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Sources and mass inventory of sedimentary polycyclic aromatic hydrocarbons in the Gulf of Thailand: Implications for pathways and energy structure in SE Asia

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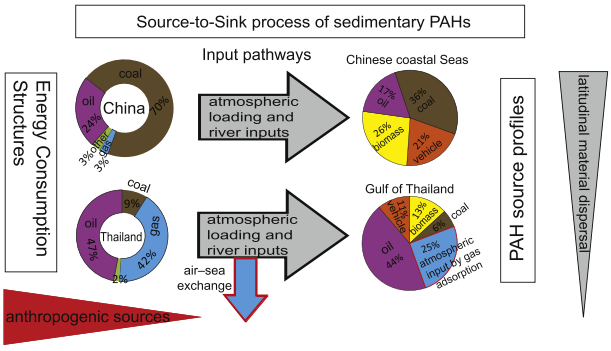
HIGHLIGHTS

- Distribution, sources and mass inventory of sedimentary PAHs in the GOT were studied.
- Atmospheric loading could be important for the sink of PAHs in the open GOT.
- PMF model apportioned a factor with air-sea exchange for the LMW PAHs in open area.
- Comparative sediment PAH mass inventory implies Asian regional energy structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Surface sediments obtained from a matrix of 92 sample sites in the Gulf of Thailand (GOT) were analyzed for a comprehensive study of the distribution, sources, and mass inventory of polycyclic aromatic hydrocarbons (PAHs) to assess their input pathways and impacts of the regional land-based energy structure on the deposition of PAHs on the adjacent continental margins. The concentration of 16 PAHs in the GOT ranged from 2.6 to 78.1 ng/g (dry weight), and the mean concentration was 19.4 ± 15.1 ng/g. The spatial distribution pattern of 16 PAH was generally consistent with that of sediment grain size, suggesting the influence of regional hydrodynamic conditions. Correlation and principal component analysis of the PAHs indicated that direct land-based inputs were dominantly responsible for the occurrence of PAHs in the upper GOT and the low molecular weight (LMW) PAHs in the coastal region could be from petrogenic sources. A positive matrix factorization (PMF) model apportioned five contributors: petroleum residues (~44%), biomass burning (~13%), vehicular emissions (~11%), coal combustion (~6%), and air–water exchange (~25%). Gas absorption may be a significant external input pathway for the volatile PAHs in the open GOT, which further implies that atmospheric loading could be important for the sink of PAHs in the open

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Asia continental margin
Energy structure

sea of the Southeast Asia (SE Asia). The different PAH source patterns obtained and a significant disparity of PAH mass inventory in the sediments along the East and Southeast Asia continental margins can be ascribed mainly to different land-based PAH emission features under the varied regional energy structure in addition to the depositional environment and climatic conditions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), an important and ubiquitous class of environmental contaminants, are derived mainly from both natural (e.g., fossil fuels, fires) and anthropogenic (e.g., incomplete combustion of fossil fuels, petroleum residues) sources (Yunker et al., 2002; Saha et al., 2009; Bouloubassi et al., 2012). Because PAHs are xenobiotic chemicals, their influx into the marine environment and resulting effects are major issues giving rise to concerns on local, regional, and global scales (Ohkouchi et al., 1999; Arzayus et al., 2001; Ghosh et al., 2003; Bouloubassi et al., 2012). Coastal and shelf areas are important oceanic realms having sensitive and vulnerable responses to impacts from adjacent human-induced pressures (Halpern et al., 2008), and fine-grained marine sediments distributed on continental shelves are usually regarded as the major sink for most land-derived contaminants (including PAHs) (Tsapakis et al., 2003; Lima et al., 2005; Guo et al., 2006; Pietzsch et al., 2010). Therefore, assessments of the distribution and sources of sedimentary PAHs in the coastal margins are important to examine their input pathways, fate, and response to adjacent land-based impacts from industrialization and social development (Pereira et al., 1996; Zakaria et al., 2002; Latimer and Zheng, 2003; Lin et al., 2011; Zhang et al., 2011; Liu et al., 2012).

It has been shown that atmospheric PAHs over the marginal seas of Asia are impacted significantly by continental outflow and have a close relationship to emission activities on land (Xu et al., 2012; Liu et al., 2014). PAHs emitted from China have been associated mainly with coal/biomass burning (Xu et al., 2006), and the differences in PAH emissions resulting from regionally varied energy consumption structures and environmental conditions in different latitude regions have caused differences in the flux and compositions of sedimentary PAHs in the Chinese marginal seas (Guo et al., 2006; Hu et al., 2011; Liu et al., 2012). These findings could imply that the tropical coastal margins of Southeast Asia (SE Asia) may also archive specific information about the sedimentary PAHs, considering the varied sources of emission, energy structures and climatic conditions in these low latitude regions (Saha et al., 2009). For example, widespread input of petrogenic PAHs to Malaysian waters has been found, caused by the frequent heavy rainfall inherent to tropical Asia, which may facilitate the transfer of these petrogenic and combustion-derived substances (e.g., PAHs and black carbon) into the adjacent marginal sea (Zakaria et al., 2002; Hu et al., 2016). Records of sedimentary PAHs in coastal regions reveal that the energy structure in the tropical environments of SE Asia differs from those of China in the mid-latitudes of Asia and Western industrialized countries (Xu et al., 2006; Boonyatumanond et al., 2007a; Saha et al., 2009). However, to date, the characteristics of and a comparison of the sedimentary PAHs on the continental shelves of these tropical regimes remain sparsely studied.

The Gulf of Thailand (GOT), a typical and semi-enclosed shelf sea in SE Asia, has been subjected to a significant contribution of PAHs from vehicular emissions, oil spills, biomass burning, and fossil fuel consumption (Saha et al., 2009; Sahu et al., 2011). The ecosystem of the GOT is especially vulnerable to human activities (Srisuksawad et al., 1997), and the increased anthropogenic activities have induced severe environmental pollution, especially in the upper Gulf where there is a significant land-based export of contaminants by the Chao Phraya River (Wattayakorn et al., 1998). Oil spills in the GOT, with its higher levels of petroleum hydrocarbons, have occurred mainly in the navigated areas along shipping routes and around several estuaries in the upper GOT (Ivanov and Zatyagalova, 2008; Wattayakorn, 2012). Previous studies of sedimentary PAHs in the GOT focused mainly on the nearshore region, and the results of these studies showed a dominant river influence with mixed pyrogenic- and petrogenic-origin PAHs in the upper Gulf and a widely observed pyrogenic signature along the coast of the lower Gulf (Boonyatumanond et al., 2006). The primary sources of PAHs in Thailand estuarine sediment have exhibited pyrogenic patterns, although petroleum contamination is obvious in the aquatic water (Wattayakorn and Chaipuriwong, 2006; Wattayakorn, 2012). However, the majority of previous studies of PAH deposition in the GOT have been restricted mainly to the nearshore region, and only limited sampling sites cover the open areas (e.g., >50 km from the coast). Therefore, toward the tropical continental shelf in SE Asia, the source apportionment, input pathways and mass inventory of PAHs remain poorly understood within the context of their source-to-sink processes and different regional energy structures as noted above.

In this study, the large-scale occurrence of PAHs in continental shelf sediments of the GOT was examined for the first time from a source-to-sink viewpoint to provide an understanding of the spatial distribution, source apportionment, input pathways, and comparative features of the mass inventory of the sedimentary PAHs in the context of the varying energy structure and depositional environments along the Asia continental margins.

2. Materials and methods

2.1. Study area and sampling

As a semi-enclosed tropical marine embayment located in the South China Sea, the GOT is relatively shallow with a mean depth of 45 m. It is usually divided into two parts, the upper Gulf and the lower Gulf (Fig. 1). The upper Gulf, covering approximately 10,000 km^2, is the northernmost part of the Gulf. It receives large amounts of sewage, runoff, and sediments, especially from the Chao Phraya River, which flows through several cities including the megacity of Bangkok (Wattayakorn et al., 1998; Boonyatumanond et al., 2006). Overall, the Gulf is poorly flushed, with little mixing, especially in its upper region (Wattayakorn et al., 1998), which results in the majority of fluvial sediments and associated contaminants being deposited in the upper Gulf (Srisuksawad et al., 1997).

In this study, 92 surface sediment samples were strategically collected on a regional scale during three cruises conducted by the R/V *Boon-Lerd Pa-Sook* and the R/V *SEAFDEC 2* (SEAFDEC, i.e., Southeast Asian Fisheries Development Center) during 2010–2012. The samples were collected using a stainless steel box corer deployed from the vessels. All sediment samples (0–3 cm) were wrapped in pre-combusted aluminum foil and stored at −20 °C until analysis.

2.2. Analytical procedures

The PAH analysis procedure and QA/QC were followed that described by Mai et al. (2003) and Hu et al. (2011). Briefly, about 20 g of the freeze-dried sample was spiked with a mixture of recovery standards containing five deuterated PAHs and then extracted with dichloromethane (DCM) in a Soxhlet apparatus for 48 h, with activated copper added to remove the sulfur. The extracts were concentrated and