Oxygen Demand of the Sediment from the Semariang Batu River, Malaysia

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Abstract: The Semariang Batu River is located near the city of Kuching, with residential and shrimp farming activities which may impact the quality of the sediment. However, sediment of this river had not been investigated. Therefore, the objectives of this study were to determine the sediment oxygen demand (SOD) at different locations along the river and the relationship between SOD and the characteristics of the sediment. Surface sediments were collected at five stations for analysis. Results indicated that sediment total phosphorus values ranged from 288-1446 mg/kg. The station near the residential, seafood and boat landing jetty and the station near shrimp farm discharge recorded the highest sediment phosphorus and nitrogen. SOD ranged from 0.76 gO2/m2/day at the station with the least human activities to 21.4 gO2/m2/day at the station with shrimp farm discharge. SOD near the jetty was also high 16.2 gO2/m2/day which ranked the second highest in value among the five stations. SOD values were significantly correlated with phosphorus, nitrogen and clay content of the sediment.

Key words: Sediment oxygen demand · Shrimp effluent · Domestic discharge · Nitrogen · Phosphorus

INTRODUCTION

Water quality of many rivers in the world has been investigated to gain more understanding on the impact of agriculture, aquaculture, sewage, household and industrial effluents on the receiving water bodies [1-5]. However, not as much studies are done on the sediment. The study of sediment is important as sediment is a sink for organic materials and other contaminants such as heavy metals, antibiotics and pesticides and these contaminants could affect the quality of water which is in contact with the sediment for a long time. Nelson et al. [6] reported that the Klang River in Malaysia showed low dissolved oxygen due to the high oxygen demand of sediment that rests on the bottom during neap tides and was resuspended during spring tides. Chau [7] reported that even though the exogenous organic materials dissolved in the overlying water of a land-locked embayment in Hong Kong had been reduced substantially, the soft bottom sediment continued to act as sources of nutrients. Contaminants were reported to reduce the richness and evenness of marine communities [8].

The Semariang Batu River is a tidal influenced river located near Kuching city, Malaysia. The rapid development of the city is encroaching on the river where traditionally a village is located upstream and in the 1990’s due to the bloom in shrimp industry; it became a site for shrimp aquaculture. Impacts of shrimp aquaculture on the water quality have been reported in different parts of the world [9-11]. The input of shrimp aquaculture into the river and coastal areas include nutrients and organic matter [12]. Preliminary investigation of the Semariang Batu River water quality indicated phosphate was highest at the station downstream of shrimp farm discharge and ammonia-nitrogen was highest at the station near the residential area [13]. Shrimp pond bottom soil was found to be high in nutrients such as nitrogen and phosphorus and organic matter and as a result high oxygen demand was reported [11, 14, 15]. For residential areas, discharge into the rivers includes untreated or partly treated sewage and greywater with high organic matter and high nutrients [12, 16-18]. These potentially results in eutrophication and oxygen depletion of the receiving water bodies [11, 12]. Sediment oxygen demand plays an important role in determining the dissolved oxygen level in water bodies.
Hantush [19] reported an almost linear relationship between steady-state sediment oxygen demand and bulk water oxygen. Therefore, in this study, nutrients and oxygen demand of the sediment from different stations were investigated.

**MATERIALS AND METHODS**

**Sampling Location:** Sediment samples were collected from five stations along the Samariang Batu River, Malaysia (Fig. 1). Station S1 was located about 4 km downstream of the shrimp farm discharge point at Loba Bodoh Besar; station S2 was located at the Semariang Batu Village jetty which was also near downstream of urban residential area; station S3 was located at Loba Kara which was near the shrimp farm effluent discharge point; station S4 was located at Lemidin River where a small construction work was observed and station S5 was located at Mangkuang River where no human activities was observed.

At each sampling station, four undisturbed sediment cores were collected (three for sediment oxygen demand (SOD) measurement and one for sediment characteristic analysis) and capped on the top and at the bottom with PVC caps. The inner diameter and height of the sediment core were 5.1 cm and 12.7 cm respectively. The sediment was collected from the bottom of the river during low tide. Water samples were collected from the river using plastic containers. The sediment samples were packed in cooler box with ice and transported to the laboratory with minimum core disturbance. Sediment samples for sediment characteristic analysis were preserved at 4°C prior to analysis.

**Oxygen Demand Analysis:** SOD analysis method in this study follows that of Truax et al. [20]. Immediately upon the samples’ arrival at the laboratory, the sediments were equilibrated to the room temperature. Two chambers consisting of sediment chamber (Fig. 2) and blank

![Fig. 1: Study area and sediment collection stations](image1)

![Fig. 2: Sediment oxygen demand analysis setup in laboratory](image2)
chamber with the height of 24.0 cm and inner diameter of 24.2 cm were set up in the laboratory. The volume of each chamber was 11 litres. The clean chambers were filled to three-fourths full by using the river water. Three core samples were placed in the sediment chamber and the chamber was filled to the top with channel water. The chamber was covered, calibrated dissolved oxygen (DO) meter was inserted and entrapped air was removed before being sealed with silicon seal. Six chambers were set up simultaneously. The chamber was left for 10 minutes to allow suspended sediments to settle. DO value was recorded at 10 minutes intervals for three hours.

The SOD rate was calculated from a graph of DO concentration in the chamber versus time. The slope of the oxygen depletion line was determined through linear regression. SOD was computed according to Equation 1 [21].

\[
SOD_r = 1.44 \frac{V}{A} (a - b)
\]  

where SOD_r was the sediment oxygen demand (g O₂/m²/d), V was the volume of the chamber (L), A was the surface area of the sediment (m²) and b was the regression slope of the DO concentration with time (mg/L/min). Measured SOD rates were corrected to 20°C and 25°C using modified van’t Hoff form [Equation 2] of the Arrhenius relationship [22].

\[
SOD_{20} = \frac{SOD_r}{1.065^{T_{20}}}
\]  

where T was the water temperature (°C), SOD_20 was the SOD rate at 20°C (g O₂/m²/d) and SOD_r was the SOD at temperature T (g O₂/m²/d).

Sediment Analysis: The sediment samples were air-dried, treated with H₂O₂ and hexametaphosphate (HMP) before particle size analysis (PSA) was carried out according to the Pipet Method [23]. pH of sediment solution was measured using a pH meter (Jenway 3305) in a ratio of 1:5, sediment: distilled water. Organic matter analysis was carried out according to Loss on Ignition (LOI) method [24]. TOC was calculated by using equation [3].

\[
TOC = OM\% \times 0.58
\]  

Total Kjeldahl nitrogen (TKN) was analyzed by using the moisture samples [25]. TKN was determined according to the Total Kjeldahl Method (Nessler Method) [26], after digestion in concentrated HSO₄ and Kjeldahl high selenium catalyst tablets (FOSS Tecator 2006 digestor unit). Colorimetric determinations of TKN and total phosphorus (TP) were carried out by using a spectrophotometer DR2010. For determination of TP, 2 g of sample was digested with HClO₄ [27] and the digested sample was measured for TP (in the form of reactive phosphorus) using ascorbic acid method [26]. All samples were analyzed in triplicates.

Statistical Analysis: For each parameter of the sediment, mean values from different stations were compared for significant difference by using one-way ANOVA and multiple comparison tests (Fisher’s Least Significant Difference). Relationships between SOD and sediment characteristics were analyzed using correlation and linear regression analyses. All data analysis was conducted using SPSS version 17.0 package.

RESULTS

The sand, silt and clay content of the sediment from the five stations are shown in Table 1. Station S1 sediment was loamy, stations S2 and S3 were clayey and stations S4 and S5 were clay loams. Sand was the highest at station S1 and the lowest at station S3. On the other hand, clay was the highest at station S3 and the lowest at station S1. Multiple comparisons indicated that sand, silt and clay at all pairs of stations were significantly different (P = 0.002, P = 0.019, P = 0.021 respectively).

Table 2 shows the concentrations of TOC, TP, TKN and SOD_20 of the sediment from the five sampling stations. TOC content ranged from 6.1% at S4 to 15.4% at station S3 (Table 2). TOC values were in decreasing order of S3>S2>S1>S5>S4. All stations were significantly different in TOC (P = 0.0005) except amongst station S1, S4 and S5 (0.07 = P = 0.73).

Table 1: Mean and standard deviation values of sand, silt and clay of sediment at the five sampling stations and their textural classification

<table>
<thead>
<tr>
<th>Fraction (%)</th>
<th>Station</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>47.21 ± 1.34*</td>
<td>32.18 ± 2.04*</td>
<td>20.60 ± 0.69*</td>
<td>Loam</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>26.30 ± 0.76*</td>
<td>27.46 ± 2.18*</td>
<td>46.24 ± 1.42*</td>
<td>Clay</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>21.10 ± 0.73*</td>
<td>23.58 ± 1.42*</td>
<td>55.31 ± 0.70*</td>
<td>Clay</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>31.77 ± 0.52*</td>
<td>40.86 ± 0.71*</td>
<td>27.33 ± 0.92*</td>
<td>Clay loam</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>28.39 ± 1.08*</td>
<td>47.37 ± 1.69*</td>
<td>24.14 ± 0.56*</td>
<td>Clay loam</td>
<td></td>
</tr>
</tbody>
</table>

Means in the same column with the same superscript are not significantly different at 5%.
Table 2: Mean and standard deviation values of TOC, TP, TKN and SOD of the sediment taken at the five sampling stations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Station 1 (S1)</th>
<th>Station 2 (S2)</th>
<th>Station 3 (S3)</th>
<th>Station 4 (S4)</th>
<th>Station 5 (S5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (%)</td>
<td>7.48 ± 0.99a</td>
<td>11.39 ± 1.11b</td>
<td>15.35 ± 0.49c</td>
<td>6.14 ± 0.53d</td>
<td>7.25 ± 0.72e</td>
</tr>
<tr>
<td>TP (mg/kg)</td>
<td>495.8 ± 71.9a</td>
<td>1437.5 ± 55.6b</td>
<td>1445.8 ± 46.9c</td>
<td>322.9 ± 50.1d</td>
<td>287.5 ± 99.2c</td>
</tr>
<tr>
<td>TKN (mg/kg)</td>
<td>581.2 ± 31.1a</td>
<td>1131.3 ± 45.1b</td>
<td>1277.1 ± 231.0c</td>
<td>793.8 ± 31.3d</td>
<td>508.3 ± 29.5e</td>
</tr>
<tr>
<td>SOD (gO₂/m²/day)</td>
<td>6.00 ± 1.26a</td>
<td>16.24 ± 0.48b</td>
<td>21.35 ± 0.78c</td>
<td>2.27 ± 0.66d</td>
<td>0.76 ± 0.33e</td>
</tr>
</tbody>
</table>

Means in the same row with the same superscripts are not significantly different at 5%.

Fig. 3: Regression of SOD on (a) organic carbon and (b) clay

Fig. 4: Regression of SOD on (a) TKN and (b) TP

TP ranked the highest at station S3 at the mean value of 1446 mg/kg followed by stations S2, S1, S4 and S5 in that order with the lowest value of 288 mg/kg at station S5. TP at stations S2 and S3 were 3-5 times higher than S1, S4 and S5. Least significant difference analysis of the means indicated that stations S2 and S3 (P=0.883) came from populations of the same mean and stations S4 and S5 also came from populations of the same mean (P=0.535). TKN trend was similar to TP except for stations S1 and S4 where station S4 showed significantly higher mean TKN than S1 (P=0.037) but lower mean TP (P=0.011). For TKN, pairwise comparisons indicated that mean TKN of stations S2 and S3 came from populations of the same mean (P=0.129) and stations S1 and S5 came from populations of the same mean (P=0.428). Both TP and TKN were found to be highly correlated with clay with 88.5 and 94.3% of the total variations explained by the regression (Figure 3) (P=0.017 and P=0.006 respectively).

Mean SOD values ranged from 0.76 gO₂/m²/day at station S5 to 21.4 gO₂/m²/day at station S3 (Table 2). SOD values at stations S2 (16.2 gO₂/m²/day) and S3 (21.4 gO₂/m²/day) were much higher than the other stations (= 6 gO₂/m²/day). Least significant difference analysis showed that the mean SOD values were
significantly different among all pairs of stations \((P=0.036\) between \(S4\) and \(S5\), \(P<0.0005\) for all other pairs). The trend of \(\text{SOD}_{20}\) in decreasing order was \(S3>S2>S1>S4>S5\). Figures 4 and 5 showed regression of \(\text{SOD}_{20}\) on other characteristics of the sediment. It was found that \(\text{SOD}_{20}\) was highly correlated with TOC \((r=0.965, P=0.008)\), clay content \((r=0.942, P=0.017)\), TKN \((r=0.929, P=0.023)\) and TP \((r=0.977, P=0.004)\). Furthermore, \(\text{SOD}_{20}\) was found to be significantly negatively correlated with silt content \((r=0.929, P=0.022)\).

**DISCUSSION**

The high organic carbon and nutrients (nitrogen and phosphorus) at station S3 is most likely due to the discharge from shrimp ponds during harvesting. High concentrations of carbon \((1-20\%)\), nitrogen \((1,000-20,000\text{mg/kg})\) and phosphorus \((1,000-20,000\text{mg/kg})\) were reported to accumulate in the sediment of aquaculture ponds [14]. Nutrient budget studies of Thakur and Lin [28] showed that major sink for nutrients were the sediment which accounted for 14-53% nitrogen and 39-67% of phosphorus of the total input and the drained water at harvest contained 114-28% nitrogen and 12-29% phosphorus. It was also reported that shrimp could only accumulate 23-31% nitrogen and 10-13% phosphorus of the total input and that the majority of the input was the feed. Lemonnier and Faninnoz [29] reported that for semi-intensive shrimp ponds, 19-46% of nitrogen input from feed and water was exported to the coastal environment and the outflow water showed an increase in organic soluble and sestonic organic forms expressed in terms of particulate nitrogen, particulate organic carbon and chlorophyll a. Paez-Osuna et al. [30, 31] reported that 63.5% and 47.2% respectively of the phosphorus accumulated in the sediment of shrimp ponds. Therefore, during harvesting, organic materials with nutrients are transferred to the receiving stream.

For \(\text{SOD}_{20}\), the highest value was found at station S3. This is due to the availability of organic matter from the shrimp farm discharge. As a result, the bottom sediment became a favorable site for the development of microbial communities that led to high consumption of oxygen by bacteria [14]. According to calculation [32], benthic oxygen uptake rate of shrimp ponds at stocking rate of 45,000 and 105,000 animals/ha and an overall feeding rate ranging from 1-5% of the body feeding rate per day range from 32.8-39.2 \(\text{gO}_2/\text{m}^2/\text{day}\). For the present study, the stocking rate was about three times that of 105,000 animals/ha. Therefore, it is not surprising that the \(\text{SOD}_{20}\) was so high at the stream receiving the discharge. Ling et al. [33] also reported that stations downstream of fish aquaculture showed elevated \(\text{SOD}_{20}\) of 10.4 \(\text{gO}_2/\text{m}^2/\text{day}\) when compared with the lowest value of 5.6 \(\text{gO}_2/\text{m}^2/\text{day}\) upstream.

For station S2, the concentrations of TP and TKN were also very high (not significantly different from station S3) and TOC and \(\text{SOD}_{20}\) ranked second highest. This is due to the discharge mainly from residential and commercial areas. The individual septic tank mainly treated solids and other nutrients overflowed to the receiving water. This probably explains the non-significant difference between station 2 and 3 for nutrients. There was likely contribution from untreated household greywater which included kitchen waste. Furthermore, it is located near the jetty where boats and seafood landed. These activities also contributed the high organic materials thus supporting the benthic communities giving high \(\text{SOD}_{20}\). This is proven by the significant positive correlation between \(\text{SOD}\) values with TOC, TP and TKN. High correlation between \(\text{SOD}_{20}\) and sediment organic matter, TP and TKN were also reported in the Serin River [33].

Station S1, located downstream of S3 was ranked third highest in TOC, TP and \(\text{SOD}_{20}\) and ranked fourth for TKN. Being downstream of shrimp farm discharge point, though 4 km away, as the tide water flooded and
subsequently receded, some of the pollutants were likely brought to station S1. For station S4, the TKN values ranked the third and it was significantly higher than S1 likely due to the presence of new construction activities. Station S5 is considered a clean site with no visible human activities and thus the values of TOC, SOD, and nutrients were the lowest amongst all the stations. When results of mean SOD from the present study were compared with those of other studies [7, 20, 22, 33-39] as shown in Table 3, it was found that mean SOD values from Station S5, S4 and S1 were in 12, 7 and 5 respectively of all the ranges listed. However, mean SOD values from stations 2 and 3 which were the highest among the five stations only fell in the range reported for Eastern United States rivers [22].

High concentrations of sediment TP were due to the great capacity of the sediment for adsorption of phosphorus [40]. This is also shown by the significant correlation between phosphorus and clay content. The high concentrations of phosphorus in the sediment from stations S2 and S3 due to residential and commercial activities is similar to the report of Xiangxi River sediment in China (757.7-1438.5 mg/kg) which received industrial and urban wastewater input [41]. Phosphorus values of the other three stations, S1, S4 and S5, falls in the range (37-453 mg/kg) reported in Florida bay [42].

It is recommended that shrimp farm effluents and household waste be treated and recycled. This is because phosphorus, applied as a fertilizer to produce food, is dependent on phosphorus derived from phosphate rock which is a non-renewable resource and the current reserve may be depleted in 50-100 years [43]. Therefore, when phosphorus and nitrogen from households and shrimp farm waste are recycled, not only the aquatic species are protected, nutrients from the waste will be recovered for use in food production.

**CONCLUSIONS**

This study shows that sediment oxygen demand was the highest at the station that received shrimp farm effluent and second highest at the station near residential areas and boat jetty and the lowest at the station with no obvious human activities. The sediment oxygen demand values were significantly correlated with organic carbon, clay content, total phosphorus and total nitrogen of the sediment.

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