Marine Pollution Bulletin 88 (2014) 366–372

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Baseline distributions and sources of Polycyclic Aromatic Hydrocarbons (PAHs) in the surface sediments from the Prai and Malacca Rivers, Peninsular Malaysia

Mehrzad Keshavarzifard [a], Mohamad Pauzi Zakaria [a,*], Tan Shau Hwai [b], Ferdius@Ferdius Mohamat Yusuff [c], Shuhaimi Mustafa [d], Vahab Vaezzadeh [a], Sami M. Magam [a], Najat Masood [a], Sadeq A.A. Alkhadher [a], Fatemeh Abootalebi-Jahromi [a]

[a] Environmental Forensics Research Center (ENFORCE), Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] School of Biological Science, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia
[c] Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[d] Halal Products Research Institute, Universiti Putra Malaysia, 4300 UPM Serdang, Selangor, Malaysia

ARTICLE INFO

Article history:
Available online 28 August 2014

Keywords:
Polycyclic Aromatic Hydrocarbons (PAHs)
Pollution sources
Pyrogenic
Malacca River
Prai River
Malaysia

ABSTRACT

In this study, the surface sediments of the Malacca and Prai Rivers were analyzed to identify the distributions, and sources of Polycyclic Aromatic Hydrocarbons (PAHs). The total PAH concentrations varied from 716 to 1210 and 1102 to 7938 ng g^{-1} dw in the sediments of the Malacca and Prai Rivers, respectively. The PAH concentrations can be classified as moderate and high level of pollution in the sediments of the Malacca and Prai Rivers, respectively. The comparison of PAHs with the Sediment Quality Guidelines (SQGs) indicates that the PAHs in the sediments of the Malacca and Prai Rivers may have the potential to cause adverse toxicity effects on the sampled ecosystems. The diagnostic ratios of individual PAHs indicate both petrogenic- and pyrogenic-origin PAHs with dominance of pyrogenic source in both rivers. These findings demonstrate that the environmental regulations in Malaysia have effectively reduced the input of petrogenic petroleum hydrocarbons into rivers.

1. Introduction

During the last several decades, Southeast Asian countries, such as Malaysia, have experienced a drastic increase in urbanization and industrialization, resulting in an immense increase in petroleum hydrocarbon consumption. For example, Malaysia saw an increase of the number of registered vehicles during the last decade. By the end of 2012, there were 22.7 million vehicles (personal cars, commercial vehicles, public vehicles and motorcycles) registered in Malaysia, compared to 10.6 million in 2000 (JPJ, 2013), an increase of almost 12 million vehicles or 114%. These changes had caused a significant input of Polycyclic Aromatic Hydrocarbons (PAHs) into freshwater and marine ecosystems in Malaysia (Zakaria et al., 2002). Moreover, the high amount of precipitation in Malaysia (Fig. 1) causes intensive erosion from the watershed, resulting in massive wash-out of street dust, used crankcase oil, and other oily materials, into Malaysian rivers. Recent studies indicate that the rivers and coastal areas of this country are still receiving significant inputs of petroleum hydrocarbon pollution, most of which is from petrogenic sources, such as used crankcase oil (Zakaria et al., 2002; Bakhtiari et al., 2009; Saha et al., 2009; Shahbazi et al., 2010; Sakari et al., 2012; Mirsadeghi et al., 2013).

Among Southeast Asian countries, Malaysia has experienced extremely rapid industrialization, motorization, and urbanization. Penang and Malacca are two atypical Malaysian cities that have undergone rapid growth in population, industrialization and urbanization. The population size and density of Penang and Malacca has experienced continuous growth during the last two decades. In 2013, data on population rose from 1.33 million in 2000 to 1.65 million for Penang and from 0.46 million in 2000 to 0.85 million for Malacca (DOSM, 2014a,b), indicating a significant increase of population for Penang (24%) and Malacca (83%). Penang was founded by Sir Francis Light in 1786 and has since become one of the biggest ports in the region. The island has become a global ecotourism magnet and experienced extraordinary economic growth with a high population density. The immense pressure on the island's ecosystem makes the study of the Prai River necessary to safeguard its ecosystem health. In contrast, the Malacca River dissects Malacca City and snakes through highly dense population

* Corresponding author. Tel.: +60 3 8946 6764; fax: +60 3 8943 6766.
E-mail address: mpauzi@upm.edu.my (M.P. Zakaria).

http://dx.doi.org/10.1016/j.marpolbul.2014.08.014
0025-326X/

and industrial centers before exiting into the Straits of Malacca. Malacca City was a major trading post in the Malay Archipelago at the height of the *Spice Trade* by the Europeans in the 1500s. Immense growth has turned the city and its river into a potential receptacle of petroleum hydrocarbon pollution. Baseline information on compound-specific hydrocarbons in major urban rivers in Malaysia is poorly documented and understood. This study attempts to enrich our knowledge regarding the short- and long-term conservation and historical heritage of the Malacca and Prai Rivers and their hinterlands.

PAHs are hydrophobic, and their molecular structures consist of two or more fused benzene rings (Neff, 1979). The molecular structure of PAHs has a major influence on their toxicity. Some members of this group are carcinogenic, mutagenic, and teratogenic and can produce cascades of adverse effects on aquatic organisms (Karami et al., 2012) and humans (Masiol et al., 2012).

Based on the number of benzene rings, PAHs are divided into two major groups, namely low-molecular-weight (LMW) and high-molecular-weight (HMW) PAHs. LMW PHAs, such as naphthalene and anthracene, have two to three fused benzene rings, whereas HMW PAHs, such as pyrene, consist of more than three benzene rings. LMW PAHs are more water-soluble (Shahbazi et al., 2010), and biodegradable (Xu et al., 2012) than HMW PAHs. In contrast, HMW PAHs are more resistant to volatilization and biodegradation. They can be readily adsorbed onto the organic particles that are widely present in sediments (Berto et al., 2009) and become more available to benthic organisms, particularly filter feeders and sessile organisms (Yender et al., 2002).

The release of PAHs into natural environments is mainly governed by anthropogenic activities (Tiwari et al., 2012) and, to a much lesser extent, by natural events, such as forest fires (Manoli et al., 2000). Based on their source of release into natural environments, PAHs are divided into two groups, pyrogenic and petrogenic. Pyrogenic PAHs comprise of the products of incomplete combustion of organic matter, such as the combustion of fossil fuel, vehicular engines combustion, garbage incinerators, and coal combustion (Ergut et al., 2006). Petrogenic sources consist of unburned crude oil and its derivatives, such as gasoline, diesel fuel, lubricating oil, and asphalt (Ravindra et al., 2008). In order to minimize environmental pollution, Malaysia had implemented the Environmental Quality Act in 1974 known as EQA (1974). The regulation is generally aimed at waste solution fractions of the environmental pollutants (EQA, 1974). Hence, with EQA (1974) there is a provision in dealing with persistent organic pollutants (POPs) as specified under the Schedule Waste (waste of oil or oily sludge) especially the oil spill and used crankcase oil. The Schedule Waste aims at reducing spilling of the oily waste with punitive damages. Over the last decade, the level of compliance and awareness among the industries, household and general public of the EQA (1974) has significantly increased. Hence, the results of this study revealed that the industrial community and the general public spill less used crankcase oil and other oily waste. Consequently, there is a decrease of petrogenic PAHs (low-molecular-weight PAHs) as this study has clearly shown.

Surface sediment samples were collected at six locations in the Prai River and Malacca River from January 2013 to May 2013 using an Ekman Dredge sampler (Fig. 2). The samples were sliced from the top 4 cm of the collected sediment cakes to indicate modern input. At each sampling station, the shell debris and organisms were carefully removed. The samples were then transferred into previously cleaned aluminum foil, immediately stored in double pre-cleaned Ziploc bags, and then placed on ice in a cooler box. The samples were transported to the laboratory and stored at −20 °C until further analysis. Prior to additional analyses, the samples were freeze-dried and stored frozen if necessary.

The samples were purified and fractionated according to the procedures described by Zakaria et al. (2002). In brief, 8 g of freeze-dried sediment from each sample was transferred into a cellulose thimble and carefully placed into a Soxhlet extractor. Each sample was spiked with 50 μL of 10 μg/g deuterated surrogate internal standards (SIS), which included naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The sample was extracted using 300 mL of high-purity dichloromethane (DCM) for 8–10 h. The extract was rotary-evaporated to near dryness, rinsed with 3:1 *n*-hexane DCM, and volumetrically transferred to the top of a first-step glass column (0.9 cm i.d. × 9 cm height), which was previously packed with 5% H_2O-deactivated silica gel (60–200 mesh size, Sigma Chemical Company, USA) and high-purity hexane. The non-polar compounds, such as hydrocarbons, were eluted with 20 mL of hexane/DCM (3:1 v/v). The eluent from the first-step column was sequentially fractioned in the second-step column chromatography (0.47 cm i.d. × 18 cm height) using 4 mL of high-purity hexane, a subsequent batch of 4 mL of high-purity hexane, and 16 mL of hexane/DCM (3:1 v/v) to obtain *n*-alkanes, and hopanes, linear alkylbenzenes (LABs), and PAHs fractions, respectively. The n-alkane and LAB fractions were not analyzed in this study. The PAH fraction was decreased using a rotary evaporator to approximately 1 mL and then transferred into a 2-mL amber vial. Subsequently, the fraction was concentrated to near dryness using a gentle stream of pure nitrogen gas (N_2). The fraction was then re-dissolved in 200 μL of isooctane containing a 10-ppm internal injection standard (IIS), p-terphenyl-d_{14}.

The PAH compounds were analyzed using a GC–MS Shimadzu QP5050A model and a BPX-5MS fused-silica capillary column (30 m by 0.25 mm i.d., 0.25-μm film thickness). The carrier gas was high-purity helium (He). The GC–MS temperature program

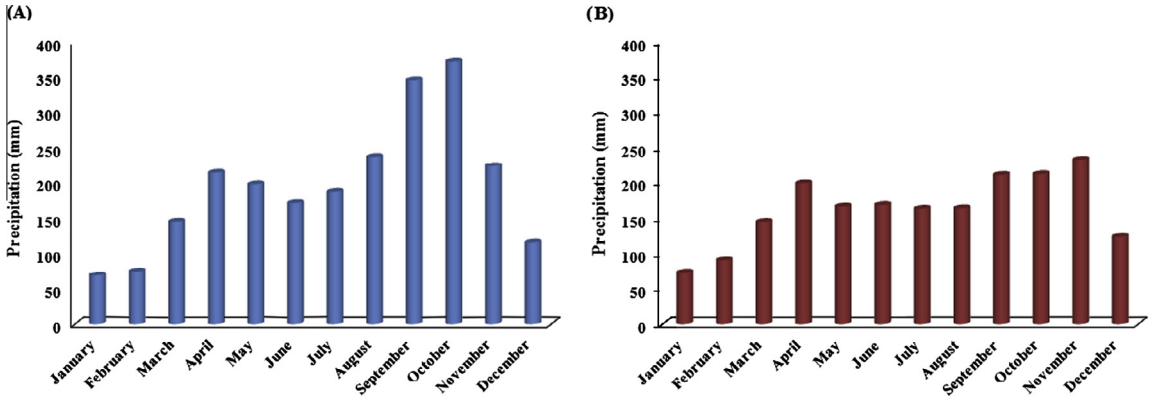

Fig. 1. The monthly mean precipitation (mm) in (A) Penang and (B) Malacca (MetMalaysia, 2014).