SEDIMENT OXYGEN DEMAND AND SEDIMENT CHARACTERISTICS OF SANTUBONG RIVER

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List of Abbreviation

PSA-Particle size analysis
SOD- Sediment oxygen demand
OM-Organic matter
OC-Organic carbon
TP-Total phosphorus
TKN-Total kjeldahl nitrogen
TAN-Total ammonia nitrogen
TON-Total organic nitrogen

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Sediment Oxygen Demand and Sediment Characteristics of Santubong River

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Abstract

The objective of this study was to determine the sediment oxygen demand and sediment characteristics of the Santubong River. This study aimed to examine the relations between sediment oxygen demands and the sediment characteristics of the Santubong river due to human activities in the watershed. Particle size analysis was also conducted in order to determine the content of clay, silt and sand in the bottom sediment of Santubong river. The highest clay content was from station 2, while for silt and sand, the stations that gave the highest content was from station 5 and 1 respectively. The organic matter and organic carbon gave a positive correlation with the sediment oxygen demand. Total phosphorus determined from the orthophosphorus phosphorus, total Kjeldahl nitrogen, total ammoniacal nitrogen, total organic nitrogen, all shows a significant difference among the stations. For heavy metals, the sediments samples were taken at five stations along the river bank, the station that has the most lead concentration were station 3, station 1 and station 5, nickel and chromium respectively. The station with the highest SOD was obtained from station 1 and the lowest from station 5.

Key words: Sediment oxygen demand, sediment characteristics, Santubong River

Abstrak

CHAPTER 1

Introduction

Rapid urbanization such as the construction of the residential area along the Santubong River and the increasing number of the new cage culture along the river might cause an impact on the river hydrology and geomorphology. The discharge of waste from the nearest shrimp pond culture into the Santubong River is one of the sources of pollution on Santubong River. Agricultural activities in the area are mostly carried out along the bank of the Santubong River, and agricultural wastes are discharged directly into the river or flowed in runoff into the river after rainfall.

Waste products from the shrimp are produced continuously during the shrimp culture. When some of these waste materials are removed during the water discharge, the nutrients content in the pond might be lost and this might as well lead to the pollution of the water resource such as rivers where the water from the shrimp ponds are discharged (Swindlehurst, 1992; Limsuwan, 1993). The higher content in nutrient in shrimp ponds discharge is not good for other aquatic life in the water reservoir as it may cause pollution to the water body. Therefore, it is important to understand and to know the characteristics of sediment by their particle size distribution, the nutrients content and the concentration of heavy metals in order to understand more on the effect it may cause to the environment and human health.

This study was conducted using sediments collected along the Santubong River. In this study, analysed the Santubong River sediment oxygen demand and sediment characteristics, which included both physical and chemical characteristics. For the physical analysis, the particle size of the sediment was analysed in order to determine the percentage of the clay, silt, and sand. For the chemical analysis, organic matter, total
carbon, organic carbon/organic matter, total organic nitrogen, total phosphorus and heavy metals that were found in the sediment were determined.

The objectives of this study were to determine sediment oxygen demand of Santubong River and the sediment characteristics through various parameters.
CHAPTER 2

2.1 Sediments in river

Sediments and soil particles in rivers are primarily derived from rock weathering processes. There are two major natural sources of sediment:

1) Products of continental rock and soil erosion; and

2) Autochthonous materials which are formed within the water body.

Apart from water, sediments are also responsible of nutrients and pollutant transportation in aquatic environment. Sediments are known to capture hydrophobic chemicals pollutants entering water bodies (McCready, 2006). River sediment is the potential pollution source of toxicity to aquatic organisms and water quality. Physical and chemical sediment measurements are important components of marine monitoring programs designed to assess the environmental effects of wastewater discharges around ocean outfalls (Bilyard, 1987). Sediment characteristics are considered sensitive indicators of sewage-derived pollution not only because sediments adsorb and retain pollutants, but also because of the important interaction between the sediments and the benthic invertebrates that inhabit them.

According to Marcus (1991), sediment serves as diffuse sources of contamination to the overlying water body; slowly releasing the contaminant back into the water column. Therefore, ensuring good sediment quality is crucial to maintain a healthy aquatic ecosystem, which ensures good protection of human health and aquatic life.
2.2 Sediment oxygen demand

Sediment oxygen demand (SOD) is a combination of all of the oxygen-consuming processes that occur at or just below the sediment/water interface. Sediment Oxygen Demand (SOD) is the sum of all biological and chemical processes in sediment that utilize (take up) oxygen. Where the sediments are particularly enriched and where oxygen demand is substantial, it is important to simulate the uptake rates of oxygen and the release rates of nutrients from the sediment to the overlying water.

Most of the SOD at the surface of the sediment is due to the biological decomposition of organic materials and the bacterially facilitated nitrification of ammonia, while the SOD several centimetres into the sediment is often dominated by the chemical oxidation of species such as iron, manganese, and sulphide (Wang, 1980; Walker and Snodgrass, 1986).

Table 1: Level of SOD related to sediment quality (Butts and Evans, 1978)

<table>
<thead>
<tr>
<th>Range of SOD at 25 °C (g/m²/day)</th>
<th>Quality of benthic sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.5</td>
<td>Clean</td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>Moderately clean</td>
</tr>
<tr>
<td>1.0-2.0</td>
<td>A little polluted</td>
</tr>
<tr>
<td>2.0-3.0</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>3.0-5.0</td>
<td>Polluted</td>
</tr>
<tr>
<td>5.0-10.0</td>
<td>Very polluted</td>
</tr>
<tr>
<td>&gt; 10.0</td>
<td>Possibly sewage sludge</td>
</tr>
</tbody>
</table>
2.3 Physical characteristics of sediment

Sediment is the material that settles at the bottom of a liquid. Commonly, the word is used to describe the dirt, silt, soil, or polluted material that settles at the bottom of a lake, river, or stream. Sediment in the river consists of various type of soil as the size of individual particle contained in the sediment is not the same with one another. The particle-size analysis is basically conducted in soil science in order to evaluate the texture of soil. Soil texture is the combination of different combination of sand, silt and clay that make up the particle-size distribution of soil sample (Klute, 1986).

Sediments are capable of transporting loads of adsorbed nutrients, pesticides, heavy metals, and other toxins. Sediment particles can contain heavy metals as a part of the structure, as exchangeable cations, or as sorbed and precipitate matter. Sediment size across the river varies with the rate of water circulation. In areas with still or slow moving water, fine particles suspended in the water are allowed to sink to the bottom. The deposit areas are created because small sediment grains have greater surface area available for adsorption of organic and chemical compounds (Thompson and Lowe, 2004).

The quantity of heavy metals retained in sediments is also affected by the characteristics of the sediment into which they are adsorbed. Sediments with a high percentage of small grains, have high surface-to-volume ratios and this means that smaller particle size of soil such as silt and clay, have the ability to adsorb more heavy metals than sediments composed of large grains, such as sand. Total organic carbon is added to sediments primarily through the decomposition of plant and animal matter. Organic carbon can directly adsorb heavy metals from solutions applied to sediments (Liber et al., 1996). Nonetheless, high percentages of organic matter and/or small grains in sediment are
generally associated with reduced heavy metal bioavailability and toxicity (Ankley et al., 1996).

### 2.4 Nutrient and organic matter in sediment

Nitrates and nitrites are formed in many ways, both natural and industrial. Among the natural pathways are nitrification of ammonia and precipitation of nitric and nitrous oxides. Nitrites can be formed from nitrates by denitrification in sediments that lack oxygen. When total nitrogen is in excess it can contribute to eutrophication (Valiela et al., 2004). Fertilizer use, release of industrial and municipal wastes, and leaching of farm animal wastes and septic tanks are major sources of nitrates.

However, excessive phosphorus inputs from municipal, industrial, and residential sources as well as from agriculture can have detrimental effects on adjacent or down gradient aquatic systems by increasing the biological productivity of surface water. Increases in biomass and microalgae blooms decrease oxygen availability in the water acting as a stressor on aerobic organisms within the environment (Valiela and Bowen, 2002). The resultant eutrophication may cause taste-and-odour problems to the consumers, degrade habitat for aquatic life, and discourage recreational use of the affected water body.

Organic matter in sediment consists of carbon and nutrients in the form of carbohydrates, proteins, fats and nucleic acids. Bacteria quickly eat the less resistant molecules, such as the nucleic acids and many of the proteins. Organic matter is a vital food source for a variety of organisms, but may lead to oxygen depletion as organisms break down the carbon (Hyland et al., 2005). Sediment organic matter is derived from plant and animal detritus, bacteria or plankton formed in situ, or derived from natural and anthropogenic
sources in catchments. Sewage and effluent from food-processing plants, pulp and paper mills and fish-farms are examples of organic-rich wastes of human origin.

2.5 Heavy metals in river and the consequences

Among the various contaminants, heavy metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risks. Heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Tam and Wong, 2000). They inhibit primary productivity, nitrogen fixation, mineralization of carbon, nitrogen, sulfur and phosphorus, litter decomposition and enzyme synthesis and activity in soils, sediments and surface water. Unlike organic pollutants, heavy metals are not biodegradable and undergo a global eco-biological cycle in which natural waters are the major pathways (Nürnberg, 1984).

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic, highly toxic or poisonous at low concentrations. These anthropogically derived inputs can accumulate in local sediments. Although metals (copper, lead, chromium, zinc, etc.) exist naturally in ecosystems, if they are in high enough concentrations, then metals can have detrimental effects on the health and behaviour of animals. The most serious kind of river pollution is the pollution by heavy metals discharged from factories in industrial zones, especially those located upstream of rivers (Chan, 1999). According to Mateu et al. (1996) trace metal levels can be indicators of the concentrations of other pollutants to which they are potentially related.

Heavy metals such as cadmium, mercury, lead, copper, and zinc, are regarded as serious marine pollutants because of their toxicity, tendency to be incorporated into food chains, and ability to remain in an environment for a long time (Kishe and Machiwa, 2003). Lead
occurs naturally in the environment, natural lead levels are almost zero and any concentration above this level indicates contamination (Goldberg et al. 1983). However, most lead concentrations that are found in the environment are a result of human activities, natural and anthropogenic sources. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. When dissolved lead enters the water column, it is dispersed by water circulation, complexes with particulate matter suspended in the water column, and adsorbed into the sediment (Williamson and Morrisey, 2000).

Lead enters estuaries by atmospheric deposition from vehicle exhaust, and air pollution, and as run-off from parking lots and roads. Studies indicate that lead in sediment varies in proportion to the number of people living in the area (O'Connor, 2002). Automobile fuels have historically contained lead additives for valve lubrication, but their usage is slowly being phased out. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water.

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (IARC, 1990). Adverse health effects from cadmium exposure may occur at lower exposure levels than previously thought, primarily in the form of kidney damage (Järup, 2003).

Nickel is a compound that occurs in the environment only at very low levels and is essential in small doses but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of
animals, mainly for those that live near refineries. The most common application of nickel is an ingredient of steel and other metal products.

Table 2: Regulatory limits of heavy metals applied to soil (Adapted from U.S. EPA, 1993)

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Maximum concentration in sludge (mg/kg or ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>75</td>
</tr>
<tr>
<td>Cadmium</td>
<td>85</td>
</tr>
<tr>
<td>Chromium</td>
<td>3000</td>
</tr>
<tr>
<td>Copper</td>
<td>4300</td>
</tr>
<tr>
<td>Lead</td>
<td>420</td>
</tr>
<tr>
<td>Mercury</td>
<td>840</td>
</tr>
<tr>
<td>Nickel</td>
<td>75</td>
</tr>
<tr>
<td>Selenium</td>
<td>100</td>
</tr>
<tr>
<td>Zinc</td>
<td>7500</td>
</tr>
</tbody>
</table>

2.6 Environmental effect of river pollution

In Malaysia today, the state of the river is appalling and in urban areas rivers have been turned into open sewers. There are various sources of pollution occurring in Malaysia rivers, mainly from agriculture, livestock farming domestic homes, urban areas and industries. According to Hj Keizrul bin Abdullah (2002), the worse cases of pollution are when the rivers flow through urban area as they are subjected to heavy solid and liquid waste disposal from the settlements, drainage effluents from commercial area, food centres and wet markets.

Nowadays, the most important environmental concern facing the aquaculture industry is the disposal of the nutrient rich effluent water produced during the culture of aquatic animals (Goldburg and Triplett, 1997). The direct discharge of shrimp farm waste into the river will also pollute the water in the river. When the harvesting season ended, the shrimp ponds are drained and the accumulated sediment is often treated by flushing the bottoms, drying the sediment and removing it (Hopkins, 1986). The deposition of detrital loads,
resulting from plankton and other organisms, increases in eutrophic waters (Jickels, 1998). Based on the study, the sediment processes in shrimp ponds can contribute substantially to the nutrient discharge loads, particularly in the form of NH$_4^+$ (Funge-Smith and Briggs, 1998; Preston et al., 2000). The excess nutrients in runoff stimulates high production of plankton. Turbidity of water increases further decreasing light penetration. Benthic plants die and epiphytic algae are the only bottom plant.
CHAPTER 3

Materials and methods

3.1 Area description

The main source of the samples were taken from Sungai Santubong. Five (5) sampling stations (ST 1, ST 2, ST 3, ST 4, and ST 5) were established along the Santubong River. Table below gives a detailed description of each sampling station. Three replicate of sample are collected from each station.

Table 3: Description of sampling stations

<table>
<thead>
<tr>
<th>Station</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST 1</td>
<td>Residential area (Santubong village)</td>
</tr>
<tr>
<td>ST 2</td>
<td>Discharge area</td>
</tr>
<tr>
<td>ST 3</td>
<td>Cage culture</td>
</tr>
<tr>
<td>ST 4</td>
<td>Cage culture</td>
</tr>
<tr>
<td>ST 5</td>
<td>Clean area (upstream)</td>
</tr>
</tbody>
</table>
3.2 Sampling and collecting sediment

Three replicates of sediment samples from each station were collected at different times between December 2008 and March 2009. Only one replicate was taken for every trip, this means there were three trips for each sampling of replicate which were taken on 12\textsuperscript{th} December 2008, 19\textsuperscript{th} February 2009 and 26\textsuperscript{th} March 2009. Five hundred grams of samples were collected from the upper 30 mm layer of sediment using a shovel for each location. The sample collected was packed separately in a hand-held plastic jars and stored in sealed plastic bags in a refrigerator at 4 °C in order to minimize the bacterial activities and chemical changes due to processing. The sediment collected was for sediment
characterizations, for SOD analysis, samples were collected using PVC tube and both end of the tube were seal after the sediment were collected.

3.3 Sediment Oxygen Demand

For each station 3 cores of soil samples were collected with seal cores and packed in ice and 6 gallons (25 litres each) of channel water were collected for transportation to laboratory. In order to determine the sediment oxygen demand the procedure below were followed:

After the samples arrived at the laboratory, the sediments were immediately equilibrated to the test temperature (about 20 °C). Then, the clean chambers were filled with three-fourths full with the channel water and we allowed the channel water temperature to adjust to the test conditions, which is in this case the laboratory condition. After that, we placed the core samples in a chamber and finish filling the chamber with channel water in such a way as to minimize suspension of core sediments. The cover was placed on the chamber and calibrated DO meter (Adwa, AD610) was inserted. Any entrapped air was removed and any opening was sealed using silicone. Any suspended sediments were allowed to settle. As the pump operation (HAQOS SP500) began, the recording data on DO, time and temperature at selected intervals was recorded. The flow rate of the chamber was at 900 L/H.
Calculation of sediment oxygen demand

The SOD rate was calculated from a graph of DO concentration in the chamber versus time. The slope of the oxygen depletion was determined through linear regression. The following equation was used to calculate the SOD rate (Doyle and Lynch, 2005):

\[
SOD_T = 1.44 \frac{V}{A} (-b) \quad [1]
\]

Measured SOD rates were corrected to 20°C using a standard van't Hoff equation:

\[
SOD_{20} = \frac{SOD_T}{1.065^{T-20}} \quad [2]
\]
3.4 Physical Analysis of the Sediment

3.41 Particle Size Analysis

The Pipette Method (Phin, 2000)

Pretreatment

Ten grams of soil was weighted into a 2 litre tall form beaker. After adding 20 millilitre of H$_2$O$_2$, the sample was left to stand overnight. On the following morning, the mixture was boiled carefully to avoid any soil frothing over. More H$_2$O$_2$ was added when the reaction subsided and boiling was repeated. The addition of H$_2$O$_2$ was repeated until most of the organic matter had been destroyed judged by the rate of reaction and the bleached colour of the sample. The side of the beaker was rinsed occasionally. After the final addition of H$_2$O$_2$, the sample was heated for about one hour to destroy excess H$_2$O$_2$.

Dispersion

Five millilitre of the sodium hexametaphosphate solution was pipetted into the peroxide treated sample. The soil mixture then transferred to 1 litre electric stirrer container and the volume was made up to about 500 millilitres. The sample was stirred for 10 minutes with a high speed stirrer, then the stirrer blades was washed down as they were removed from the suspension.

Separation by sieving and sedimentation (simplified for USDA system)

The dispersed soil suspension was then transferred through a 0.050 millimetre sieve into a 1 litre measuring cylinder. It was done by placing a large funnel below the sieve to channel all the suspension and subsequent washings into the cylinder. The particle on the sieve was washed carefully until all the fine particles were washed through into the cylinder. The
fraction remaining on the sieve was the sand fraction >0.05 millimetre. All the sand fraction on the sieve was transferred into an evaporating dish by rinsing it with water. The evaporating dish was placed in an oven set at 105 °C and leaved it to dry until constant weight. The suspension was made up by adding the water into 1 litre measuring cylinder with distilled water and then placing it in water bath maintained at 28 °C. The suspension was stirred thoroughly with a special hand plunger using up and down movement. The plunger was removed and when the swirling motion stopped. Immediately 20 millilitres was pipetted from 6 centimetre depth. It was transferred to an evaporating dish and the sample was dried in an oven at 105 °C. The stirring was repeated, 20 ml of the sample was pipetted from 10 centimetre depth after 6 hours 39 minutes. Then the sample was dried in the oven at 105 °C and weighed after cooling.

3.5 Organic Carbon and Organic Matter Analysis

3.51 Dry Ash Method (Boyd, 1995)

A clean crucible was tared and 2 gram of air-dried soil was added into the crucible. Then the sample was placed in an oven at 105 °C for 24-48 hours. The sample was removed from the oven, cooled in a desiccator, and weighed. The sample was placed in a muffle furnace at 350 °C for 8 hours, after 8 hours the sample then was removed from the furnace, cooled in desiccators, and reweighed. The resulting weight loss would caused mainly by the oxidation of organic matter to carbon dioxide and water if a soil was ignited at 350 °C for several hours. The temperature should not exceed 350 °C to prevent loss of water from clay minerals and decomposition of calcium carbonate to calcium oxide and carbon dioxide. The organic matter concentration is compute as follows:

\[
OM = \frac{W_{TS} - W_F}{W_{TS} - W_T} \times 100
\]
Where

\[ OM = \text{organic matter concentration (\%)} \]

\[ W_T = \text{tare weight of crucible (g)} \]

\[ W_{TS} = \text{tare weight of crucible and oven dry soil (g)} \]

\[ W_F = \text{weight of crucible and soil after ashing (g)} \]

In order to determined the organic carbon concentration instead of organic matter concentration, the organic matter concentration was multiplied by 0.58. The value of 0.58 was used because soil organic matter has a carbon content about 58%.

\[ OC = OM \times 0.58 \]

### 3.6 Total Phosphorus Analysis

#### 3.61 Digestion with perchloric acid (Jackson, 1958)

Two gram of air dried soil was placed in a 250 volumetric flask and 30 ml of 70% HClO₄ was added and it was covered with pyrex funnel to ensure the reflux of the HClO₄. The mixture was digested in a preheated sand bath on a hot plate at 350 °C in a well ventilated, stainless steel hood until the dark colour due to the organic matter disappeared. The heating was continued at 203 °C for 20 minutes.

When the digestion was completed, heavy white fumes of HClO₄ appeared and the silica becomes white. One or two millilitre of HClO₄ was added to wash down any particle sticking to the sides of the flask. For the soil that contains a high organic matter content, 20 millilitre of concentrated HNO₃ was added and heated to oxidize the sample. When the digestion was completed, the flask was removed from the sand bath to cool down the mixture. The sample then was diluted with deionized water to 250 millilitres and mixed
well. The solid material was allowed to settle then the reactive P concentration in the sediment was determined using Hach instrument (DR2010 Soectrophotometer using the PhosVer 3 (Ascorbic Acid) method.

3.7 Determination of TKN

Determination of total Kjeldahl Method

Total Kjeldal Nitrogen were determined by following Regular Kjeldahl Method (Bremner, 1996). A sample of 0.300 gram was placed in a micro-Kjeldahl digestion flask. One tablet of high selenium kjeldahl catalyst and 3 millilitre of concentrated H$_2$SO$_4$ were added into the flask. The flask was heated on the digestion stand using FOSS Tecator 2006 digestor unit. When the frothing has ceased, the heat was increased, until the digest clears. After that, the mixture was boiled gently for 2 hours. The heating was regulated during this boiling so that the H$_2$SO$_4$ condenses about one-third of the way up the neck of the digestion flask. After the digestion has complete, the flask was allowed to cool. Then the procedure of determining the total kjeldahl nitrogen was continued by following the steps provided in the Hach laboratory manual of Nessler method (Hach, 1996).

Determination of Total Ammoniacal-N (NH$_3$ + NH$_4^+$)(TAN)

The determination of Ammoniacal-N is also carried out by following Kjeldahl Method described in the method for determination of TKN. However, the digestion step is omitted since the analysis for TAN did not involve the amount of nitrogen in organic form.