River, Balik Pulau showed that agricultural activities at the upstream area increased the nutrient level (Nurul Ruhayu, 2011; Nurul Ruhayu & Khairun, 2017). A similar study by Richards and Host (1994) indicated that agricultural activities changed the quality and quantity of water runoff. Despite the anthropogenic activities within a small area at the upstream, its influences could contributes to a greater contamination to the entire river basin up to the downstream (Peters & Meybeck, 2000). Therefore, the usage of fertilisers and pesticides (Bellos et al., 2004) in agriculture sectors can lead to river pollution (Nurul Ruhayu, 2011). Intensively cultivate fields, along with the heavy use of fertilisers and pesticides contribute to this problem (Sims et al., 1999; Sharpley et al., 1999; Rekolainen et al., 1999). Excess nutrients will later stimulate chlorophyll production that leads to hypoxia (dissolved oxygen, DO < 3 mg/L) (Rabalais & Nixon, 2002; Howarth & Marino, 2006).

The main fertiliser used for agricultural activities are nitrogen, phosphorus and potassium (Todd, 1989). According to Todd (1989) and Tredoux (1993), only a part of the nitrogen fertiliser solution is absorbed into the soil and used by plants while, the leftovers would flows through underground water subsequently entering the river system.

Furthermore, the application of fertilisers in agricultural land adjacent to the river increases the chances of it to move quickly to the river flow through leaching process (Peters & Meybeck, 2000) and also depends on the quantity and quality of runoff during heavy rains (Ngoye & Machiwa, 2004). Sedimentation from agricultural activities contributes negative effect on the recreational value of any ecosystem (Harker et al. 2000). Amon-Armah et al. (2013) reported that the TSS loading could act as a medium for transferring harmful bacteria and viruses into water system.

The increase of nitrogen (Arheimer & Linden, 2000; Castillo et al., 2000; Goolsby et al., 2000; Bramley & Roth, 2002) and phosphorus (Fisher et al., 2000; Bramley & Roth, 2002; Schaffelke et al., 2005) from the leaching of agricultural activities at watershed area can lead to contamination of drinking water sources and eutrophication in water surface of the river (Gomann et al., 2004). In durian orchard, the amount of fertiliser needed is 9 – 40 kg of organic fertiliser (which contain nitrogen (N), phosphorus (P) and potassium (K)) for each tree per year (PPDM, 2010). Meanwhile, in palm oil plantation, each tree need 1.2 kg N, 0.4 kg P and 2.0 kg K fertilisers annually to promote the tree growth and fruit production (Hishamudin et al., 1987). Thus, application of fertilisers in agriculture sectors along river corridors will be the non-point source of pollution in river systems (Das et al., 2011; Bagalwa et al., 2015).

The usage of pesticide for eradication of pest in plantation could lead to contaminants the water bodies through leaching. The pesticide residue can cause toxic and reduction of oxygen content in rivers (Griffin et al., 1979). On the other hand, it contributes carcinogens and mutagens on estuary aquatic life and can cause long-term effects of the disease to humans (Dermott, 1979).

Other anthropogenic activities that lead to water pollution are from domestic discharge. Studies show that unplanned housing construction without water treatment systems channel the waste from domestic activities, small industries and warehouses directly into the river system i.e. the use of detergents, foodstuffs, oil, urine and faeces (Jothy, 1976; Wan Maznah, 2002; Schaffelke et al., 2005). Direct discharge from domestic waste increased the concentrations of biological oxygen demand (BOD), nitrates, organic chemicals and bacteria in the soil as well as causing water to be very turbid and produce a fouls odour (Todd, 1989; Yap et al., 2006; Das et al., 2011).

Increased concentrations of nutrients released into the domestic river system may increase the problem of eutrophication in marine waters (Ahyaudin, 2000). Goldberg (1976) reported that soluble products such as faecal waste released into rivers have been identified to be carried as far as 10 km from where it is released depending on the quantity and the tide.

Aquaculture pond area usually lies between 2 and 20 hectares from mangrove estuary skirt (Sasekumar, 2000). Aquaculture ponds are a major factor contributing to the destruction of mangrove ecosystems (Todd, 1989; SAM, 2004; Khairun et al., 2012). Aquaculture wastes containing excess uneaten pellets, urine and manure can cause eutrophication in the river system and this will increase nitrate and phosphorus and the increment of suspended solids (Defur & Rader, 1995). Organic pollution and high nutrient in the river can lead reduce the dissolved oxygen in the river system (Kautsky et al., 2001; SAM, 2004). In addition, the reduction of oxygen could