TITLE: BIOMAGNIFICATION PROFILE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN MANGROVE ECOSYSTEM ELUCIDATED BY $\delta^{13}C$ AND $\delta^{15}N$ ISOTOPES RATIOS AS GUIDES TO TROPHIC WEB STRUCTURE.

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M.Sc (GS24153)
1st Semester

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are natural, ubiquitous substances in marine environments; they consist of two or more benzene rings fused in various arrangements. A range of biological effects has been demonstrated for these compounds, including acute toxicity, carcinogenicity, mutagenicity, teratogenicity and endocrine disrupting activity (Takeuchi et al., 2009). There are two types of anthropogenic sources of PAHs: petrogenic and pyrogenic. Petrogenic sources include crude oil and petroleum products such as kerosene, gasoline, diesel fuel, lubricating oil, and asphalt. Pyrogenic sources form by the incomplete combustion of organic matter (e.g., coal, petroleum, and wood) in industrial operations and power plants that use fossil fuels, smelting, garbage incinerators, and vehicle engines powered by gasoline or diesel fuel, and forest fires (Saha et al., 2009). Being persistent in the sediment, PAHs can continually affect bottom-dwelling organisms and high trophic level animals via food webs. It has been clarified that while relatively high concentrations are often detected in macroinvertebrates, and macroinvertebrates have been widely used as bioindictors to monitor spatial and temporal trends of PAH concentrations the concentration in animals at high trophic levels is relatively low and the primary concern is the potential of some PAHs' metabolites to cause damage to DNA, RNA, and cellular proteins.

In this study, mangrove ecosystem has been chosen to elucidate the level of PAHs through its food web. Mangrove areas both ecologically and economically important. Mangroves area is thought to be highly productive communities, sometimes being important primary producers in the estuarine food, leading to commercial fish and shellfish. The ecological mangrove is varied. Mangroves are important nursery, breeding, feeding grounds for finfish and shellfish is well documented worldwide. While for the biomagnifications, the process usually occurs with trophic level and defines as the bioaccumulation of a substance up the food chain by transfer of residues of the substance in smaller organisms that are food for larger organisms in the chain. It generally refers to the sequence of processes that result in higher concentrations in organisms at higher levels in the food chain (at higher trophic levels). These processes result in an organism having higher concentrations of a substance than is present in the organism's food. Biomagnifications can result in higher concentrations of the substance than would be expected if water were the only exposure mechanism.

Problem statement

East Coast of Malaysia is subject to oil pollution since South China Sea is a very busy pathway for many ships from worldwide. The mangrove ecosystem in the East Coast of Malaysia also is not excluded from its outcomes. Besides, oil sources are very prominent over there. PAHs are present in the fossil fuels also formed by incomplete combustion of carbon-containing fuels. PAHs also are one of the most widespread organic pollutant and very persistent in the environment. Several study need to be conducted to discover it's disreputable towards living organisms.

Significance of study

Numerous studies have done for evaluating the PAHs level of contaminant and also the sources, but fewer studies have been conducted to figure out the risk on the biota particularly through the trophic level of mangrove ecosystem. PAHs are notorious by its acute toxicity, carcinogenicity, mutagenicity and endocrine disrupting chemicals. Hence by estimating the level of contaminant through trophic level, the threat for the life will bring into focus and their safeguard will further emphasized.

Research objectives

1- To determine the level of contaminants and types of organisms exposed to high accumulation risk of PAHs in mangrove ecosystem.
2- To study the biomagnifications profile of PAHs in mangrove ecosystem.

Literature review

Monitoring the impact of pollutants on aquatic life forms is challenging due to the differential sensitivities of organisms to a given pollutant, and the inability to assess the long term effects of persistent pollutants on the ecosystem as they are bio-accumulated at higher trophic level (Torres et al., 2008). The studies of concentration, distribution and source of polycyclic aromatic hydrocarbon (PAHs) which one of the most widespread organic pollutants were mostly conducted in marine water, bottom sediment as well as biota. Y. Liang et al., 2007 reported that aqueous route dominated accumulation of non-biodegradable PAHs in tilapia because higher levels were detected in larger fish than in smaller ones. In the report also stated that viscera appeared to be promising tissue for indicating PAHs level in talapia, because it contained much higher concentration than the muscle. Takeuchi et al., 2009 reported that PAHs undergo "biodilution" which is the organisms at higher trophic level may rapidly metabolize PAHs or they may assimilate less of them.

Mangrove ecosystems, important inter-tidal estuarine wetlands along the coastline of trophical and subtrophical regions, are exposed to oil pollution by accidental or chronic oil spills. The unique features of mangroves systems such as high primary productivity, abundant detritus, and rich organic carbon, anoxic and reduced conditions

favour the retention and accumulation of PAHs (Ke et al., 2002). Mangrove environments also have relatively high organic matter and sulphide content in their sediments, anoxic conditions, low energy nature of the environment, and reduced current flow, make them a preferential site for the deposition and accumulation of contaminants such as PAHs in mangrove sediments (Bernard et al., 1996). The major inputs of the PAHs contamination in environment are mainly from anthropogenic activities such as transportation, automobiles, oil spills and combustion which are creating serious threat to coastal ecosystem such as mangroves.

The potential sources of oil pollution on the East Coast of Peninsular Malaysia are mainly associated with oil fields in Terengganu and accidental spills form supertankers transporting oil form the Western hemisphere to the North East (K. Chandru et al., 2008). Although the South China Sea is one of the most important routes for oil tankers, data on the contaminants level for organisms in the mangrove ecosystem particularly have not been well documented.

Methodology

Study Area:
Mangroves area, Kuala Terengganu, Malaysia

Sampling procedures:
Several quantities of lichens, macroalgae, molluscs, crustacean, fishes, and otter will be collected. Samples were mixed/ homogenized and weighed approximately 20g. Sodium sulphate (Na_2SO_4) anhydrous was added, stirred well until the wet samples become dry. Then the samples were stored at -18˚C.

Samples Analysis Procedures:
The weighed samples were extracted with soxhlet extractor using dichloromethane (DCM) for more than 8 hours. The extracted samples were added with surrogate internal standard mixture (SIS) prior to purification and fractionation. The copper treatment was also applied to remove sulphur contents in the samples. The samples were introduced to 5% deactivated silica gel to collect the hydrocarbon contents with 25% DCM in hexane solvent. In the second step column chromatography, 100% fully activated was used to collect the third fraction containing PAHs with similar solvent. Gas Chromatography- Mass Spectrometer was used to analyze PAHs in the samples.

Stable isotopes determination:

Muscle tissues from samples were dissected out and dried for 24 hours at 60˚C. Dried samples were ground to powder and immersed in chloroform: methanol (2:1) solution to remove lipid. Stable carbon and nitrogen were measured and results were presented a part per thousand deviations from the standards, expressed as $\delta^{13}C$ and $\delta^{15}N$.

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