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TOTAL ORGANIC CARBON (TOC) AND CARBON/NITROGEN RATIO IN SURFACE SEDIMENTS IN KUALA SUNGAI BARU, MELAKA

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ABSTACT: Total Organic Carbon and Carbon/Nitrogen ratio were determined from the sediments samples collected from eleven study areas in Kuala Sungai Baru Melaka. The high percentage of organic carbon observed in Station 8 ranging 1.88% and this could be attributed to organic matter from industrial, residential and municipal wastewater around the study areas. Comparatively higher C/N ratio was found in Station 1 of 68.04 which is in the sea; this could be the result of the rain that happened the day before we collected the samples. With various agricultural wastes from the palm oil and rubber plantation, forest, padi field and the effluent from the pig farm attribute to the higher number of C/N ratio which is most likely accumulated in Station 1. However, overall results can support the idea that sediments in Kuala Sungai Baru were mostly derive from the primary production in the sampling sites. The result results show that the water quality in all the sampling stations is classified as Water Supply II category based on Interim National Water Quality Standards for Malaysia.
Keywords: Total organic carbon, carbon, nitrogen, sediments, Melaka

1. INTRODUCTION

Water is the basic element of life without it life would not exist on earth. It is important resource for human, and yet it is taken for granted because water is everywhere and it flows freely when we turn on the tap. The usage for water increases as population grows until the demand sometimes overshoots the supply or availability of water. Surface water resources have played an important function throughout the history of human civilization. About one third of the drinking water requirement of the world is obtained from surface sources like rivers, canals and lakes (Das & Acharya, 2003). Every time we use water, we affect it in some way. Once used, water flows out as quickly as it comes - down the drain and into our rivers. The gunk and grease that is flushed down into the drain unthinkingly every day will ultimately find their way to a nearby river and polluting it in the process (Kailasam, 2006). Within Asia, some 90% of sewage is untreated and is discharged directly into freshwater bodies and the sea (UNEP, 2001). In Malaysia, rivers provide 97% of drinking water (WWF, 2009). Although rivers in Malacca do not have serious sewage contamination and marine pollution, the rapid population increase and the increasing commercialization and industrialization are important factors to assess the level of pollution status in Kuala Sungai Baru waters. All land-basedpollution ends up in the sea, obviously containing mixture of harmful substances directly and indirectly affecting human health. Domestic and industrial wastewaters also contribute organic contaminants in various amounts. As a result of any accidental spills or leaks, industrial organic wastes may enter streams. Some of the contaminants may not be completely removed by treatment processes; therefore, they could become a problem for drinking water sources. It is important to know the organic content in a waterway (Holt, 2000). Oxygen is often used as an indicator of water quality, such that high concentrations of oxygen usually indicate good water quality. Salinity also influences dissolved oxygen concentrations, such that oxygen is low in highly saline waters and vice versa. The amount of any gas, including oxygen, dissolved in water is inversely proportional to the temperature of the water; as temperature increases, the amount of dissolved oxygen (gas) decrease (Carr et al, 2006). As our population grows worldwide and as industries refine their processes, water quality is increasingly important. Organic contaminants in water represent a unique threat to public health. In the environment, discharged organics enter the ecosystem, where they compete for food and oxygen, or become nutrients. Excess nutrients can create an imbalance in surface water that results in algae blooms. Detecting and quantifying concentrations of organics in water helps to protect human populations, industrial processes, and our environment (Carr et al., 2006).Total Organic Carbon in river sediments is a key component in a number of chemical, physical and biological processes. It contributes significantly to acidity of natural waters through organic acids (Goni & Hedges, 1995; Hernes & Benner, 2002), biological activity through light absorption and carbon metabolism and water chemistry through the complexion and mobilization of metals and organic pollutants. By forming organic complexes, TOC can influence nutrient availability and control the solubility and toxicity of contaminants (Cho et al., 1998). TOC consists of Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC). Dissolved Organic Carbon work has been done on the organic matter, both in the sediment and in the suspended sediment in Malaysia rivers (Alongi et al, 2004). The main objectives of this study are to (i) investigate the Total Organic Carbon (TOC) in Kuala Sungai Baru; and (ii) determine the organic matter ratio of Carbon to Nitrogen (C/N) in the study areas.

2. LITERATURE REVIEW

The world's 10 largest rivers contribute about 40% of organic carbon burial in deltaic and coastal environments (Hedges & Keil, 1995). There is a need to evaluate the terrestrial contribution of organic matter to the ocean sediments from different oceanic settings, particularly off major rivers, which deliver huge amounts of freshwater and sediments to the ocean (Nittrouer et al, 1995). Continental margin sediments are significant sites for organic carbon burial because of high sedimentation rates and biological productivity. Off major river mouths, continental margins also receive significant amounts of organic matter of terrestrial origin (de Haas et al, 2002). Although the determination of total carbon (TC) content in marine sediments is straightforward by a carbon–hydrogen–nitrogen (CHN) elemental analyzer that of organic carbon (OC) presents difficulties (King et al., 1998; Leong and Tanner, 1999). These arise because organic material is a complex mixture, and some of these components may be lost from the sediment at temperatures both above and below those for the loss of other materials, such as structural water and carbonates (Mook and Hoskin, 1982). The determination of organic carbon is usually a tedious and lengthy procedure, involving weighing of the sediment sample, careful pretreatment of the sample by a suitable acid to remove inorganic carbon (IC), analysis of the sediment solution extract for soluble organic carbon (SOC), drying of the sediment, weighing of the sediment and analysis of the sediment by CHNS analyzer.

2.1. Melaka Environmental Outlook

Although Straits of Melaka do not have serious sewage contamination and marine pollution, the rapid population increase and the increasing commercialization and industrialization are important factors to assess the level of pollution status in Melaka waters. All land-based pollution ends up in the sea, obviously containing mixture of harmful substances directly and indirectly affecting human health. In Kuala Sungai Baru in Alor Gajah, Melaka and surrounding areas, the Government of Malaysia has been looking for finding ways and means to reduce the pollution effect due to pig farming. Kuala Sungai Baru river and sea basins are chosen its tributaries flow through lands with varies activities such as township, oil palm plantation and there is also a pig farming nearby in Sungai Tanjung. In Kuala Sungai Baru in Alor Gajah, Malacca and surrounding areas, the Government of Malaysia has been looking for finding ways and means to reduce the pollution effect due to pig farming and reduce the present pollution effect, for instance the river and beach from TanjongBidara to Telok Gong in Masjid Tanah constituency due to pig farming that has been going on without control for decades (Lim, 2009). The issue on pollution in Malacca has become a political agenda on which the politicians have their own opinions and suggestions but until today they did not come up with a collective idea on how to solve the existing problem. An estimated 12 million tonnes of animal wastes were produced by cattle, swine, poultry, sheep and goat in year 2000 (Choo&Yogendran, 1989). For the last 50 years the Government of Malaysia have been trying to find solutions on how to reduce the present pollution effect of pig farms on the river and beach from, Kuala Sungai Baru to Tanjong Bidara to Telok Gong in Masjid Tanah. This has been going on without control for decades. This has been dragged for a long time mainly because of political reasons. Many times that people in Malacca had rallies for the Paya Mengkuang pig farms closures but it went to deaf ears. The pig farmers said that it is the issue of pollution in Paya Mengkuang that the government is going for because they are not complying with the environmental standards from the Department of Environment (DOE) for pig rearing.

2.2. Water Quality Trend

The Department of Environment (DOE) started monitoring river water quality in Malaysia in 1978. As of 2003, there were 926 manual stations located in 120 river basins. In addition to the manual stations, 15 automatic water quality stations have been installed at major rivers to capture real time data on specific parameters to monitor river water quality changes continuously (Sien et al., 2001). The trend of the river basins water quality is shown Figure 1 below. The decrease in the number of river basins was attributed to 2 factors. First, an increase number of polluting source such as sewage treatment plants, agro-based factories and pig farms which contributed to an increase in the pollutant load. Secondly the decrease in the amount of waterfall in the states of Pahang and Sarawak resulted in 5 and 11 deteriorated from clean to slightly polluted. A change of water quality index caused a major shift in the category of rivers.

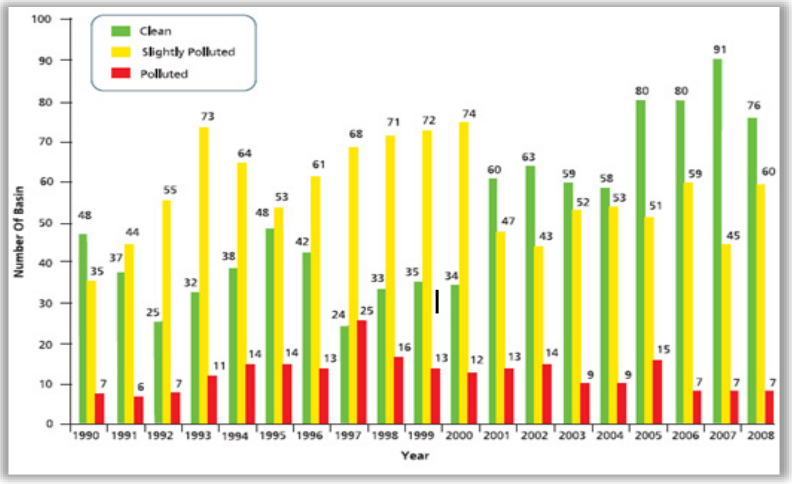

Figure 1. Malaysia: River Basin Water Quality (1990 -2008)
Source: Department of Environment (DOE)

2.3. River Quality Monitoring

The DOE has established a river monitoring network since 1978 to establish the status of river water quality, to detect changes in the water quality and wherever possible to identify pollution sources of rivers. It also serves to support environmental management and planning in the country. There are 1085 water quality monitoring stations sited within 140 river basins throughout the nation. The monitoring programme includes both the in-situ measurements and laboratory analyses of as many as 30 physico-chemical and biological parameters. In addition, 15 automatic water quality monitoring stations are installed to detect changes in river water quality on a continuous basis at strategic locations on major rivers basins. Water quality levels for specific parameters can be transmitted real-time to the DOE (Daud, 2008).

2.4. Sources of Water Pollution in Malaysia

Water Pollution is a main environmental problem cause by pig farming according to The Malaysian Environmental Quality Report; rivers in the state were polluted with ammoniac nitrogen (NH_3-N) due to pig farming and domestic wastes in 1997. Water pollution cause by pig farming occurred due to malfunction of waste lagoon or accidentally spill over from flooded lagoon or deliberate flushing of wastes directly into river system. Water may turn reddish brown and may destroy the fragile ecosystem. Pollution from nutrients contained in animal manure, namely phosphorous and nitrogen is one of the most serious problems, leading to excess algae growth, robbing water of oxygen which may lead to mass destruction of fish (Nasip Eli & Oming, 2008). Water pollution is caused by point and non-point sources. Point sources include sewage treatment plants, manufacturing and agro-based industries and animal farms. Non-point sources are defined as diffused sources such as agricultural activities and surface runoffs. In 2006, the Department of Environment (DOE) registered 18,956 water pollution point sources comprising mainly sewage treatment plants (9,060: 47.79% inclusive of 601 Network Pump Stations), manufacturing industries (8,543: 45.07%), animal farms (869: 4.58%) and agro-based industries (484: 2.55%) represents the distribution of industrial water pollution sources from agro-based and manufacturing industries compiled by the DOE in 2006 through field surveys and questionnaires. A total of 9,027 sources were identified with Selangor having the highest number of water pollution sources (1,850: 20.49%), followed by Johor (1,774: 19.65%) (DOE, 2008).

According to statistics compiled by the Veterinary Department of Malaysia, the total standing pig population for 2006 was about 1.67 million, a decrease of 1.76 percent compared to 1.7 million in 2005. Correspondingly, the number of pig farms decreased to 869 farms compared to 898 in the previous year. The number of sewage treatment plants under the management of Indah Water Konsortium Sdn. Bhd. (IWK) had increased to 9,060 in 2006 compared to 8,782 plants in 2005. Selangor had the largest number of sewage treatment plants (2,563: 28.3%), Perak (1,343: 14.8%), Johor (1,010: 11.1%) and Negeri Sembilan (928: 10.2%) (DOE, 2008).

2.4.1. Domestic Sewage

The highest percentage is from domestic sewage. Pollution by sewage from domestic, industrial and commercial sources is of more concern than that from agricultural sources. Many of the uses of river water require water of a high standard; pollution by sewage would therefore result in the need to find alternative sources (Sien, 2001). Domestic sewage is 99.9% water and 0.1% total solids on evaporation. About two-thirds of the solids are organics, comprising mainly of nitrogenous compounds (proteins and urea), carbohydrates (sugars, starches and cellulose), fats (soap, cooking oil and greases). The inorganic compounds include chloride, metallic salts and road grit when the combined sewage is used. Thus sewage is a dilute, heterogeneous medium that tends to be rich in nitrogen (Lester 1996). Damage done by untreated sewage depends on the value of the resources damaged and the extent of the damage. Its effects may be contamination of fisheries and aquaculture, the formation of red tides that kill fish and enhancement epiphytes and phytoplankton blooms, which smother underwater plants. The presence of untreated sewage and its impact on coastal and marine resources varies greatly and is complicated by numerous other factors (Sien, 2001). Domestic sewage discharge, in the form of treated sewage and partially treated sewage, remained the largest contributor of organic pollution load with an estimated biochemical oxygen demand (BOD) load of 883,391.08 kg/day. The estimated BOD loading contributed by other major sectors were agro-based and manufacturing industries (76,790.77 kg/day) and pig farming (213,215.00 kg/day). Table (1) indicates the total BOD load in kg/day discharged from sewage treatment plants throughout Malaysia in 2006 (DOE 2008).

Table 1. Total BOD Load (kg/day) from Sewage Treatment Plants in Malaysia

State	No. of STP	Total PE	Flow (m^3/day)	BOD Load (kg/day)
Selangor	2,563	5,908,450	1,329,401	332,350.31
Perak	1,343	1,300,430	292,597	73,149.19
Johor	1010	1,198,417	269,644	67,410.96
Negeri Sembilan	928	931,458	209,578	52,394.51
Kedah	755	556,637	125,243	31,310.83
Melaka	725	570,192	128,293	32,073.30
Pulau Pinang	650	2,149,001	483,525	120,881.31
Pahang	486	314,830	70,837	17,709.19
WP Kuala Lumpur	299	2,571,877	578,672	144,668.08
Terengganu	224	75,184	16,916	4,229.10
Perlis	36	16,156	3,635	908.78
WP Labuan	32	39,265	8,835	2,208.66
WP Putrajaya	9	72,833	16,387	4,096.86
Total	9,060	15,704,730	3,533,563	883,391.08

Source: Indah Water Konsortium Sdn. Bhd.

2.4.2. Pig Farming

In a survey of pig farms in Melaka, Malaysia (1980), approximately 68 % of the farms had constructed retaining ponds for pig wastes, however these pond were considered too small and thus over-loaded and non-functional (Nasip et al., 2008). Pig farming in Malaysia has become more active over the years as it yields high annual turnover of estimated 2 billion Malaysian Ringgit. The increase in pig farming activities has brought about changes in environmental qualities in the forms of organic matter pollution and trace metals pollution. Many earlier studies have indicated the presence of high levels of trace metals in sediment from estuarine receiving effluent from pig farming. This study shows that there are high concentrations of copper, zinc and lead in sediment and gastropods sampled close to the pig farm but this reduced about 100 fold towards the river mouth. Pig farming cannot continue to be a backyard industry if it is to flourish in the country. This industry has a high demand for water and discharges large quantities of wastewater into rivers with a high organic content. Designated pig farming areas are required not only to ensure a proper control of its wastewater discharges but also for disease control (Ismail & Ramli, 2007).

2.5. Total Organic Carbon

TOC has been recognized as an analytic technique to measure water quality during the drinking water purification process. TOC in source waters comes from decaying Natural Organic Matter (NOM) and from synthetic sources. Humic acid, fulvic acid, amines, and urea are types of NOM. Detergents, pesticides, fertilizers, herbicides, industrial chemicals, and chlorinated organics are examples of synthetic sources. Before source water is treated for disinfection, TOC provides an important role in quantifying the amount of Natural Organic Matter in the water source. In water treatment facilities, source water is subject to reaction with chloride containing disinfectants. When the raw water is chlorinated, active chlorine compounds react with NOM to produce chlorinated disinfection byproducts (DBPs). Many researchers have determined that higher levels of NOM in source water during the disinfection process will increase the amount of carcinogens in the processed drinking water. The analysis of total particulate carbon and its component organic and inorganic phases is fundamental to many studies of the biogeochemistry of natural waters. For example, oceanic carbon flux programmes such as the Joint Global Ocean Flux Study, require the accurate quantitative determination of the organic and inorganic carbon content of particulate matter in order to optimise the evaluation of carbon cycling processes. The proper investigation requires both representative sampling and accurate analysis. Whilst not underestimating the errors that may occur during sampling (Altabet et al., 1992; Gust et al, 1992; Gardner et al., 1993) and storage (Hedges et al., 1993). Available instrumentation allows carbon measurements to be made fairly easily, but the accuracy of these techniques for natural water particulates has rarely been evaluated. The realisation that such carbon determinations are not straightforward (Weliky et al., 1983). The definition of organic carbon, therefore, remains largely operational, and there is a need for fully instrumental method of determination, which is accurate, rapid and free from interferences. Some previous studies of soil and sediment have taken advantage of the convenience of spectrometric techniques for quantification. Visible reflectance spectrometry has been utilized for predicting soil organic matter, from the comparison with results from wet oxidation (Krishnan et al., 1980) or loss of mass on ignition (Ben-Dor & Banin, 1994). Near-infrared (IR) spectrometric measurements of soil and sediment samples have been correlated with results from wet oxidation (Morra et al., 1991; Dalal & Henry, 1986), "carbonate-corrected" total carbon (Stenberg et al., 1995; Malley et al., 1996), total carbon (Malley et al, 1996), carbonate content (Ben-Dor & Banin, 1994) and humus fractions (Krischenko et al., 1991). Nguyen et al. (1991) compared the use of mid-infrared diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) in soil analysis with that of the pressed halide disc method. A modified partial least squares method has been used to fit DRIFTS data to carbonate-corrected total carbon from soil samples (Janik & Skjemstad, 1995). Many of the above studies have, thus, compared the spectral data with experimentally determined quantities that have vague physical significance. Reeves et al. (2002) have compared DRIFTS data for soil samples with their OC contents by assuming that the soil samples did not contain inorganic carbon. The absorption of IR radiation of a particular energy by a sediment sample may result in the excitation of a certain vibration, with the same energy, in a chemical species in the sample. The amount of absorption, quantified by integration of the appropriate spectral peak, thus, provides an indication of the amount of the chemical species in the sediment. The technique is very selective because only a narrow energy region of IR radiation is absorbed, corresponding to the discrete energy of a particular vibration, and the IR instrument provides good spectral energy resolution. The new method presented herein utilizes the clear IR spectroscopic signature of IC, which is present in sediment as the carbonate ion.The role of the structural properties of the organic matter associated with the sediment particles has not been thoroughly evaluated. In the case of dissolved organic matter, changes in the structure can alter the observed partition coefficient even on a carbon normalized basis (Gauthier et al., 1987; Kukkonen & Oikari, 1991). In soil systems, some studies have demonstrated that partitioning varies with soil organic matter composition. For instance, the organic carbon normalized partition coefficient decreases for a particular compound with increases in the soil organic matter polarity expressed as the (O + N)/C ratio (Rutherford et al, 1992). Accumulation of sediment-associated contaminants may occur either via the aqueous phase, i.e., passively through direct contact with pore water, or through ingestion of contaminated sediment particles. The importance of these routes to contaminant accumulation depends on the ecology and feeding behaviour of the organism and characteristics of the sediment and chemicals. There is evidence that assimilation from ingested material can be a significant accumulation route for lipophilic compounds (Landrum, 1989; Boese & Lee, 1992; Harkey et al., 1994). Furthermore, accumulation via particle ingestion depends on the feeding rate of the organism, assimilation efficiency, and contaminant concentration in the ingested good particles, which may be significantly different than the concentration in the bulk sediment (Lee et al., 1990; Lydy & Landrum, 1992).

2.6. Sources of Carbon and Nitrogen

2.6.1. Carbon Rich Waste

Woody materials are high in carbon. Shredding or clipping these materials increases the surface area and makes decomposing easier for the microorganisms. Dry leaves, corn stalks, straw, bark, sawdust, rice stalks and etc are good sources of carbon. Carbon sources are often referred to as "browns" (Giesel & Seaver 2009).

2.6.2. Nitrogen Rich Waste

Nitrogen sources are often referred to as "greens."Grass clippings are a good source of nitrogen, especially if the lawn has been fertilized. Other sources are kitchen scraps and animal manures, including cow, horse, and poultry (Giesel & Seaver, 2009). As the Table (2) illustrates most materials available for composting don't have the ideal carbon to nitrogen ratio. One way to speed-up composting is to balance the numbers. It helps to think of materials high in nitrogen as "greens," and woody, carbon-rich materials as "browns." There is often a visual correlation between high nitrogen content in green plant material, and high carbon content in brown materials. For instance, a mixture of one-half brown materials tree leaves (40:1 ratio) could be used with one-half fresh, green grass clippings (20:1 ratio) to make a pile with the ideal 30:1 ratio. This balancing works best on a weight, rather than volume, basis. The leaves from different types of trees vary in the C/N balance. There are also some confusing exceptions to green-nitrogen, brown-carbon correlations. For instance evergreen leaves are low in nitrogen, and brown-colored animal manures are often high in nitrogen. The best way to become familiar with C/N balancing is to try to be specific about it for a while, then relax into an intuitive assessment of what a pile needs. Write down the type and quantity of materials used, and take note of the temperature your pile reaches and the quality of the finished compost. After a while, the process becomes intuitive (Giesel & Seaver, 2009*)*.

Table 2. Reference Chart for Carbon: Nitrogen ratios of selected materials

Material	C:N	Material	C:N
Bark	120:1	Paper	170:1
Coffee Grounds	20:1	Pine Needles	70:1
Cow Manure	20:1	Poultry Manure	10:1
Corn Stalks	60:1	Sawdust	500:1
Grass Clippings	20:1	Straw	40-100:1
Horse manure	25:1	Vegetable Wastes	12-20:1
Leaves	60:1	Wood Chips	100-500:1
Leguminous	15:1		

Source: United States Department of Agriculture, University of California, Placer and Nevada Counties

2.7. Carbon to Nitrogen Ratio

The Carbon to Nitrogen Ratio can be computed as the dry weight content of organic carbon divided by the total nitrogen content of the waste. Soil microbes use carbon to build new cells, and use nitrogen to synthesize proteins. Excess nitrogen is converted (or mineralized) from organic nitrogen to inorganic ammonium, which is then available for plant growth. For minimal plant growth, it is recommended that the Carbon to Nitrogen Ratio be below 20 to 1. If the Carbon to Nitrogen ratio exceeds 20 to 1, soil micro-organisms outcompete plant roots, resulting in reduced plant growth. The carbon and nitrogen isotopes have been used for indicating the likely source of organic matter in estuarine systems (Hedges & Oades, 1997). The Carbon to Nitrogen (C/N) ratio is important in a biological process. Mixed microfloras from sewage or compost are usually used in biological hydrogen production from organic wastes (Lin & Chang, 1999). Microflora requires a proper nitrogen supplement for metabolism during fermentation. A proper C/N-ratio value for pure culture is necessary to optimize anaerobic hydrogen production from organic substrate. It is necessary to maintain proper composition of the feedstock for efficient plant operation so that the C/N ratio in feed remains within desired range. It is generally found that during anaerobic digestion microorganisms utilize carbon 25-30 times faster than nitrogen. Thus to meet this requirement, microbes need a 20-30:1 ratio of C to N with the largest percentage of the carbon being readily degradable. Waste material that is low in C can be combined with materials high in N to attain desired C/N ratio of 30:1 (Yadvika et al., 2004). Some studies also suggested that C/N ratio varies with temperature.

2.8. Dissolved Oxygen

Dissolved oxygen is vital to aquatic life, as it is needed to keep organisms alive. Coastal waters typically require a minimum of 4.0 m g/l and also do better with 5.0 mg/l of oxygen to provide for optimum ecosystem function and highest carrying capacity. Main source of oxygen is aquatic plants also provide atmosphere, but much during photosynthesis, oxygen may fall to unhealthy levels if water is polluted. Example if sewage and other wastes (e.g. from food processing) with high Biological Oxygen Demand (BOD) are discharged into the sea (Clark, 1996). Temperature affects the speed of chemical reactions, the rate at which algae and aquatic plants photosynthesize, the metabolic rate of other organisms, as well as how pollutants, parasites, and other pathogens interact with aquatic residents. Temperature is important in aquatic systems because it can cause mortality and it can influence the solubility of dissolved oxygen (DO) and other materials in the water column (e.g., ammonia) (Carr et al., 2006). Many aquatic ecosystems rely heavily on external subsidies of organic matter to sustain production. However, excess inputs of organic matter from the drainage basin, such as those that may occur downstream of a sewage outfall, can upset the production balance of an aquatic system and lead to excessive bacterial production and consumption of dissolved oxygen that could compromise the integrity of the ecosystem and lead to favourable conditions for growth of less than ideal species (Carr et al., 2006). COD is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate (Chapman 1996). There are two important factors that can influence the amount of dissolved oxygen present: water temperature and organic matter (Kenimer et al., 2005). The greater the temperature, the lower saturated the DO, lower temperature, the greater the saturated DO. If water is too warm, there may not be enough oxygen in it. When there are too many bacteria or aquatic animal in the area, they may overpopulate, using DO in great amounts. Oxygen levels also can be reduced through over fertilization of water plants by run-off from farm fields containing phosphates and nitrates (the ingredients in fertilizers). Under these conditions, the numbers and size of water plants increase. Then, if the weather becomes cloudy for several days, respiring plants will use much of the available DO. When these plants die, they become food for bacteria, which in turn multiply and use large amounts of oxygen. And this depleting all the oxygen. If oxygen is available, organic material requires oxygen to decompose and organic material may also decompose in the absence of oxygen. More organic material requires more DO, and will tend to deplete water of DO. Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. The lower the concentration, the greater the stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills. The level of oxygen is a much more important measure of water quality than feacal coliform. Dissolved oxygen is absolutely essential for the survival of all aquatic organisms not only fish but also invertebrates such as crabs, clams, zooplankton, etc. Moreover, oxygen affects a vast number of other water indicators, not only biochemical but esthetic ones like the odor, clarity and taste. Consequently, oxygen is perhaps the most well-established indicator of water quality. A high DO level in a community water supply is good because it makes drinking water taste better. However, high DO levels speed up corrosion in water pipes. For this reason, industries use water with the least possible amount of dissolved oxygen (Lomborg, 2001).

3.MATERIALS AND METHODS

3.1. Study Area

Kuala Sungai Baru is a small town in Alor Gajah district, Melaka, Malaysia. Kuala Sungai Baru is situated midway between Kuala Linggi and Pengkalan Balak. The nearest town is Masjid Tanah approximately 15 kilometers. The economic activities in Kuala Sungai Baru is mainly fishing, where many small boats parking at the town's river but with fishmongers from all across Melaka coming here to buy the sea products. The study was conducted in December 2009 at the Kuala Sungai Baru in Melaka. Eleven sampling stations were selected, 3 from the seabed and 8 from riverbed. The locations of the sampling stations are as shown in Figure (2). The physical and chemical characteristics monitored included temperature, pH, Dissolved Oxygen, Depth and salinity were determined *in situ* as shown in Table 3 using YSI Environmental Monitoring System Model 610 D and salinity was measured using salinometer.

Table 3. Coordinate and Parameter *In-Situ*

Station	Latitude (N)	Longitude (E)	Temperature (°C)	pH	Salinity (psu)	Depth (m)	DO
1	02° 20.06	102° 02.20	28.65	7.78	31.25	4	5.63
2	02°20.913	102° 02.005	28.61	7.82	31.22	4.1	5.66
3	02°20.984	102° 01.874	28.62	7.79	31.26	3.8	5.73
4	02°21.244	102° 02.060	28.87	6.68	12.24	2.4	4.38
5	02°21.390	102° 02.197	29.89	6.55	7.90	1.3	4.31
6	02°21.586	102° 02.361	30.12	6.9	0.23	0.8	4.74
7	02°21.630	102° 02.406	29.54	6.7	0.29	0.5	4.24
8	02° 21.624	102° 02.684	30.19	6.45	0.42	2.2	3.97
9	02°21.618	102° 02.652	29.7	7.53	0.35	1.7	6.88
10	02°21.789	102° 02.815	31.16	6.65	0.29	1.2	4.22
11	02° 21.824	102° 02.817	29.01	6.1	0.23	2.5	6.79

The probe end of the meter was dipped into the water while the value at the pointer of the scale was read off and recorded. Dissolved Oxygen was measured in milligrams per liter (mg/l); temperature in °C (degrees centigrade) and salinity was in practical salinity units (psu). The data collected from 11 stations along the Kuala Sungai Baru is in upstream and downstream. The river banks are low, steep, and some are has shrubs and plants and the seabed sediments are collected in different depth. Sediments collected are mostly muddy.

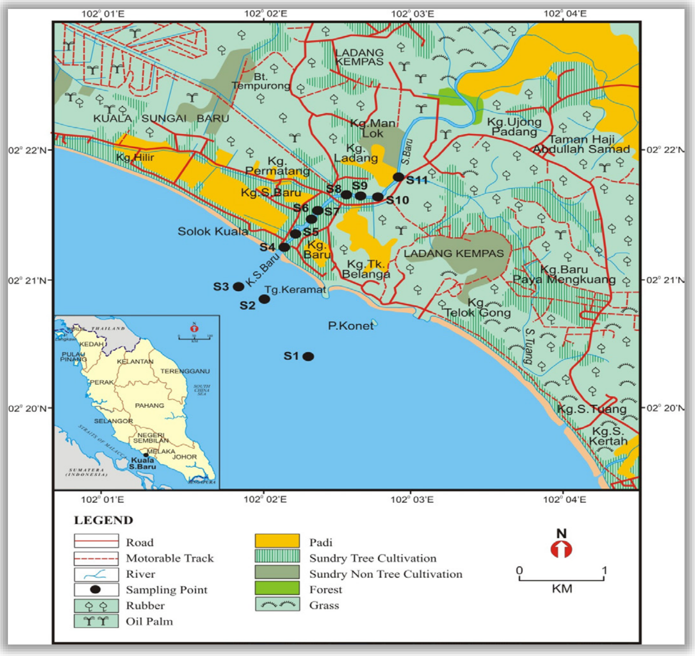

Figure 2. Geographical locations of 11 sampling stations in Kuala Sungai Baru

3.2. Collection and Preservation

Global Positioning System (GPS) was used to determine the actual coordinates of sampling stations. The parameters used such as temperature, salinity and pH of water were taken using single parameter Model 610D probe. Latitude and longitude of each station also taken using the coordinate detector (Global Positioning System). Sediments were put in individual bottles and labeled according to sampling stations and covered with aluminum. These sediment samples were transported back to Universiti Kebangsaan Malaysia (UKM) laboratory in a cooler where they were well preserved by ice and were later transferred to freezer in the laboratory for further analysis.

3.3. Method for the determination of organic matter

3.3.1 Procedure

Frozen sediment samples were removed from the freezer and thawed in sealed containers for approximately 24 hours. Placing a small amount of sample weight in aluminum foil and was burned in furnace for 3-4 days at 60 °C. Samples were weighing after burning from the furnace to get the actual dry weight. The removal of water from the sample is essential during the determination of TOC by the dry combustion methods by drying the sample at 150 °C for 24 hours. Then the samples homogenize manually with mortar and pestle. Once homogenization is complete, the samples were then sieved, the ground sample through a 100 mesh sieve. About 2 mg of the samples which passes through the sieves were used for the analysis of Total Organic Carbon (TOC) and Carbon and Nitrogen Ratio. The two main advantages of using a dry combustion method are that the elevated temperatures ensure combustion of all carbon forms present in the sample and that sample preparation is minimal. The two main disadvantages of using a dry combustion method are that a leak-free gas flow path must be maintained, or else a false positive value will be obtained due to cross-contamination with atmospheric CO_2, and the initial expense of purchasing the equipment may be high, especially if an automated system is used (Nelson & Sommers, 1996). Numerous comparison studies have been performed examining the efficiency of TOC methods (Nelson & Sommers, 1996).

3.4. Total Organic Carbon by Loss on Ignition (LOI) Method

The loss-on-ignition (LOI) method for the determination of organic matter involves the heated destruction of all organic matter in sediment (Nelson & Sommers 1996; ASTM 2000). The sample is then cooled in a desiccator and weighed. Organic matter content is calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights were corrected for moisture/water content prior to organic matter content calculation. LOI method temperatures were maintained below 500C° to avoid the destruction of any inorganic carbonates that may be present in the sample. One concern with this technique is that some clay minerals will lose structural water (i.e., water that is part of their matrix) or hydroxyl groups at the temperatures used to combust the samples. The structural water loss will increase the total sample weight loss leading to an overestimation in organic matter content (Schumacher et al., 1995). TOC content can be measured directly or can be determined by difference if the total carbon content and inorganic carbon contents are measured with the following equation:

$$\% TOC = [(\text{Dry Sediment weight} - \text{Burnt Sediment weight}) / \text{Dry Sediment weight}] \times 100\%] \quad (1)$$

3.5. Analysis Method of C/N Ratio

Frozen sediment samples were removed from the freezer and thawed in sealed containers for approximately 24hours. Placing a small amount of sample weight in aluminum foil and was burned in furnace for 3-4 days at 60 °C. Samples were weighing after burning from the furnace to get the actual dry weight. Then the samples homogenize manually with mortar and pestle. Once homogenization is complete, the samples were then sieved, the ground sample through a 100 mesh sieve. 2mg of the samples which passes through the sieves were used for the analysis of Carbon and Nitrogen Ratio using CHNS Analyzer.

4. RESULTS AND DISCUSSIONS

4.1. Total Organic Carbon derived By Loss on Ignition (LOI)

LOI can be strongly dependent on the exposure time. The fact that some authors do not mention exposure times at all (Belis et al, 1999; Lamoureux, 1999) suggests that a common assumption is that at 550 °C organic matter is burned rapidly and thereafter no further weight loss takes place. Researchers should be aware that other reactions than burning of organic matter can take place at 550 °C, e.g. dehydration of clay minerals or metal oxides, loss of volatile salts, or loss of inorganic carbon. The determination of total organic carbon is important part of any site characterization or ecological assessment since its presence or absence can markedly influence how chemicals will react in the soil or sediment. Chemical procedures for the determination of total organic carbon in seawater are usually elaborate because of the presence of inorganic materials and the large variations in organic materials. Previous work has shown that sea depth is only a weak determinant of bacterial biomass in sediments (Deming & Yager, 1992), considering that the organisms utilize and respond to solute concentrations and gradients within the sediment (Deming & Baross, 1993; Dixon & Turley, 2000). Table 2 shows the summary results of Total Organic Carbon (TOC) and Carbon/Nitrogen (C/N) ratio after a thorough analysis using the procedure that was mentioned in details in the methodology section.

Table 3. Analysis Result of TOC and C/N Ratio

Station	Original samples weight before burning (g)	Original samples weight after burning (g)	TOC %	Nitrogen %	C/N ratio
1	9.0673	8.9655	1.12	0.0165	68.04
2	8.384	8.2286	1.85	0.0621	29.84
3	8.2705	8.1554	1.39	0.0514	27.07
4	5.8908	5.8241	1.13	0.047	24.09
5	2.8199	2.7714	1.71	0.3046	5.64
6	7.6391	7.5906	0.63	0.0198	32.06
7	6.3519	6.2862	1.03	0.2469	4.18
8	5.6045	5.4991	1.88	0.1417	13.27
9	4.1923	4.1239	1.63	0.2405	6.78
10	5.6208	5.5465	1.32	0.1398	9.45
11	8.6393	8.5646	0.86	0.0426	20.29

The organic carbon distributions in this study were presented in Fig. 3 below. The organic carbon content averaging 1.32% and varied from 0.63% to 1.88%. The highest TOC variability was observed in Station 8 and Station 2 with 1.88% and1.85% respectively. Burns et al. (2008) reported that the organic carbon was highest in mixing zone where the processes of flocculation were maximums. Overall the average value was higher than the sediment from the open ocean (Cha et al, 2007; De Vittor et al, 2008).

The reasons for the higher percentage of organic carbon would be probably the primary productivity input of terrestrial organic matter, decomposition and grazing by benthic organisms which is washed to the sea from the Kuala Sungai Baru as it was raining the day before we collected the samples or from municipal and industrial wastewater, septic tanks, feed lot discharges, animal wastes (including pigs, birds and fish), runoff from fertilized agricultural field such as the rubber and palm plantations and lawns and discharges from car exhausts near the bus station. Most of the organic matter input to the sediment was from pelagic and benthic primary producers. Organic Carbon distributions are much dependent upon the combination of physical forces such as freshwater runoff, tidal currents and waves (Warnken et al., 2008). The high concentration of organic carbon observed in Station 8 could be attributed to organic matter from industrial, residential and municipal wastewater. Shallow water sediments are sites where most organic matter mineralization in marine sediments takes place (Jorgensen, 1983). High TOC effluent makes natural waters uninhabitable to fish and other wildlife and so destroys the entire natural ecosystem of the affected water body. The main economic activity in Kuala Sungai Baru is mainly fishing that is big indicator, too, that the TOC concentration is not that high to affect the habitat of the fishes. The lowest TOC percentage is in Station 6 with 0.63% TOC value only. This station has very less or no human activities. In this site, too, we can not see any or animal manures or any livestocks. Only green waste we can see from this station such as green clippings and leaves which decompose very rapidly. Appendix F shows the actual site where we can see bridge and bit further can see residential houses. In the past several researchers reviews several methods that have been used for organic carbon analysis. TOC provides an important role in quantifying the amount of natural organic matter in the water source. The organic material of photoautotrophic origin mixes with continental organic matter near the coast and is usually transported by turbidity currents to the abyssal plain (Gordon & Goñi, 2004). Total Organic Carbon (TOC) and Total Nitrogen (TN) concentration in benthic sediments can be used individually, or in conjunction with denitrification efficiencies, to predict changes in water quality and the extent of eutrophication (Heggie et al., 1999). Organically rich sediments have high TOC, TN & TP concentrations, and are found in environments characterised by high phototrophic productivity, little oxidation of organic matter by aerobic processes, and rapid burial and preservation of organic matter (Heap et al., 2006)

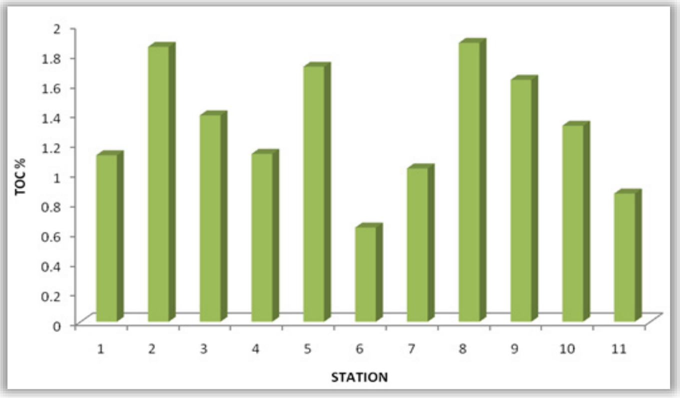

Figure 3. Total Organic Carbon

4.2. Carbon/Nitrogen Ratio

All living organisms need relatively large amounts of the element carbon (C)and smaller amounts of nitrogen (N). The balance of these elements in a material is called the carbon-nitrogen ratio (C/N). This ratio is an important factor determining how easily bacteria are able to decompose an organic material. Table 5 shows the organic C/N ratios in all 11 sampling stations. This ratio can be used to help identify the origin of the organic matter in sediments (Shipboard Scientific Party, 1998). C/N ratios of 5-8 indicate unaltered algal organic matter such as in Station 5, 6 and 9, whereas C/N ratios of 25-35 indicate fresh land-derived organic matter such in Stations 1, 2, 3 and 6 (Emerson & Hedges, 1988; Meyers, 1994). Low C/N values in sediment containing low organic carbon may be biased by the tendency of clay to absorb ammonium ions generated during the degradation of organic matter (Müller & Suess, 1977) like in Station 5 where the sediments sample was collected at 1.3 m depth only. With good measurements of organic C, N, and the input of organic matter to the sediments, the turnover of organic matter may be compared from environment (Seki & Parsons, 1968). Nitrogen in deep-sea sediments is mostly organic (Hedges et al., 1988). i.e. Station 1 of which the sediment sample was collected 4 meter deep and it was 300 meter away from the shore.

Station 1 C/N ratio is 68.4, sediments were collected in the sea at the depth of 4 m and since it is deeper seawater the salinity is higher 31.25 and so with the dissolved oxygen of 86.6%. Since nitrogen sources in freshwater should be transported mostly in upper layers, the occurrence of high concentration of nitrate should be due to input from the sea. This may indicate, too, that the crop residue that has been washed to the sea settled down in the seabed. The C/N ratios in the other areas varied from 5.64 to 32.06 with the average mean of 21.89. Such accumulation patterns of organic carbon and nitrogen should depend upon the distribution of water masses and currents (Takahashi et al, 1984). Although the C/N ratios of particulate organic matter might be changed because of the variation in decomposition process, these ratios have been employed as source indicators of sedimentary particulate organic matter by numerous workers (Prahl et al., 1980). Benthic oxidation of the increased flux of organic matter overwhelms the supply of dissolved oxygen at the sea bottom. When compared with other studies, the organic carbon content in the study areas were relatively higher than the coastal water of Terengganu (Chandru et al, 2008) and are generally lower than those reported by Al-Ghadban (1990) in the Arabian Gulf. Values of carbon-nitrogen atomic ratio (C/N) which suggest an organic matter input derived from vascular plants (Meyers, 1994), characterized by limiting nitrate concentration (Mari et al., 2001). Organisms that decompose organic matter use carbon as a source of energy and nitrogen for building cell structure. They need more carbon than nitrogen. If there is too much carbon, decomposition slows when the nitrogen is used up and some organisms die. Other organisms form new cell material using their stored nitrogen. In the process more carbon is burned. Thus the amount of carbon is reduced while nitrogen is recycled. Decomposition takes longer. Previous literature suggests that a C/N ratio of 20:1 or 30:1 is better than a 10:1 ratio for various wastewater treatment such as poultry waste, cow manure, and coffee waste (DeRenzo, 1977; Sathianathan, 1975; Boopathy & Mariappan, 1984).

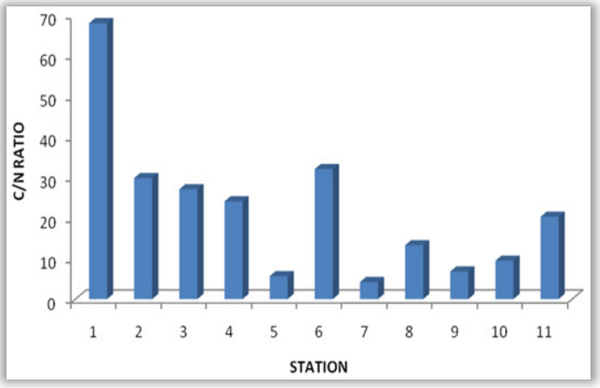

Figure 4. C/N Ratio by sampling sites

5. CONCLUSION

The concentration of organic carbon wasparticularly high in almost all the sampling stations. It is likely that the high concentration of organic carbon were due to the river outfall of organic matter from land run-off, domestic sewage, livestock waste discharges, trade effluents, mariculture activities, etc. In general, OC contents were highest in sediments on the Sungai Kuala Baru in Station 8 and 2 where intermediate water masses with low dissolved oxygen concentrations. It contains enough dissolved oxygen it is maybe influence by organic matter and the tropical water temperature. The result of this study indicates that water quality in Kuala Sungai Baru in Melaka is slightly polluted and it requires conventional treatment based on Interim National Water Quality Standards for Malaysia (INWQS) from the Department of Environment. In conclusion, study results indicate that the content of organic carbon in sediment is much influenced by many factors including the physical, biological and chemical processes.

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