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Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand

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Abstract

To assess the status of polycyclic aromatic hydrocarbon (PAH) contamination in coastal and riverine environments in Thailand, we collected 42 surface sediment samples from canals, a river, an estuary, and coastal areas in Thailand in 2003 and analyzed them for PAHs with 3–7 benzene rings by gas chromatography–mass spectrometry (GC–MS). The total concentration of PAHs ranged from 6 to 8399 ng/g dry weight. The average total PAH concentrations were 2290 ± 2556 ng/g dry weight ($n = 8$) in canals, 263 ± 174 ($n = 11$) in the river, 179 ± 222 ($n = 9$) in the estuary, and 50 ± 56 ($n = 14$) in coastal areas. Comparison of the concentration range with a worldwide survey of sedimentary PAH concentrations ranked PAH contamination in Thai sediments as low to moderate. The ratio of the sum of methylphenanthrenes to phenanthrene (MP/P ratio) allows discrimination of PAH sources between petrogenic (>2) and pyrogenic (<0.5) origins. Sediments from urban canals in Bangkok showed the highest PAH concentrations and petrogenic signatures (MP/P = 1.84 ± 0.98 [$n = 6$] in canal sediments) with abundant alkylated PAHs, indicating major sources of petrogenic PAHs in the city. To identify the sources of the petrogenic inputs in Thailand, we analyzed triterpanes, biomarkers of petroleum pollution, in the sediment samples and in potential source materials. Hopane profiles were remarkably uniform throughout the nation, suggesting a diffuse single source (e.g. automobiles). Molecular profiles of hopanes and PAHs in sediments from the urban canals were similar to those in street dust, indicating that street dust is one of the major sources of petrogenic PAHs in the urban area. On the other hand, low levels of PAHs (~50 ng/g) with a pyrogenic signature (MP/P ratio ≈ 0.5) were widely recorded in remote areas of the coast and the Chao Phraya River. These pyrogenic PAHs may be atmospherically transported throughout the nation. Middle and lower reaches of the Chao Phraya River, the river mouth, and the upper Gulf of Thailand showed intermediate concentrations and profiles of PAHs, indicating mixtures of petrogenic and pyrogenic origins. Perylene was abundant in sediments, representing up to ~60% of total identified PAHs. High inputs of soil due to frequent heavy rains could contribute to the high perylene abundance in the sediments. Sedimentary PAH concentrations decreased offshore with a half distance of ~10 km in the upper Gulf off the mouth of the Chao Phraya River. This is probably due to active deposition of laterally transported riverborne particles.

Keywords: Polycyclic aromatic hydrocarbons; Hopanes; Gulf of Thailand; Sediment; Coastal zone; Street dust

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of lipophilic anthropogenic chemicals that are ubiquitously distributed in the environment. PAHs consist of two or more fused benzene rings in various arrangements (Blumer, 1976). They form an important class of environmental contaminants, because some exhibit carcinogenic or mutagenic potential. There are several reports of increased incidence of cancer in marine animals from the vicinity of oil spills (Al-Yakoob et al., 1994; Colombo et al., 2005). Concern about PAHs in the environment arises also from the fact that many of them are persistent (IARC, 1983).

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Because of their hydrophobic and persistent nature, they accumulate in bottom sediments of coastal and oceanic environments. Sedimentary PAHs are a source of exposure of PAHs directly to benthic organisms and indirectly (i.e. via resuspension) to pelagic organisms. Therefore, many studies have examined PAHs levels in coastal and oceanic sediments. However, no comprehensive surveys of PAHs in coastal environments have been done in Thailand. Thus, we examined the distribution of sedimentary PAHs around the Thai coast, especially the Gulf of Thailand and the Chao Phraya River, a major river flowing into the Gulf.

Thailand has 2600 km of tropical coastline from the westerly Andaman Sea to the easterly Gulf of Thailand. Thailand benefits from the coast through extensive economic and industrial activities, including major development projects, developments in shipping, oil and gas, a large and important fishery sector, intensive coastal aquaculture, and extensive tourism. Wastes associated with such anthropogenic activities could increase the inputs of contaminants, including PAHs. The Gulf of Thailand extends from the shallow western part of the South China Sea over 750 km to the northwest between the Malay Peninsula and Indo-China. It is situated between latitudes 5°00′N and 13°30′N and longitudes 99°00′E and 106°00′E. It is a semi-enclosed sea, covering an area of about 320 000 km^2, with average and maximum depths in the central part of about 45 and 75 m. Thus, it is relatively shallow, and the large amounts of water flowing in from several rivers make the water low in salinity (30.5%–32.5%) and rich in sediment. The Gulf of Thailand contains several structurally complex trans-tensional basins. These are made up of asymmetrical grabens filled with non-marine to marginal marine Tertiary sediments as old as Eocene. Underlying the graben sediments are a variety of Paleozoic marine carbonates, granitic intrusive rocks, and metasediments. Recent sediments in the Gulf of Thailand are non-marine in origin, mainly fluvio-lacustrine deposits (Supaporn, 1999). Four large rivers flow into the upper Gulf. Among them, the Chao Phraya River is suspected to be most polluted with PAHs, because it runs through the capital city, Bangkok. The river basin occupies the southern part of the central plain of Thailand, with an area of 162 000 km^2. The river basin is also very important for environmental conditions, in part owing to the large volume of run-off (917 $m^3 s^{-1}$ on an annual average) that discharges into the upper Gulf in Samutprakhan province (Piyakarnachana, 1989; Piyakarnchana, 1999; Pauly and Chuenpagdee, 2003). Thus, we assessed sedimentary PAHs, focusing on the Gulf of Thailand and the Chao Phraya River.

The identification of PAH sources is essential to the regulation of PAH inputs to marine environments because there are various potential sources. Sources of PAHs to the environment can be categorized into two groups: pyrogenic and petrogenic. Pyrogenic (pyrolytic) PAHs are generated through incomplete combustion of organic matter (e.g. coal, petroleum, wood). Pyrogenic sources include industrial operations and power plants using fossil fuels, smelting, waste incinerators, exhaust from vehicles powered by gasoline or diesel fuel, and forest fires. Most pyrogenic PAHs are emitted to the atmosphere as soot or gas and are finally brought to marine environments through direct atmospheric fallout and surface run-off. Crude oil and petroleum products contain PAHs and form another important primary source of PAHs (petrogenic source). Petroleum products include kerosene, gasoline, diesel fuel, lubricating oil, and asphalt. They are emitted directly to marine environments through oil spills and routine tanker operations (e.g. discharge of ballast water). Used crankcase oil contains both petrogenic PAHs derived from unburned fuel and fresh lubricating oil and pyrogenic PAHs generated through the combustion process in the engine. Recently, Zakaria et al. (2002) indicated that dumping of used crankcase oil could be a major source of petrogenic PAHs in the tropical Asian countries. In addition, petrogenic PAHs can be introduced to rivers and coastal zones through run-off of street dust, which potentially contain petrogenic PAHs derived from spilled fuel and crankcase oil, asphalt, and tire-wear material. Although natural oil seepage generally brings petrogenic PAHs directly to coastal environments, this is not the case in the Gulf of Thailand.

Many studies have been conducted to elucidate the possible origins of PAHs present in marine sediments. Most of the studies were conducted in industrialized countries situated in moderate to cold climatic zones. They indicated that sedimentary PAHs are derived mainly from pyrogenic sources (Lipiatou et al., 1993; Garrigues et al., 1995; Simcik et al., 1996; Budzinski et al., 1997; Zeng and Vista, 1997; Pereira et al., 1999; Notar et al., 2001; Stout et al., 2004), although there are some reports indicating accumulation of petrogenic PAHs in coastal sediments (Magi et al., 2002). Recently, Zakaria et al. (2002) demonstrated widespread inputs of petrogenic PAHs to the Malaysian coastal zone and ascribed them to used crankcase oil and frequent washout of the oil by the strong rain inherent to tropical Asia. Thailand is also situated in the tropical zone and, therefore, its coastal environment may similarly receive petrogenic PAHs. However, the socio-economical setting (e.g. primary energy sources) and environmental regulations differ among the tropical Asian countries. For example, the number of automobiles in Bangkok (3.5 million) is greater than that in Kuala Lumpur (1.8 million), so a larger input of petrogenic PAHs is likely. However, Thailand has some advanced environmental regulations to control used crankcase oil, which may thus not be a significant source of PAHs in the Thai coastal zone. In these contexts, we discriminated between pyrogenic and petrogenic sources as the first step toward identifying the source of sedimentary PAHs in Thai coastal sediments.