

ASSESSMENT OF SEWAGE CONTAMINANTS USING LINEAR ALKYL BENZENES (LABs) IN SEDIMENTS COLLECTED FROM SOUTH CHINA SEA

Najat Abdullah Ebrahim*, Mohammad Pauzi Zakaria , Normala Halimoon

M.Sc (GS21079)
3rd Semester

Introduction

The seas are being polluted by organic and inorganic wastes from sewage, from agricultural and industrial wastes, and from run-off containing oil, hydrocarbons, and heavy metals. All of these contribute to sediment run-off and increased turbidity. Construction and land reclamation has caused changes in water circulation and has increased sedimentation.

In the last 50 years the production of synthetic organic chemicals for industrial and domestic use has increased dramatically from 7 million tones in 1950 to 63 million tones in 1970 (Maugh, 1978).

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 (Chaloux 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.

These organic pollutants can be found in water, soil and in the air because it will produce from the natural processes and sources. Such as from organisms, natural seeps, from automobiles, industries, agriculture, surface run off, rain, from atmosphere such as dust, and from biological process such as food chain (Zakaria and Mahat, 2006). Some hydrocarbon pollutants are carcinogenic and mutagenic effects in organisms. These will affect the biological process, the marine food; ecosystem and it also give impact to human health.

Some of hydrocarbons pollutants have been found in the river, lake and ocean. These hydrocarbons include the polychlorinated Biphenyls (PCBs), polycyclic Hydrocarbons (PAHs), Linear Alkylbenzenes (LABs), Alkanes and Hopanes. These pollutants maybe

released many years ago and it can accumulate in the ocean, lake or river. This pollutant also can stay for a long time in the water.

The LABs consist of a set of 26 secondary phenylalkanes with chain lengths ranging from 10 to 14 carbon atoms. Commercial LAB mixtures are principally used as raw material in the production of the widely used anionic surfactants. During sulfonation, 1–3% of LABs remain unreacted. Thus, LABs remain as a trace residue in cleaning products and detergents, and enter the aquatic environment wherever are being used and released.

Linear alkylbenzenes (LABs) are synthetic compounds used as precursors for the manufacture of linear alkylbenzene sulfonates (LAS) and which have been previously used as molecular tracers of sewage contamination. LABs are anionic surfactants commonly used in commercial detergents and both LAB and LAS are introduced to the aquatic environment through wastewater discharges. The present paper reports the concentrations of linear alkylbenzenes (LABs) in sediment samples from The Wash and the Thames and Humber Estuaries.

The alkylbenzenes are widely used as raw materials for detergents. Two kinds of alkylates have gained industrial importance as intermediates for the production of anionic surfactants by subsequent processing to alkylarysulfonates. The branched chain type, referred to as “hard detergent alkylate” [known after sulfonation as ABS (alkylbenzene sulfonate), BAS (branched alkylbenzene)].

Long-chain linear alkylbenzenes (LABS), have been identified in wastes, sediments, sinking and suspended particles [Takada and Ishiwatari 1987].

These compounds are produced industrially as precursors for the anionic surfactants; linear alkylbenzene sulfonates (LAS). Their presence in wastewater effluents is thought to result from incomplete sulfonation and carry-over in detergents, or from desulfonation of LAS [Eganhouse *et al.* 1983a].

The potential use of the LABS as sewage tracers has been discussed [Eganhouse *et al.* 1983a; Eganhouse 1985; Eganhouse *et al.* 1988].

The LABs have both an aliphatic and aromatic nature because of their unique structure. This results in their having physical properties in the same range as other hydrocarbons of interest, such as saturated hydrocarbons, polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

In addition to LABs, many other pollutants, both inorganic and organic are released into the sea through industrial and municipal wastewater. Pollutants whose chemical behavior is similar to that of LABs may also have the same fate. This study was to investigate the extent of the impact of municipal water discharges on SCS.

Linear alkyl benzene (LABs) considered as one of the organic pollutants that has resistant degradation and toxicity influence in the environment. 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.

PROBLEM STATEMENT

The South China Sea - the busiest shipping lane and surrounded by some of the most rapidly industrializing countries in the world - is becoming a sink for regional environmental pollution.

South China Sea has been sewage pollutants with land based pollution, this sewage pollution might be one of the important parameters to be measured.

RESEARCH OBJECTIVES

- 1- To determine the distribution of LABs in selected core sediment of South China Sea.
- 2-To determine the concentration of LABs in sediments at specific location of South China Sea.

LITERATURE REVIEW

Linear alkylbenzene (LAB) was introduced in the mid-1960s as a raw material for cleaning products. Since then, continuing and explosive research on its biodegradation and on its environmental and human toxicity has been performed. (Takada and Eganhouse, 1998).

Since the first reports on the occurrence of LABs in the environment and their utility as molecular markers in 1983 (Eganhouse et al., 1983; Ishiwatari et al., 1983), LABs have been widely employed as markers of anthropogenic inputs in many regions of the world.

LAB can potentially be transported via suspension of fine particles to which it has adsorbed. An examination of sediments in Tokyo Bay suggested LAB did not decrease in concentration between estuarine and offshore sediments, indicating the LAB in estuarine sediment can be transported seaward (Takada *et al.* 1992).

To quantitatively express the isomer composition, a ratio of internal to external isomers (I/E ratio) has been proposed as an index of the degree of LAB degradation (Takada and Ishiwatari, 1990).

Massive amounts of oil pass through the waters of the South China Sea; all major shipping routes are polluted to some degree. Over 100,000 oil tankers and container and cargo vessels transit the Straits of Malacca and Singapore each year. These tankers carry over 3 million barrels of crude oil through the straits each day (Tookey 1997).

These oil spills have seriously affected marine life and sea birds. They can also have a very negative effect of fisheries stocks and human health.

The problems of environmental pollution around the South China Sea are generally due to population growth and urbanization in coastal cities, economic growth and increased material consumption, and highly polluting technologies for energy production and primary resource extraction (David Rosenberg, 1999).

During most of the past two decades, industrial output and energy consumption have grown faster in the countries around the South China Sea than anywhere else in the world, driven by the region's rapid economic growth and increasing population. For the same reasons, it may also become a sink for regional environmental pollution from the industrial effluents of the littoral countries, as well as the spills and dumping of vessels in transit (David Rosenberg, 1999).

RESEARCH METHODOLOGY

Analytical procedure for sediment sample

Structures of linear alkylbenzenes are expressed as “n-Cm” where “n” means the phenyl substitution position on the alkyl carbons.

Twenty gram of sediment samples were precisely weighed put into thimble, and soxhlet extracted using 300 ml of dichloromethane (DCM) for 9 h with cycling rate of 10 min/cycle, and approximately 3g of activated copper was added and allowed to stand overnight to with elemental sulfur. The extracts were transferred to a 200 ml pear shaped flask, and 50 μ l of the alkylbenzenes surrogate internal standard mixture (5 ppm each component, 1-Cm, m=10-14) was added. The internal standards were added after the soxhlet extraction for the purpose of correcting the recoveries through the purification steps and not as a whole method recovery.

The extract was concentrated just to dryness using a rotary evaporator. The extracts were then subjected to purification, fractionation, and instrumental analysis, as described by as described by Hartmann et al. (2000). Briefly, the extracts were purified and fractionated using two-step silica gel column chromatography and the alkyl benzene fraction was determined by gas chromatography-mass spectrometry (GC-MS) in selected ion monitoring mode at $m/z = 91, 92, \text{ and } 105$.

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.

References

Eganhouse RP, Ruth EC, Kaplan IR. Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography/high resolution gas chromatography and gas chromatography/mass spectrometry. *Anal Chem* 1983; 55:2120–6.

Hartmann PC, Quinn J, King JW, Tsutsumi S, Takada H. Intercalibration of LABs in marine sediment SRM1941a and their application as a molecular marker in Narragansett Bay sediments. *Environ Sci Technol* 2000; 34:900–6.

Takada H, Ishiwatari R. Linear alkylbenzenes in urban riverine environments in Tokyo: distribution, source, and behavior. *Environ Sci Technol* 1987;21:875–83.

Zakaria M.P.,and Mahat A.A.2006. Distribution of Polycyclic Aromatic Hydrocarbons in the Langat estuary. *Costal Mar. Sci.* 30: 387-395.

"Ocean oil pollution distribution," Map from the National University of Singapore, Center for Remote Imaging, Sensing and Processing (CRISP), Singapore Straits Times, Nov. 26, 1998.