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LINEAR ALKYL BENZENES (LABS) IN SURFACE SEDIMENTS OF MALAYSIAN RIVERS

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ABSTRACT

This study focuses on sewage pollution, which is one of the most important issues concerning Malaysians. The main location of this study is in Johor Bahru as it is one of the most populated areas in Malaysia. The distribution and sources of linear alkyl benzenes (LABs) were evaluated in surface sediments collected from Johor Bahru Coast and the Kim Kim River, Peninsular Malaysia. The samples were extracted, fractionated and analyzed using gas chromatography-mass spectrometry (GC-MS). This study found that LABs concentrations ranged from 87.6 to 188.7 ng/g dw and 88.2 to 119.02 ng/g dw in surface sediments from Johor Bahru Coast and the Kim Kim River, respectively. Johor Bahru Coast showed an increasing trend of LABs concentrations due to rapid industrialization and population growth. The ratio of internal to external isomers (I/E ratio) of LABs in sediment samples from Johor Bahru Coast ranged from 1.76 to 2.04 while the I/E ratios in sediments from the Kim Kim River ranged from 1.72 to 1.91.

1. Introduction

The investigation of sewage pollution in Malaysia, especially in the Johor Bahru area, is very important for health, aesthetics and the ecosystem because the coastal and riverine environment is used for recreational activities and is a source of potable water for the highly populated municipalities surrounding it. Sewage pollution can be assessed by microbiological and chemical markers (Vivian, 1986; Takada and Eganhouse, 1998).

Linear alkyl benzenes (LABs) are a suite of chemical markers that have been successfully utilized as organic molecular markers for evaluating the source of sewage pollution (Eganhouse, 1997). Due to their exclusive association with human activities, LABs can be used as evidence of anthropogenic impact on the marine environment. Most of LABs production is used to manufacture linear alkylbenzene sulfonates (LAS), which is used in household synthetic detergents production (Eganhouse et al., 1983). Because of this, LABs are fast becoming the most common raw material in the manufacturing of household detergents.

Due to its improved biodegradability and cost-effectiveness, LABs have completely replaced the older branched alkylbenzene in the production of surfactants that have been used in household laundry detergents and dishwashing applications since the 1960s. LABs have isomers with different phenyl-substitution positions on the alkyl chains. It is easier to biodegrade external isomers (isomers whose phenyl substitution positions are close to the terminal end of the alkyl chain) than internal isomers (isomers whose substitution positions are close to the center of the alkyl chain). Besides this, the isomeric structure and concentration of LABs reflects the magnitude and types of sewage discharged into the aquatic environment, such as raw sewage versus secondary effluents (Tsutsumi et al., 2002).

Due to its improved biodegradability and cost-effectiveness, LABs have completely replaced the older branched alkylbenzene in the production of surfactants that have been used in household laundry detergents and dishwashing applications since the 1960s. LABs have isomers with different phenyl-substitution positions on the alkyl chains. Thus, the distribution of LAB isomers indicates the level of LAB biodegradation (Takada and Ishiwatari, 1990). Furthermore, the isomeric structure and concentration of LABs reflect the magnitude and types of sewage discharged into the aquatic environment, such as raw sewage versus secondary effluents (Tsutsumi et al., 2002). Because of these attributes, LABs are good indicators of human activities associated with sewage contamination in different regions around the world (Eganhouse et al., 1983; Takada et al., 1992; Isobe et al., 2004; Medeiros and Bícego, 2004; Luo et al., 2008; Martins et al., 2008; Ni et al., 2009; Venkatesan et al., 2010; Martins et al., 2012; Rinawati et al., 2012; Alkhadher et al., in press). All kinds of pollution stemming from human activities will ultimately settle down in surface sediments (Abdullah et al., 1999).

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2. Literature Review

Minor quantities of LABs are possibly being carried via LAS-type detergents and considering the massive utilization of detergents and consequent dis- charge of LABs into the aquatic environments, it is safe to conclude that municipal wastewaters are highly likely to have LABs that could be released into the environment (Eganhouse et al., 1983; Takada and Ishiwatari, 1987).
Due to their high hydrophobicity, log octanol- water partition coefficient 7–10 (Sherblom et al., 1992), LABs are predominantly associated with sewage rich organic particles (Murray et al., 1987; Takada et al., 1994).
The I/E ratio (a ratio of the total of internal to external isomers) has been proposed as an indicator of the level of LABs degradation in an aquatic environment. Thus, the distribution of LABs isomers indicates the level of LABs biodegradation (Takada and Ishiwatari, 1990). Because of these attributes, LABs is a good indicator of human activities associated with sewage contamination in differ- ent regions around the world (Eganhouse et al., 1983; Takada et al., 1992; Isobe et al., 2004; Medeiros and B´ıcego, 2004; Luo et al., 2008; Martins et al., 2008; Ni et al., 2009; Venkatesan et al., 2010; Martins et al., 2012; Rinawati et al., 2012; Alkhadher et al., 2015).
There is a strong correlation between sewage contami- nation and various waterborne diseases in tropical Asia, which are wide-ranging in these regions (Isobe et al., 2002). Therefore, the assessment of riverine and coastal area sediments for possible sewage contamination is a critical turning point towards improving water quality and reducing the risk of infectious diseases (Wang et al., 2010). All kinds of pollution stemming from human activities will, in the end, settle down in surface sediments (Abdullah et al., 1999). Thus, it is important to analyze surface sediments to identify the level of sewage contamination in coastal and riverine areas.
Most of the pollutants leave their fingerprints in sediments, thus sediment analysis offers certain advantages compared to water analysis. Peninsular Malaysia especially Johor Bahru is highly populated and urbanized with numerous rivers and coastal areas that are on the receiving end of land based anthropogenic inputs such as municipal effluents, agricultural effluents and industrial discharges (Shahbazi et al., 2010). Johor is the second largest state in Peninsular Malaysia and is located along its south Coast with an area of approximately 19000 km2 and a population of 3.5 million people (DOSM, 2014). Over the past few decades, the coastal area of Johor has undergone rapid development i.e. urbanization and industrialization (Hadibarata et al., 2012).
Such intense growth in Johor Bahru's human population and households has led to a high amount of municipal wastewaters being discharged into coastal waters (Azman et al., 2012). Hence, this study is conducted to identify the possible sources of LABs by estimating the concentrations and distribution of LABs in sediments from the Johor Bahru Coast and the Kim Kim River. The present study also aims at comprehensively assessing the anthropogenic impacts of LABs on the aquatic environment of the Johor Bahru Coast and the Kim Kim River in Johor Bahru state using data from the concentration and main sources of LABs compounds in the surface sediments. This study could also provide valuable insights into the degradation of LABs in the marine environment as well as act as a gauge for the efficiency of sewage treatment plants in this area.

3. Methodology

To evaluate the organic compound inputs from anthropogenic activities in Johor Bahru Coast and the Kim Kim River, eight sediment samples were collected from eight locations at Johor Bahru Coast and the Kim Kim River during the months of May and June 2013 (Figure 1). Surface sediment samples were collected from five locations along Johor Bahru Coast and three locations from the Kim Kim River, all of which are located in the eastern part of Johor Bahru, Peninsular Malaysia. LABs may have originated from hot spot areas such as hospitals, hotels, laundries, schools, governmental institutions, shopping centers, parks and restaurants where human activities are intense. An- other factor that contributed to the elevated levels of LABs in SBB1 is high concentration of TOC at 15.6 mg/g dw. A positive correlation be- tween the concentrations of hydrophobic organic compounds (HOCs) and TOC was previously reported by several workers (Arzayus et al., 2001; Accardi-Dey and Gschwend, 2002; Hinga, 2003). The lowest concentration of LABs was found at station SBB12 of Brunei Bay (7.1 ng g−1 dw). This can be explained by less anthropogenic influence around the station. In general, the results of this study suggested that Brunei Bay is subjected to low impact from domestic wastewater discharge.

4. Analysis

Purification and fractionation of the sediment samples was performed using a method presented by Zakaria et al. (2002). Briefly, the previously freeze-dried sample was soxhlet-extracted using 250 mL of high purity dichloromethane (DCM) for 10 h. prior each sample extraction, the 1- Cn LABs (50 ml) were added and used as surrogate standards where 1- refer to first isomer of each LABs homologue, n refer to carbon number (8-14).

The extracts were rotary-evaporated to near dryness and were transferred onto the top of 5% H2O deactivated silica gel (60–200 mesh size, Sigma Chemical Company, USA) in a glass chromatographic column (0.9 cm i.d., 9 cm height). Exactly 20 mL of high purity Hexane/ DCM (3:1, v/v) was used as an elution solvent for the hydrocarbon fraction. The extract was rotary evaporated and reduced to 1–2 mL and was sequentially fractionated with a fully activated silica gel column (0.47 cm i.d. _ 18 cm height) to get LABs fractions using 4 mL of high purity hexane. The LABs fraction was

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then transferred to a 2 mL amber vial and evaporated to near dryness using a gentle stream of nitrogen. The internal standards (biphenyl-d10, m/z 164) were added in each blank and sample extract before instrumental analyses. The reasonable efficiency of surrogate recovery (1- Cn LABs) for LABs indicates that there is a minimal possibility of loss of target compounds during analysis due to their non-volatile, non-polar nature.

Procedural blanks for LABs were conducted with each batch of samples together with the samples from extraction up to the instrumental analysis, to determine any cross-contamination during the analytical procedures and from glass- ware. Individual LABs congeners were determined using a GC–MS in the selected ion monitoring mode at m/z 91, 92, and 105. LABs congeners were quantified using average response factors generated from a five- point calibration curve, which was constructed for the concentration range of 0.25–5 mg/g. Each sample of LABs concentration obtained were recovery-corrected against the surrogate internal standards (1-Cn LABs) spiked just after extraction. Ranges of recoveries of the LABs surrogates were 89%–98%, throughout the sample analyses.

The highest concentration of LABs was observed in SJB3 (188.7 ng/g¡1.dw), situated in the center of the Johor Bahru area, which is known to be a highly populated and urbanized area. The highest level of LABs observed in SJB3 is similar to those reported in highly urbanized areas where untreated sewage was being discharged into the coastal waters (Isobe et al., 2004). Another factor affecting the increase of LABs in SJB3 is the total organic carbon (TOC), which was found to be very high in this station (30.9 mg/g). The Positive correlations between the concentrations of hydrophobic organic compounds (HOCs) and total organic carbon (TOC) have previously been reported (Arzayus et al., 2001; Accardi-Dey and Gschwend, 2002; Hinga, 2003). On the other hand, in the present study, the lowest concentration was found at station SJB2 of the Johor Bahru Coast (87.6 ng/g¡1.dw). This might be attributed to the presence and efficiency of sewage treatment plants or because the area has a lesser population. This research team believes that these spatial distributions are likely due to the differences in industrialization and urbanization rates in the wastewater outfalls of these sampling stations. The results also affirm that sewage treatment plants (STPs) directly influence the concentrations of LABs as generally low concentrations of LABs are observed wherever there are many STPs and vice versa. Because the results from this preliminary study indicated that there may be STPs around the study area, we attribute the lower LAB concentration at JB2 to its proximity to STPs.

The occurrence of LABs in Johor Bahru sediments may be attributed to lateral transport of untreated or treated domestic sewage of household and industrial waste into inshore locations of Johor Coast. Eganhouse et al. (1983) and Valls et al. (1989) observed a decrease in LABs concentration and depletion of external LABs rather than internal ones in offshore sediments com- pared to inshore or estuaries sediments. However, the fact that concentrations of LABs were higher in the mid- dle station of the study area (SJB3) than in the other sampling stations could be because this station is close to input source of LABs (anthropogenic activities) on inshore land. The second station with high concentrations of LABs was SJB5 (Figure 4). SJB5 is located within a highly populated and industrialized area causing accumulation of large amounts of municipal sewage waste. Johor Bahru has experienced rapid population growth in recent years. The population growth rate of Johor Bahru increased from approximately 1.6 to 3.5 million people from 1980 to 2014 (DOSM, 2014). During this time, increasing levels of LABs concentration was also observed at the first station and the fourth station (SJB1& SJB4) of Johor Bahru Coast. This indicates that these sampling stations are close to hot spot areas where human activities thrive, such as hospitals, hotels, laundries, schools, governmental institutions, shopping centers, parks, and restaurants. Therefore, the LABs may have originated from these anthropogenic and residential activities as well.

5. Conclusion

The highest I/E ratio was recorded in the upstream of Kim Kim River (SKK1 1.9) and the lowest I/E ratio was recorded in the downstream (SKK3 1.7), indicating that the sedimentary LABs in the upstream River were more degraded than those in the downstream River (Figure 6). This may be explained by the higher bacterial activity upstream of the River than downstream (River Est ary). The I/E ratios results in the Kim Kim River were in contrast with what was expected from incubation biodegradation experiments (Takada and Ishiwatari, 1990). This supports the explanation that LABs isomer is converted through a mechanism that involves phenyl group migration after an H-abstraction from the alkyl chain, following reacquisition of hydrogen from the ambient natural organic matter (Gustafsson et al., 2001). Some studies found that using I/E ratios as indicators of the extent of biodegradation at offshore locations seemed doubtful. For instance, Gustafsson et al. (2001) observed that I/E ratios decreased with increasing distance from source to offshore in Boston Harbor, which is in contrast to what was expected from incubation biodegradation investigations. Luo et al. (2008) found that I/E ratios decreased with increasing distance from source to offshore in South China Sea sediments (0.2–0.9) compared to those collected from other terrestrial rivers.

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