DISTRIBUTION OF ALKANES, HOPANES AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SELECTED SEDIMENTS IN SARAWAK RIVER, SEMBULAN RIVER AND TAWAU RIVER, EAST MALAYSIA

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INTRODUCTION:

Environmental pollution has become a major concern in all aspect of the world. This pollution appears to be everywhere including the coastal areas. Coastal zones, especially bays, estuaries, shoals, and reefs near large cities or the mouths of major rivers, often overwhelmed by human-caused contamination. High levels of toxic chemicals, heavy metals, disease-causing organisms, oil, sediment, and plastic refuse are adversely affecting some of the most attractive and productive ocean regions. The potential losses caused by this pollution amount to billions of dollars each year.

Rivers and estuaries in Malaysia are important for fisheries, recreational and marine activities, tourism, and maintaining biodiversity in the tropical area. However, the rivers and estuaries are under constant threat of various pollutions. One of the major threats is organic pollutants. There are varieties of potential sources such as industrial and commercial development, shipping industries and other human activities.

There are 2 important classes of hydrocarbons: Aliphatics and aromatic compounds. Alkanes are aliphatic hydrocarbons whereas hopanes are cyclic alkanes. The aromatics are benzene rings which attach together to form polycyclic aromatics. Their unique structures can provide very specific information on the origins of the compounds. Molecular markers are defined as compounds whose structures are linked to specific origins.

N-alkanes are one of the major components of petroleum. Also, n-alkanes provide useful information on weathering of petroleum. The alkanes, or aliphatic hydrocarbons, consist of fully saturated normal alkanes that are also called parrafins. Alkanes can also form branched formation of the general molecular formula (C_nH_{n+2}) where n=1 to 40.

Hopanes are molecular composition of petroleum that deposited in sediment that can be used for determination of oil pollution and the biomarker approaches have been applied to investigate on some oil spill accident. The crude oil can be characterized using biomarker compounds that include the presence of pentacyclic triterpanes such as oleanane.

16 PAHs are identified as priority pollutants by the United States Environmental Protection Agency (USEPA). As ubiquitous persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) have attracted a great deal of attention from the people

due to their carcinogenic and mutagenic properties (Zhang *et al*., 2006). Their concentration is usually high in urban zones but, due to their high diffusion rates and the ability to accumulate in particles, PAHs are easily transported through the air, and are subsequently deposited in soils and waters, sometimes far from the origin sources.

RESEARCH OBJECTIVE:

The purposes of this research are:

- Measure the concentration level of alkanes, hopanes and polycyclic aromatic hydrocarbons (PAHs) of selected surface sediments of Sarawak River, Sembulan River and Tawau River, and
- Identify the sources of pollution in selected sediment based on MP/P ratio and other diagnostic ratios by comparing with source materials

RESEARCH METHODOLOGY

Sampling collection:

20 surface sediments samples (top 2-5 cm representing recent input), 9 from Sarawak River, Kuching, 6 from Sembulan River and 5 from Tawau River, are collected using Eckman dredge and placed into previously solvent-rinsed stainless steel containers. The samples are put into zip-lock bag, transported to the laboratory in cool box and stored at -20ºC prior to further analysis. The street dust, tire rubber, asphalt, crankcase oil and used crankcase oil are also being collected.

Total Organic Carbon (TOC) Analysis:

The sediment samples were dried overnight at 60°C in oven, and then thoroughly ground to a fine powder and homogenized using mortar and pestle. Acidification procedure was used in order to eliminate inorganic carbon (carbonates) that contain in the samples. 1-2 g of each sample was weighed and 1-2 ml of 1M HCL was added drop by drop until the sample completely moist with HCl. The samples were dried at 100°C for ten hours to remove hydrochloric acid. 1 g of each sample was reweighed and then analyzed using LECO CR-412 Carbon Analyzer at 1350°C to determine TOC percentage.

Chemical analysis:

Sediment samples were defrosted at room temperature and homogenized with pre-cleaned spatula. 15-20 grams of the samples are dried with baked anhydrous sodium sulphate to remove moisture and placed in pre-cleaned cellulose thimbles and soxhlet extracted for about 8-10 hours by distilled dichloromethane (DCM). After extraction, a few of activated copper chips are added into the sample and left overnight.

Clean up step is done by using 5% H_2O deactivated silica gel to separate other unwanted polar compounds. The 5% H_2O deactivated silica gel is packed in the column until 9cm heights. The 150µl of surrogate internal standards mixture is spiked into the solvents. The extract and 20ml of Hexane/DCM (3:1 v/v) are transferred into the column to elute hydrocarbons. The eluted sample is reduced in volume to near dryness.

The 2nd step column chromatography or fraction step is done using 100% fully activated silica gel. The silica gel is packed until 18 cm height. The eluted sample from first column is added to the 2nd step column and charge through with 4ml hexane to get alkanes and hopanes fraction, then 4ml hexane added again to get LABs fraction, and finally 16ml of Hexane/DCM (3:1 v/v) is added to get PAHs fraction.

The fractions are evaporated to about 1ml, rinsed with iso-octane and transferred to glass ampoule, evaporated to dryness under gentle stream of nitrogen and re-dissolved into 150µl iso-octane containing Internal Injection Standards. The solution is analyzed with gas chromatography (GS) equipped with the mass spectrometer (MS).

RESULT AND DISCUSSION:

1. Water Quality Parameter (Sarawak River)

Station	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7	Station 8	Station 9
COD (mg/l)	8.67	6.33	9.33	33.33	5.33	7.00	7.67	38.00	10.00
DO (mg/l)	6.79	6.64	6.79	5.35	5.68	5.81	5.60	5.62	4.87
Secchi disk (m)	0.25	0.20	0.25	0.20	0.20	0.15	0.20	0.15	0.40
Turbidity (mg/l)	40.46	46.15	45.09	60.56	40.89	60.42	64.29	45.73	23.67
Conductivity (µs/cm)	195.0	45.5	45.6	46.4	56.8	43.5	43.7	101.3	63.2
pH	6.73	7.09	7.08	7.46	7.06	7.01	6.96	7.01	7.04
Temperature (ºC)	24.7	24.7	24.7	24.7	24.8	24.7	24.7	25.3	25.4
Salinity (% ppt)	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
Weather report	Rainy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy

2. Water Quality Parameter (Sembulan River)

Station	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6
COD (mg/l)	90.33	154.00	97.33	113.00	120.00	126.00
DO (mg/l)	5.84	6.60	6.80	9.30	8.10	9.90
Secchi disk (m)	0.20	0.25	0.10	0.20	0.20	0.40
Turbidity (mg/l)	23.60	16.40	14.20	8.81	1.94	0.63
Conductivity (µs/cm)	38.18	20.10	13.99	41.63	45.80	43.30
pH	6.60	6.68	5.90	7.20	7.60	7.70
Temperature (ºC)	27.8	27.8	27.8	29.4	30.9	30.4
Salinity (% ppt)	2.0	5.5	8.0	26.6	29.5	29.9
Weather report	Partly cloudy	Partly Cloudy	Partly Cloudy	Partly Cloudy	Partly Cloudy	Partly Cloudy

High chemical oxygen demand (COD) measured shows that high capacity of water to consume oxygen during the decomposition of organic matter and the oxidation

of inorganic chemicals. Low dissolved oxygen (DO) indicates that low amount of oxygen (O_2) dissolved in the water. High turbidity shows that high cloudiness of the river caused by individual particles (suspended solids). High conductivity estimates the total amounts of dissolved ions in the water are high.

SIGNIFICANCE OF STUDY:

The results from this research can determine the major sources of PAHs which might be contributed to the pollution at Sarawak River, Sembulan River and Tawau River by comparing with source materials. Diagnostic ratio that used in this research are methylphenanthrene over phenanthrene ratio (MP/P ratio), low molecular over high molecular (L/H ratio), and other diagnostic ratios by comparing with the source materials. The ratios can determine weather the anthropogenic sources are come from petrogenic or pyrogenic and which source materials that contributed to the major pollution to the rivers.

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