DISTRIBUTION OF LINEAR ALKYLBENZENES (LABS) IN SELECTED SEDIMENTS OF SARAWAK KUCHING AND SEMBULAN RIVERS

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INTRODUCTION

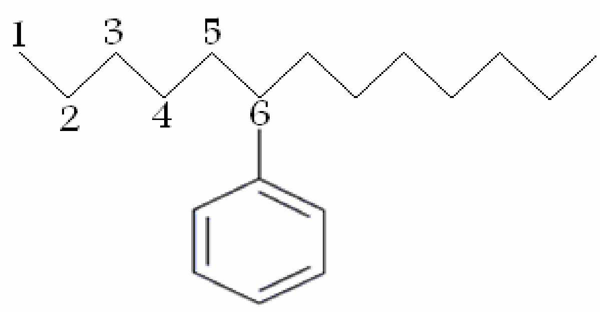
Kuching and Kota Kinabalu rivers are located in the East of Malaysia. The major activities in these cities are human; tourism activities. Linear alkyl benzene (LABs) considered as one of the organic pollutants that has resistant degradation and toxicity influence in the environment.

The term alkyl benzenes (LABs) has been used to describe a group of phenyl alkanes having a benzene ring attached at any position except the 1-position of a straight alkyl chain of between 9 and 15 carbons (Fig: 1) (Eganhouse et al.,1983). Linear alkylbenzenes (LABs) are commonly found in the environment due to their use as a precursor in the manufacture of linear alkylbenzene sulphonate (LAS) detergents, in which they remain as trace contaminants (Cirsp et al., 1979; Eganhouse & Kaplan 1982; Ishiwatari et al., 1983). Other uses include insulating oils in buried electricity transmission cables from where they may enter sediments in the event of damage to the cable sheath or joints (Gledhill et al. 1991).

Different anthropogenic activities in wide communities and cities produce considerable quantities of solid and liquid wastes, and finally discharged as domestic wastewater. As a rule, domestic wastewater carries a wide variety of pollutants to the coastal region, so that it is one of the major sources of pollutants. They are readily biodegraded under aerobic conditions but may be released into anoxic environments where they can persistent in sediments (Johnson 2003). Laboratory experiments show that LABs can be degraded under nitrate-reducing conditions, and isomeric analysis of the remaining LABs is good indicator of the degree of degradation.

The impact of LAB could be clear when this compound killing the bacteria which degrade the organic matter in the sewage. Therefore, it is used as molecular markers of sewage.

The pollution of LABs has been studied several years back. Study on LABs contents in Malaysia Rivers is still limited.



Wastewater treatment plant is considered as the main way of protection of the river environment against several pollutants that can get their way to the environment during the frequently leaking of untreated and the partially treated sewage.

Linear alkyl benzene(LABs) into aquatic environments as surfactant-related source of LABs in industrial wastewater discharge from LAS synthesis plants frequently, the behavior and fate of organic contaminants (Takada and Eqanhouse., 1998) can be examined using a widely used chemical with similar physiochemical properties. In this regard LABs have been used as molecular markers of domestic waste water (Takada and Eqanhouse, 1998) Because of their high hydrophobicity.

Rapid population growth and urbanization in most developing countries in South and Southeast Asia `since the 1990s have been accompanied by high health risks due to increasing inputs of untreated domestic wastewater to rivers and coastal environments. Establishment of municipal sewage treatment service cuts the load of sewage discharged into the aquatic environment, and it is one of the effective counter measures to reduce the risk (Isobe, 2004). As a result small amounts of LABs are likely contained in LAS-type detergents (Takada and Eganhouse, 1998), and use of detergents and subsequent disposal bring LABs into aquatic environments. Another surfactant-related source of LABs is industrial wastewater discharge from LAS synthesis plants (Takada and Eganhouse, 1998), which the phenyl group is attached near to the end of the alkyl chain) were degraded faster than internal isomers.

In the present study, linear alkylbenzenes (LABs) are used as molecular markers of sewage input. LABs with C_{10}–C_{14} normal alkyl chain are the raw material for the industrial production of linear alkylbenzenesulfonates (LAS). LAS are widely used anionic surfactants contained in domestic synthetic detergents for washing clothes and dishes. Small but significant amounts of LABs are not sulfonated during the synthesis, and the unsulfonated residue is carried over in LAS-type synthetic detergents..

Major population centres and socio-economic growth in Sabah is concentrated in the coastal area. There are four major growth centres: the state capital Kota Kinabalu, Sandakan, Tawau and Kudat; and more than 300 villages along the Sabah coastline. The majority of coastal villages depend upon fisheries as their main source of income, but agriculture and tourism are becoming more important.

PROBLEM STATEMENT

Rapid population growth, land development along river basin, urbanization and industrialization have subjected the rivers in Kuching and Kota Kinabalu Rivers to increasing stress, giving rise to water pollution and environmental deterioration. Several human activities that have directly degraded the natural environment, particularly in regard to river water quality in Kuching and Kota Kinabalu Rivers include: discharge of untreated waste water, raw sewage and disposal of the city effluent which the majority of the drain discharges their mixture of effluent and storm water.

RESEARCH OBJECTIVES

The objectives of this project are:

1- To measure the concentration level of linear alkyl benzene (LAB) in sediment samples collected from Kuching and Sembulan Rivers, Malaysia.

2- To determine the distribution of LABs in sediment samples collected from Kuching and Sembulan Rivers, Malaysia.

LITERATURE REVIEW

Costal areas are recipients of increasing amounts of land-based wastes transported by rivers and sewage outfalls, and domestic effluents are the major point sources of coastal pollution (Richard & Shieh, 1986). Discharge of wastewaters into semi-enclosed systems, where dilution processes are quite restricted and anaerobic condition often prevail, can lead to an accumulation of persistent contaminants in sediments, depending upon their phase-association in the water column (Chalaux et al., 1995).

Today, urban riverine and coastal environments are receiving massive amounts of organic pollutants derived from various sources and domestic waste is one of their major sources.

Since the first report on the occurrence of LAB in the environment and their utility as molecular markers in 1983.(Eganhouse et al., 1983; Ishiwantari et al., 1983)LABs have been widely employed as markers of anthropogenic input in aquatic environment. Linear alkyl benzene (LAB) was introduced in the mid-1960s as a raw material for cleaning products. Since then, continuing and explosive research on its environmental and human toxicity has been performed. The efficiency of linear alkylbenezene Sulfonate as surfactant is clearly established. And it is one of the safest and most cost-effective products in widespread commercial use.

The expected consequence of this analytical survey is to envisage the continuous challenges for the detergents industry in catalytic production of LAB, better control of selectivity. Replacement of corrosive and mineral liquid acid catalyst by heterogeneous acid catalyst and the maintenance of competitiveness of LAB with respect to natural alcohols.
The use of LAS-type detergents and their subsequent disposal bring LABs into aquatic environments (Eganhouse et al., 1983; Takada and Ishiwatari, 1987).

LABs are more resistant to microbial attack in the environment than LAS. It is rare to detect LAS in the marine environment due to their degradable nature, whereas LABs have been constantly detected in a wide range of marine environments due to their persistence. LABs are also hydrophobic , therefore, can potentially accumulate in sediments and biological tissue.

Material and Methods

Sampling Collection

The sediments samples were collected during December, 2008 and May, 2009. The sites of the sampling were included various stations in the Kuching River in Sarawak and Sembulan River in Sabah Malaysia. Nine surface sediment samples (top 0-4 cm representing recent input) from Kuching River in Sarawak and sex surface sediment samples from Sembulan River in Sabah were collected by Eckman dredge and placed into previously solvent-rinsed stainless steel containers. The samples transported to the laboratory in ice box and stored at -20˚C prior to further analysis to prevent any contamination.5 samples (Bitumen, Street dust, tyre rubber, Fresh crankcase oil, Used crankcase oil) collected from Kuching River in Sarawak and 5 samples (asphalt, Tyre rubber, Fresh crankcase oil, Used crankcase oil, Street dust) from Sembulan River in Sabah.

Extraction of LABs

Sediment sample was defrosted at room temperature and homogenized with baked anhydrous sodium sulphate and placed in pre-cleaned cellulose thimbles and soxhlet extracted for 9 hours by 300 ml distilled dichloromethane DCM (v/v). The extracts were subjected to activated copper and left overnight to remove the elemental sulfur. Volume of the solvents was reduced using rotary-evaporator. The extract was then put into pear shape flask using a Pasteur pipette. The sample was then concentrated to near dryness.

The extracts were then subjected to purification, fractionation, and instrumental analysis, as described by Hartmann et al. (2000). Briefly, The extract was then charged to 1st Step Column Chromatography.

Compound class separation

The explanation for packing of the 1 Step column chromatography is as the following 5% H2O deactivated silica gel was used to pack the glass column (0.9 mm internal diameter). Glass wool put in the bottom of the column. First, rinse the column with Hexane. The 5% H_2O deactivated silica gel was added until the height of deactivated silica gel reach 9 cm using Pasteur pipette. The sample was added with 20 ml of Hexane/DCM 3:1 into the column. The stopper was opened to allow all the samples with Hexane/DCM 3:1 passed through the column into 25 ml pear shape flask. Volume of solvents then was reduced to near dryness to get ready for the 2nd Step Column Chromatography.

Activated silica gel was used to pack the column with an internal diameter of 0.47 cm and the height of activated silica gel was 18 cm. First, the column was rinsed with distilled Hexane to remove unwanted compounds. The silica gel with added until the height of silica gel reach 18 cm and packed it. There would be three fractions resulting from these steps: the first fraction consists of alkanes; the second LABs; and the third PAHs. A series of elution volume of solvents was added according to fraction to be collect. To get LAB fraction, firstly the samples were rinsed with 4 ml hexane into the column, to remove the alkanes. After this 4 ml hexane was charged through the column to get the LABs fraction.

After these step, the volume of fraction was extracted to near dryness and transfer to 2 ml vial, and stored in cool room until further analysis.
LABs analysis will be done using quadruple mass spectrometer integrated with gas chromatography.

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