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Baseline distribution and sources of linear alkyl benzenes (LABs) in surface sediments from Brunei Bay, Brunei

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ABSTRACT

Sewage pollution is one of major concerns of coastal and shoreline settlements in Southeast Asia, especially Brunei. The distribution and sources of LABs as sewage molecular markers were evaluated in surface sediments collected from Brunei Bay. The samples were extracted, fractionated and analyzed using gas chromatography-mass spectrometry (GC-MS). LABs concentrations ranged from 7.1 to 41.3 ng g^{-1} dry weight (dw) in surficial sediments from Brunei Bay. The study results showed LABs concentrations variably due to the LABs intensity and anthropogenic influence along Brunei Bay in recent years. The ratio of Internal to External isomers (I/E ratio) of LABs in sediment samples from Brunei Bay ranged from 0.56 to 2.17 along Brunei Bay stations, indicating that the study areas were receiving primary and secondary effluents. This is the first study carried out to assess the distribution and sources of LABs in surface sediments from Brunei Bay, Brunei.

Discharge and emission of sewage contamination are derived from human activities such as industrial development, urbanization, tourism, etc. The control of aquatic pollution has been identified as an immediate need for sustained management and conservation of the existing fisheries and aquatic resources (Islam and Tanaka, 2004). By far, sewage is the greatest volume of waste discharged to the marine environment. Highly populated cities generate huge loads of such wastes daily which are finally washed out by the drainage systems that generally release into nearby rivers or aquatic systems. Sewage contamination can be assessed by microbiological and chemical markers (Vivian, 1986; Takada and Eganhouse, 1998).

Linear alkylbenzenes (LABs) are one group of the chemical markers which have been successfully utilized as organic molecular markers for evaluating the source of sewage pollution (Eganhouse, 1997). Owing to their source specificity, resistance to degradation and persistence in marine sediments for a long time, molecular markers such as LABs have been important for studying anthropogenically derived organic matter input and its impact on aquatic environments (Takada and Eganhouse, 1998). 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). 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).

The I/E ratio (a ratio of the total of Internal to External isomers) has been proposed as an indicator of LAB degradation level in an aquatic environment (Takada and Ishiwatari, 1990). 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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Most of the contaminants leave their fingerprints in sediments, thus sediment analysis offers certain advantages compared to water analysis.

Brunei is a Southeast Asian country consisting of two unconnected parts with a total area of 5.8 km2 on the island of Borneo and the population of Brunei is 415,000 people of which 76% live in urban areas. The rate of urbanization is estimated at 2.13% per year from 2010 to 2015 (Oxford Business Group, 2013).

The purpose of this study is to evaluate source of sewage pollution by applying LABs and I/E ratios in the surface sediments from aquatic environment of the Brunei Bay. This study provides 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 (STPs) in this area.

The present study was conducted in the Brunei Bay which is located on the northwestern coast of Borneo Island. Surface sediment samples were collected from fourteen locations at Brunei Bay during December 2013 (Fig. 1, Table 1). The sediments were sampled with a stainless steel Ekman dredge sampler. The top 4 cm of surface sediments was placed into a pre-cleaned plastic ziplock bag and stored at −20 °C. The sediments were then homogenized and freeze-dried.

Purification and fractionation of the sediment samples was performed using a method presented by Zakaria et al. (2002). Briefly, the previously homogenized, freeze-dried and precisely weighed samples were soxhlet-extracted using 250 mL of high purity dichloromethane (DCM) for 10 h. Prior to each sample extraction, the 1-Cn LAB (50 μL) were added as surrogate standards where 1- refers to the first isomer of each LAB homolog, n refers to carbon number within the range of 8 to 14. The extraction of the samples was followed by activated copper treatment to remove elemental sulfur. The extracts were rotary-evaporated to near dryness and transferred onto the top of 5% H_2O deactivated silica gel (60–200 mesh size, Sigma Chemical Company, USA) in a glass chromatographic column (0.9 cm i.d. and 9 cm height). Exactly 20 mL of high purity Hexane/DCM (3:1, v/v) was used as an elution solvent for hydrocarbon fraction. The extracts were rotary evaporated and reduced to 1–2 mL and sequentially fractionated with a fully activated silica gel column (0.47 cm i.d. and 18 cm height) to get LAB fractions using 4 mL of high purity hexane. The LAB fractions were 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) contained in 10 ppm internal injection was added to each blank and sample extract before instrumental analyses. The instrumental procedure involved the use of a GC–MS Agilent model with a 5MS fused-silica capillary column (30 m by 0.25 mm i.d. and 0.25-μm film thickness) to analyze the LABs.

The 26 congeners of LABs were analyzed. A 1-μL aliquot of purified samples was introduced into the GC–MS injector. The GC–MS temperature program started at 70 °C for 2 min, with a ramp of 30 °C per minute until 150 °C. The temperature was further increased to 310 °C with an increasing rate of 4 °C/min for 15 min. The analysis was done using selected ion monitoring (SIM) mode with splitless injection. Individual LABs were monitored in SIM mode at (mass/charge ratio) m/z = 91, 92 and 105. The oven temperature was held at 70 °C for 2 min, then continued at 30 °C/min to 150 °C, 5 °C/min to 310 °C and held for 6 min.

The mass spectrometer was scanned repeatedly at an ionization potential of 70 eV with the source at 200 °C and electron multiplier voltage at ~2000 eV.

Quantification of target compounds of LABs was carried out based on external calibration curves using a series of LAB standard mixture solutions for the 26 target compounds with different concentrations (0.25, 0.5, 1, 2.5 and 5 mg/L) were prepared. Determination of target compounds was achieved based on matching their compound ionization and retention times with the standard mixture of LABs. All of the LABs in sediment samples were calculated based on dry weight (dw).

Quality assurance and quality control were considered while conducting the analytical processes. The reasonable efficiency of surrogate recovery (1-Cn LAB) for LABs indicates that there is a minimal possibility of loss of target compounds during analysis due to their non-volatile, non-polar nature. Ranges of recoveries of the LABs surrogates

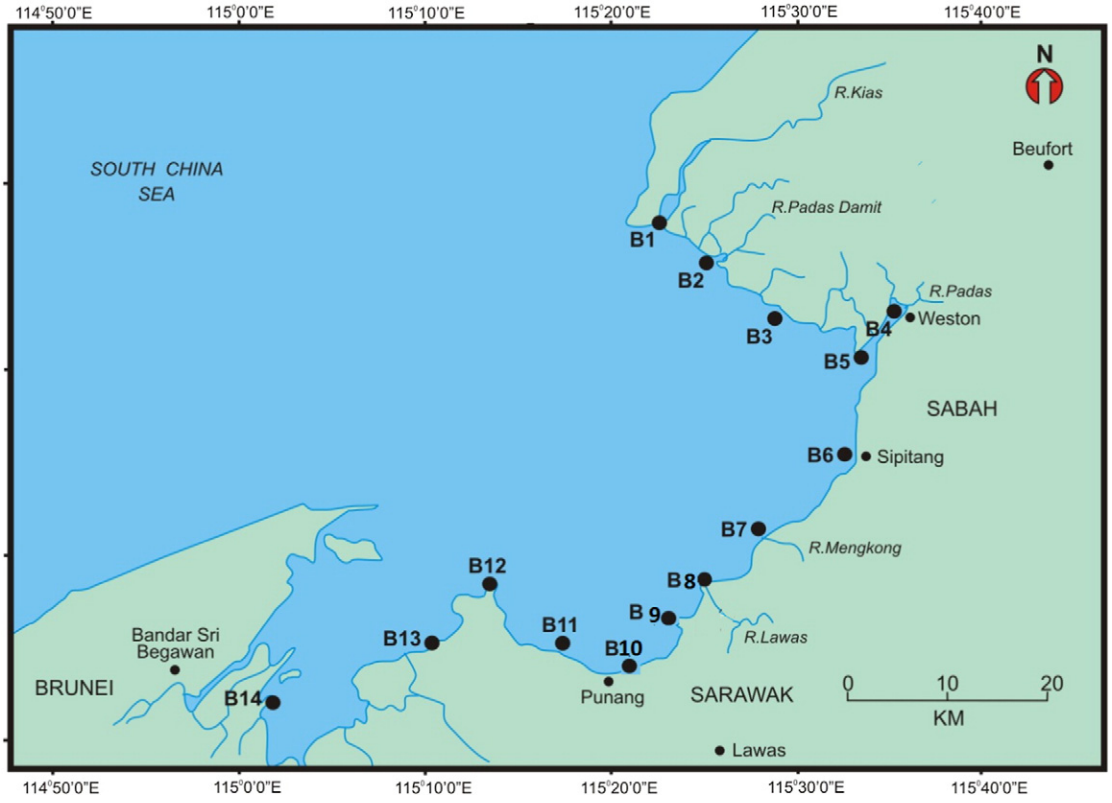

Fig. 1. Sampling stations along Brunei Bay (B1–B14).