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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Limin Hu [a,b,*], Xuefa Shi [a,b,*], Shuqing Qiao [a,b], Tian Lin [c], Yuanyuan Li [d], Yazhi Bai [a,b], Bin Wu [a,b], Shengfa Liu [a,b], Narumol Kornkanitnan [e], Somkiat Khokiattiwong [f]

[a] Key Laboratory of Marine Sedimentology and Environmental Geology, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China
[b] Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266061, China
[c] State Key Laboratory of Environmental Geochemistry, Guiyang Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China
[d] Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
[e] Marine and Coastal Resource Research Center, Samut Sakhon Province 74000, Thailand
[f] Phuket Marine Biological Center, Muaeng Phuket 83000, Thailand

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
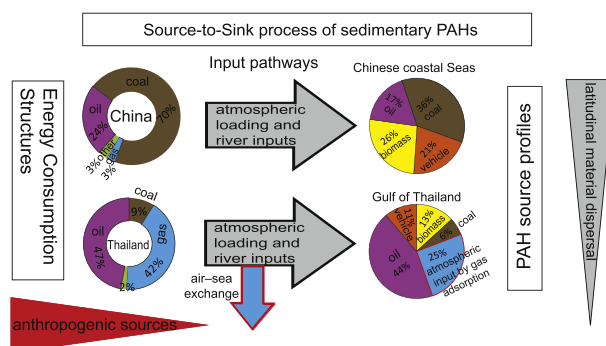
ABSTRACT

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

* Corresponding authors at: Key Laboratory of Marine Sedimentology and Environmental Geology, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China.
E-mail addresses: hulimin@fio.org.cn (L. Hu), xfshi@fio.org.cn (X. Shi).

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 near-shore 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 km², 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
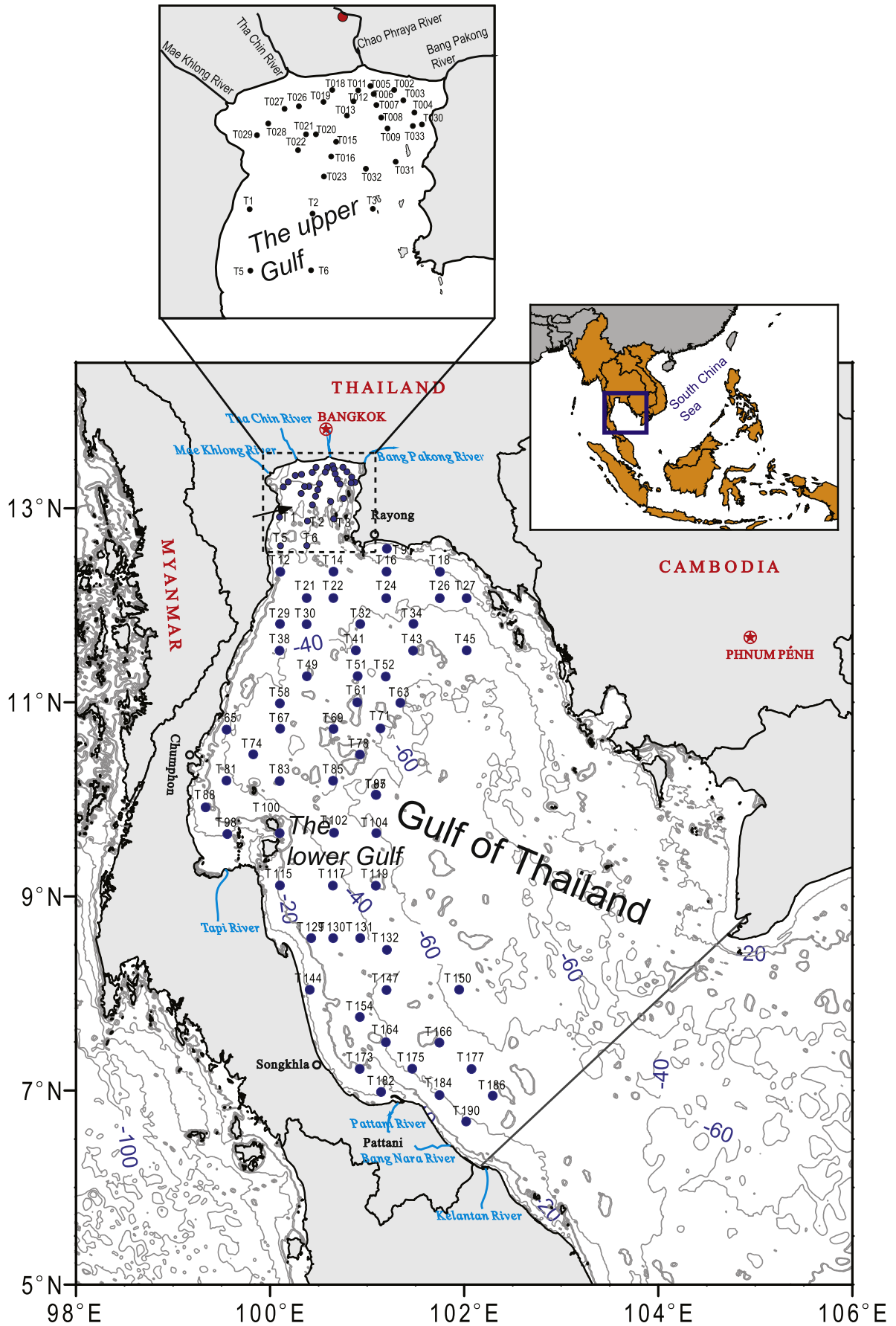
Fig. 1. Study area and sampling stations ($n = 92$) in the GOT in SE Asia, the stations located at the upper Gulf ($n = 33$) with the corresponding labels were marked in the dashed rectangle.

fractionated using a silica-alumina (1:1) column. PAHs were eluted using 35 ml of hexane/dichloromethane (1:1). Hexamethylbenzene was added as internal standard and the mixture was reduced to 0.2 ml and injected into GC-MSD (Agilent Series 5975 Mass Spectrometer interfaced to 6890 Series Gas Chromatograph). The GC was equipped with a DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific), with helium as the carrier gas (1.0 ml min^{-1}). Samples were injected in the splitless mode with an injector temperature of 280 °C. Oven temperature was programmed from 60 °C to 180 °C (1 min hold), at 8 °C min^{-1}, and from 180 °C to 300 °C (2 min hold), at 3 °C min^{-1} rate. The mass spectrometer was operated in the electron impact (EI) mode (70 eV), with the scanning range between m/z 50 and 500. Sixteen U.S. EPA proposed priority PAHs (16 PAHs) and perylene were measured in this study including naphthalene (Nap), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (InP), dibenz(a,h)anthracene (DBA), benzo(ghi)perylene (BghiP) and Perylene.

For QA/QC, procedural blanks, standard-spiked blanks, standard-spiked matrix, duplicate samples and NIST 1941 standard reference samples were analyzed simultaneously. Nominal detection limits for individual PAH ranged from 0.2 to 2 ng/g (dry weight) for 10 g of the sediments (Mai et al., 2003). Procedural blanks contained no detectable amounts of the target PAHs compounds, and the PAH recoveries of the standard-spiked matrix ranged from 75 to 93%, and the paired duplicate samples agreed to within 15% of the measured values (– 10). Recoveries of the PAHs in the NIST 1941 were between 80% and 120% of the certified values. The average surrogate recoveries were 69 ± 11% for Nap-d$_8$, 68 ± 6% for Ace-d$_{10}$, 90 ± 14% for Phe-d$_{10}$, 102 ± 14% for Chr-d$_{12}$ and 91 ± 15% for perylene-d$_{12}$, respectively. Reported concentrations here were not recoveries corrected.

The analytical methods of total organic carbon (TOC) and grain size were according to Hu et al. (2009). Replicate analysis of one sample ($n = 6$) provided a precision of ± 0.02 wt.% for TOC. For the grain size, the relative error of the duplicate samples was <3% ($n = 6$).

2.3. Principal component analysis (PCA)

PCA, a multivariate analytical tool, was used to determine the distribution of the samples and to study the relationships of the measured parameters. Before analysis, the non-detectable values were replaced with concentration values equal to one-half of the method detection limits. Then, the raw data matrix was Z-scoring standardized and mid-range normalized to eliminate the influence of the different units and to ensure that each determined variable had equal weighting in the PCA. PCA was performed using the program *SPSS 16.0* for Windows (SPSS Inc., Chicago, IL, USA).

2.4. Positive matrix factorization (PMF) modeling

PMF modeling has been successfully applied to spatially distributed data set to apportion the sources of PAHs (Wang et al., 2009; Stout and Graan, 2010; Lin et al., 2011; Yu et al., 2015). Detailed concept and application of PMF for source apportionment were described in EPA PMF 5.0 Fundamentals and User Guide (http://www.epa.gov/heasd/research/pmf.html). In principle, the PMF model is based on the following equation:

$$Xij = \sum_{k=1}^{p} AikFkj + Rij$$

where Xij is the concentration of the jth congener in the ith sample of the original dataset; Aik is the contribution of the kth factor to the ith

sample; Fkj is the fraction of the kth factor arising from congener j; and Rij is the residual between the measured Xij and the predicted Xij using p principal components.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{Xij - \sum_{k=1}^{p} AikFkj}{Sij} \right)^2$$

where Sij is the uncertainty of the jth congener in the ith sample of the original dataset containing m congeners and n samples. Q is the weighted sum of squares of differences between the PMF output and the original data set. One of the tasks of PMF analysis is to minimize the Q value. Before PMF analysis, the concentration file and its corresponding uncertainty file were inserted into the model. In this study, an uncertainty of 20% for PAHs were adopted based on the results from analyzing the replicate samples and the standard reference material, respectively (Mai et al., 2003).

3. Results and discussion

3.1. Distribution and composition of PAHs

3.1.1. Spatial variability of PAH concentrations in the GOT

The total concentrations of 16 PAHs in the GOT sediments ranged from 2.6 to 78.1 ng/g (dry weight), with a mean of 19.4 ± 15.1 ng/g (Table S1). The concentrations of the 16 PAHs in the upper and lower Gulf sediment samples varied from 4.0 to 77.4 ng/g (mean of 23.1 ± 17.5 ng/g) and 2.6 to 78.1 ng/g (mean of 17.5 ± 13.4 ng/g), respectively. The PAH concentrations in this work were much lower than those in river sediments adjacent to the upper GOT (263 ± 174 ng/g) and slightly lower than those in the coastal region (50 ± 56 ng/g) (Boonyatumanond et al., 2006), but they were comparable with those from the central Pacific (1–61 ng/g) (Ohkouchi et al., 1999). It has been reported that PAH concentrations range broadly in the sediments of tropical Asia (4 to 38,100 ng/g for $\sum$ 14 PAHs) (Saha et al., 2009). The relatively low PAH concentrations observed in this work can be ascribed to the long distance from the coast to the majority of sampling sites in the open area (Fig. 1).

Spatially, relatively high concentration levels of the 16 PAHs (>30 ng/g) were found mainly in the estuarine area in the upper Gulf, in the eastern offshore area (near Chonburi Province), and in the western part of the lower Gulf (near Samui Island). This result is consistent with the distribution of fine-grained sediments (Figs. 2a and 3a), which are regulated by fluvial input, ebb-tidal currents, and counter-clockwise water circulation (Sojisuporn and Putikiatikajorn, 1998). Pronounced low PAH concentrations (<15 ng/g) were found mainly to the south of the Chao Phraya Delta, where grain size is coarser, and/or in the central basin of the open lower Gulf, which is far from the coast (Figs. 2a and 3b). The 16 PAHs could generally be grouped into 2–3 ring and 4–6 ring types according to their source characteristics. The 2–3 ring PAHs showed a more heterogeneous spatial pattern (Fig. 3b and c), with spotty high values in the eastern offshore region (e.g., sites T14, T22, T26, T34, and T52), where there has been a higher magnitude risk for impacts by oil spills (Singkran, 2013). In contrast, the 4–6 ring PAHs exhibited a more homogenous distribution in the GOT (Fig. 3c).

Perylene, a natural diagenetic product, showed an apparent decreasing pattern with increasing distance toward the coast (Fig. 3d). Although the perylene abundance (n.d.–32 ng/g) in the present study was much lower than those from other estuarine–coastal areas with significant river input (e.g., coastal East China Sea, 7–141 ng/g) (Hu et al., 2014), it was comparable to previously reported results in the upper Gulf, which showed a high abundance of perylene constrained within 30 km off the river mouth (Boonyatumanond et al., 2006). The elevated perylene abundance in the nearshore region of the upper GOT was also comparable with the observed high sediment mass accumulation rates therein (>250 mg/cm^2/yr) (Fig. 2b) (Srisuksawad et al., 1997),
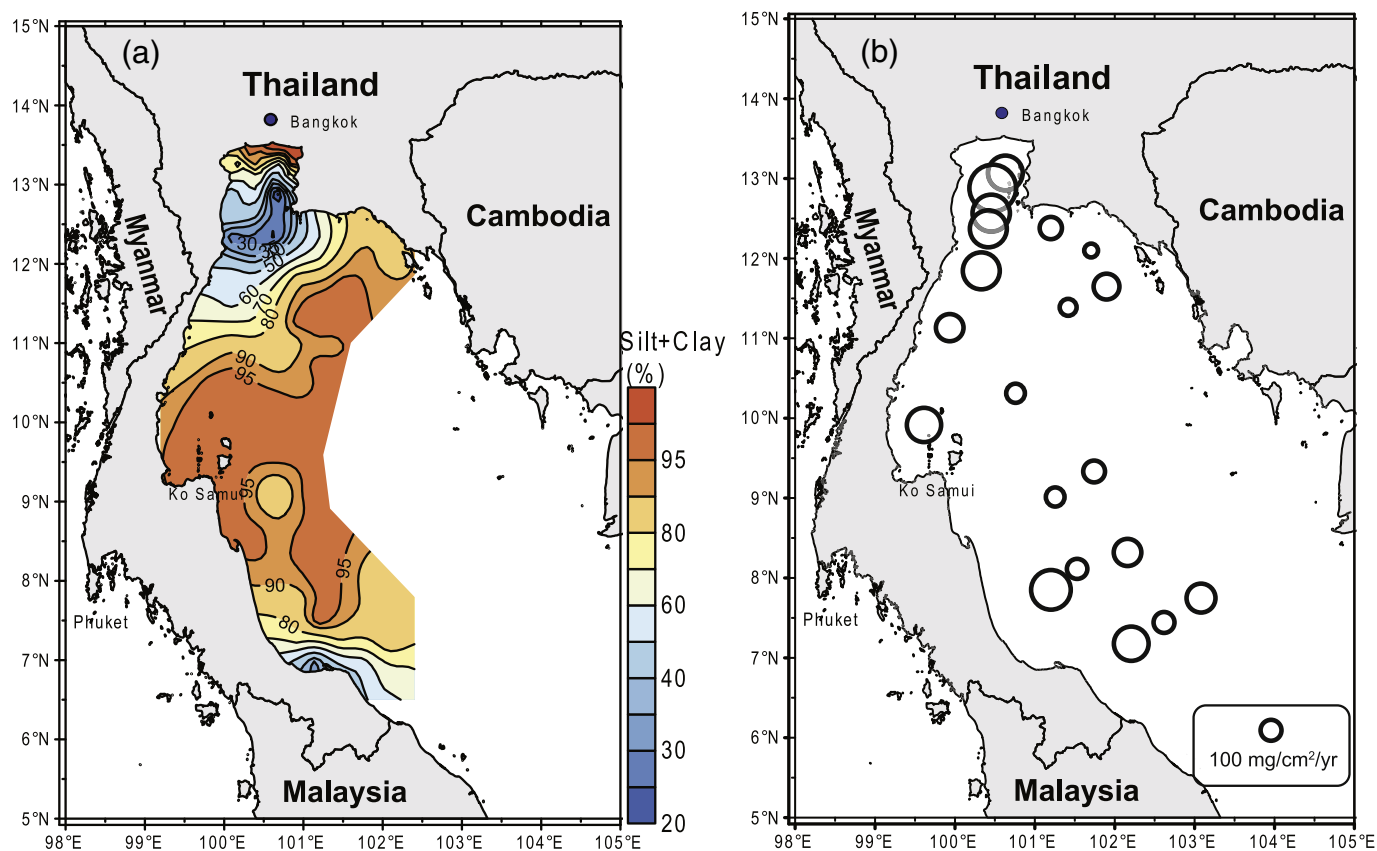
Fig. 2. Spatial distribution of the fine-grained sediments (silt and clay) (a) and mass accumulation rate (MAR) (b) in the study area.

suggesting the limited offshore dispersal of land-based sediments and its associated materials.

3.1.2. Correlation between PAHs, TOC, and grain size

A significant correlation existed between the 16 PAHs and TOC in the samples from the upper Gulf, especially between the high molecular weight (HMW) PAHs and TOC, but the lower Gulf showed poor relationship (Fig. 4). It has been suggested that river input and a subsequent off-shore transport mechanism explain the main dispersal pattern of sedimentary PAHs in the upper Gulf, especially for the inshore area within 30 km from the coast (Boonyatumanond et al., 2006), where the sedimentary TOC is a mixture of terrigenous soil-derived organic matter (OM) and marine OM (Boonphakdee et al., 2008). Furthermore, extremely high PAH concentrations (Fig. 4) were found at the outlet of the river mouth (sites T018 and T030), indicating a direct source-dependent control (i.e., river input) on PAH presence in the upper Gulf. Therefore, the significant correlation between PAHs and TOC in the upper Gulf should be ascribed to their similar absorption and/or the coupled input pathways. On the other hand, the inconsistence between TOC and PAHs in the lower Gulf (Fig. 4) could be related mainly to their heterogeneous origins, that is, a dominant supply of algal-derived OM as the predominant contributor of TOC (Kennedy et al., 2004) and sedimentary PAHs predominated by low molecular weight (LMW) PAH homologues, which could be potentially ascribed to the presence of petrogenic contamination and atmospheric loading for gas–sea exchange (see below). Additionally, the correlation between PAHs and TOC in the lower Gulf could also be weakened by the small variation in grain size, especially for those samples >50 km from the coast (Md 6–7φ; Fig. 4h).

3.1.3. Composition of PAHs from PCA

To identify the compositions and sources of sedimentary PAHs in the GOT, principal component analysis (PCA) was performed, and the first two principal components (PC1 and PC2) were responsible for 55% and 30% of the total variance, respectively. PC1 showed high correlations with LMW PAH homologues, being especially heavily weighted by Phe and Fluo, Pyr, Ace and Ant (Fig. 5a), suggesting low-temperature pyrogenic and generic petroleum (i.e., unburned fossil fuel) sources (Kavouras et al., 2001; Mai et al., 2003). PC2 was highly loaded in HMW PAHs (BaA, Chr, BbF, BkF, BaP, InP, DBA and BghiP) (Fig. 5a), which could be attributed to a mixture of combustion-derived sources.

According to Fig. 5b, the samples near the river mouth in the upper Gulf and the offshore region in the lower Gulf (e.g., sites T14, T22, T26, T34, and T52) were distinguished by high positive scores on PC1, indicating a significant petrogenic contribution. Actually, a petrogenic signature of PAHs has been identified previously in the majority of the urban sediments within tropical Asian countries (Saha et al., 2009), and petroleum contamination in the coastal GOT has also been previously reported extensively (Wattayakorn et al., 1998; Wattayakorn, 2012 and references therein). Although a pyrogenic origin of the sedimentary PAHs in the upper GOT has also been identified (Boonyatumanond et al., 2006; Wattayakorn, 2012), the presence of petrogenic PAHs in the remote area, especially near "hot spots" (e.g., discharge points or local oil spills), cannot be negligible. For example, the eastern seaboard of the GOT has been highly exposed to anthropogenic inputs of oil due to frequent oil spills from tanker/ship accidents and spillage during the last two decades (Wattayakorn, 2012; S Khokiattiwong, personal communication), and it has also been classified as a very high magnitude risk zone for oil spill impacts due to the frequent oil-related incidents and activities (Singkran, 2013). On the other hand, the group of samples with high PC2 scores was restricted mainly to the river mouth area in the upper Gulf (Fig. 5b), indicating a fluvial input of the pyrogenic PAHs in the upper GOT. Street dust via fluvial input and surface runoff
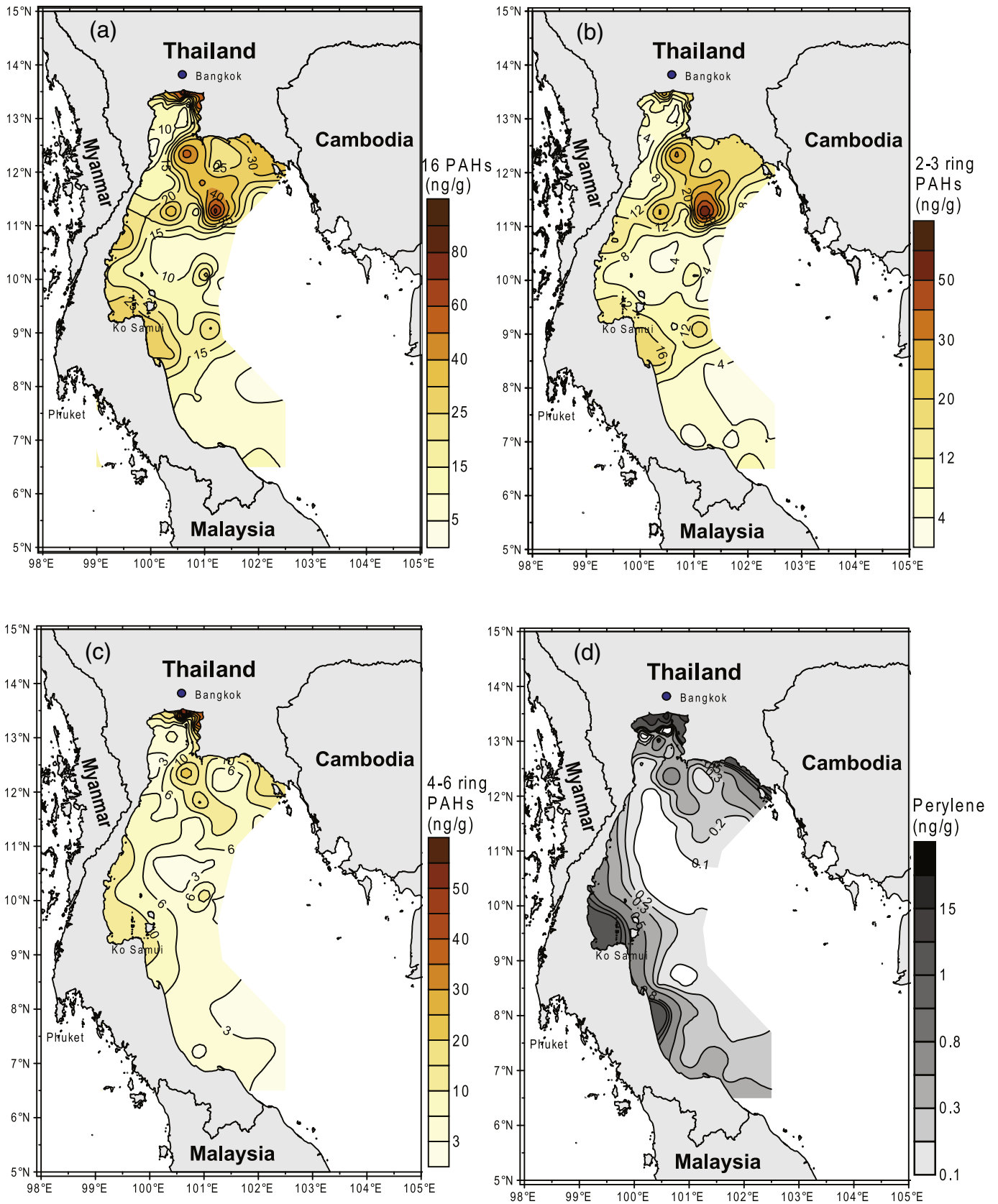
Fig. 3. Spatial distribution of 16 PAHs (a), occurrence of 2 + 3 ring PAHs (b), 4–6 ring PAHs (c) and perylene (d) in the study area.

have been reported to be constrained in the nearshore region of the upper GOT, with limited offshore dispersion (Boonyatumanond et al., 2006, 2007b), whereas the fossil-fuel combustion-derived

contribution (e.g., soot) observed in the samples from the lower GOT is likely more related to the ubiquitous atmospheric loadings (Hu et al., 2016).
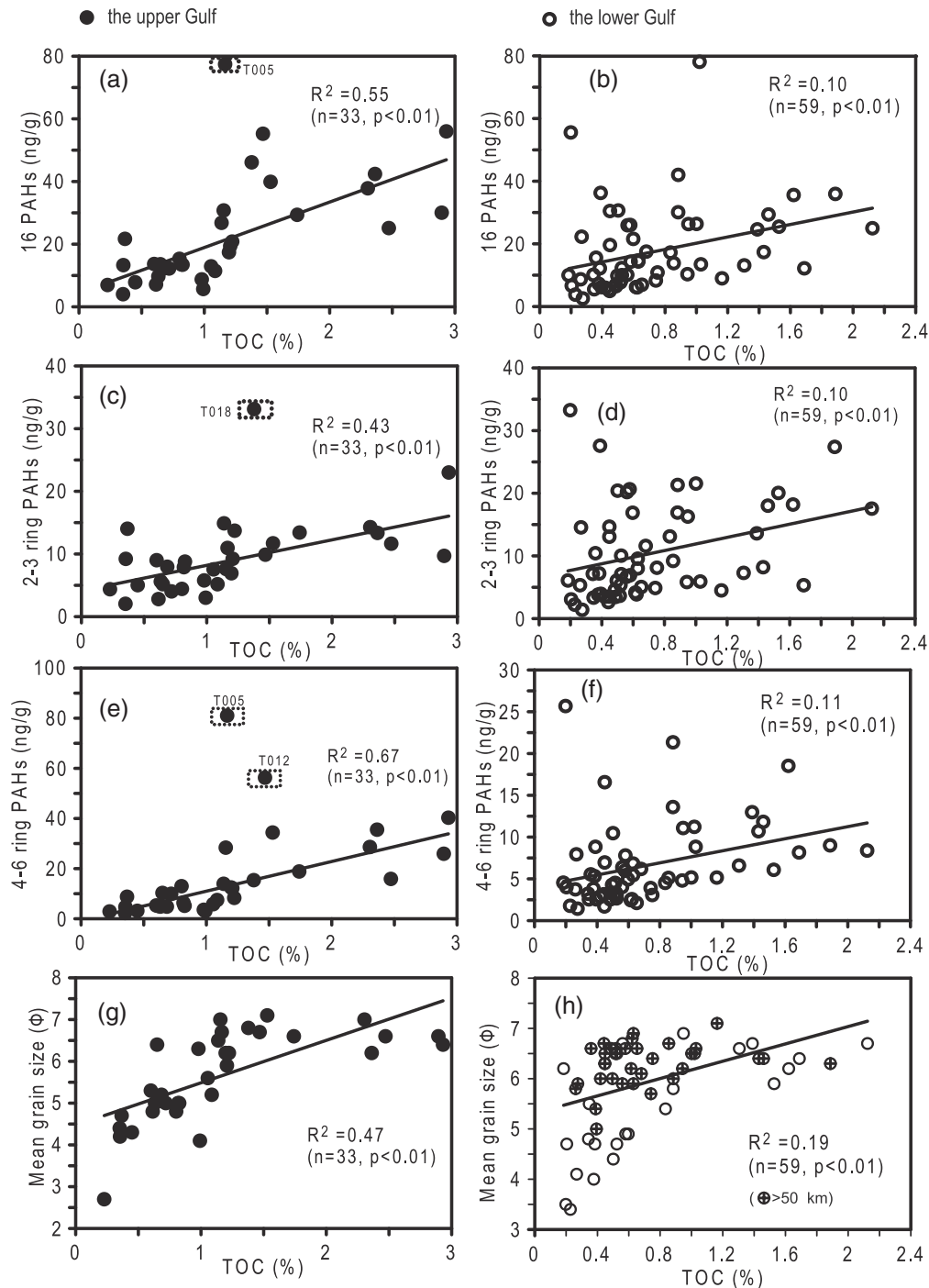
Fig. 4. Correlations of TOC with 16 PAHs (a, b), 2 + 3 ring PAHs (c, d), 4–6 ring PAHs (e, f) and mean sediment grain size (g, h) in the upper and lower GOT, respectively.

3.2. Source identification of PAHs using PMF modeling

PMF modeling, which provides an opportunity to quantitatively determine the extensive contribution of PAHs in each of the individual samples, has been used recently in several sedimentary environments (Sofowote et al., 2008; Wang et al., 2009; Stout and Graan, 2010; Lin et al., 2011, 2013; Yu et al., 2015). In this study, PMF modeling was conducted using an input dataset of 13 PAHs from 92 sediment samples using the EPA PMF 5.0 model. Because Nap, Ac, and Ace were lower than their detection limits in the majority of the sediment samples, they were excluded from the initial PMF analysis. After testing for

three to seven factors, a five-factor solution was adopted by comparing with PAH source profiles reported in SE Asia (Zakaria et al., 2002; Saha et al., 2009) and/or those commonly referenced in sediments worldwide (Li et al., 2003; Bzdusek et al., 2004; Christensen and Bzdusek, 2005; Christensen and Arora, 2007) (Fig. 6). The correlation between the estimated and measured concentrations was almost unity ($R^2 = 0.97$, $p < 0.01$; Fig. S1), suggesting that the measured concentrations were well explained by the five selected factors.

Factor 1 is dominated by Phe, Fluo, and Pyr (Fig. 6a), and this profile is believed to be related to leakage of crude oil or release of refined petroleum, which have been widely identified in the sediments of SE Asia
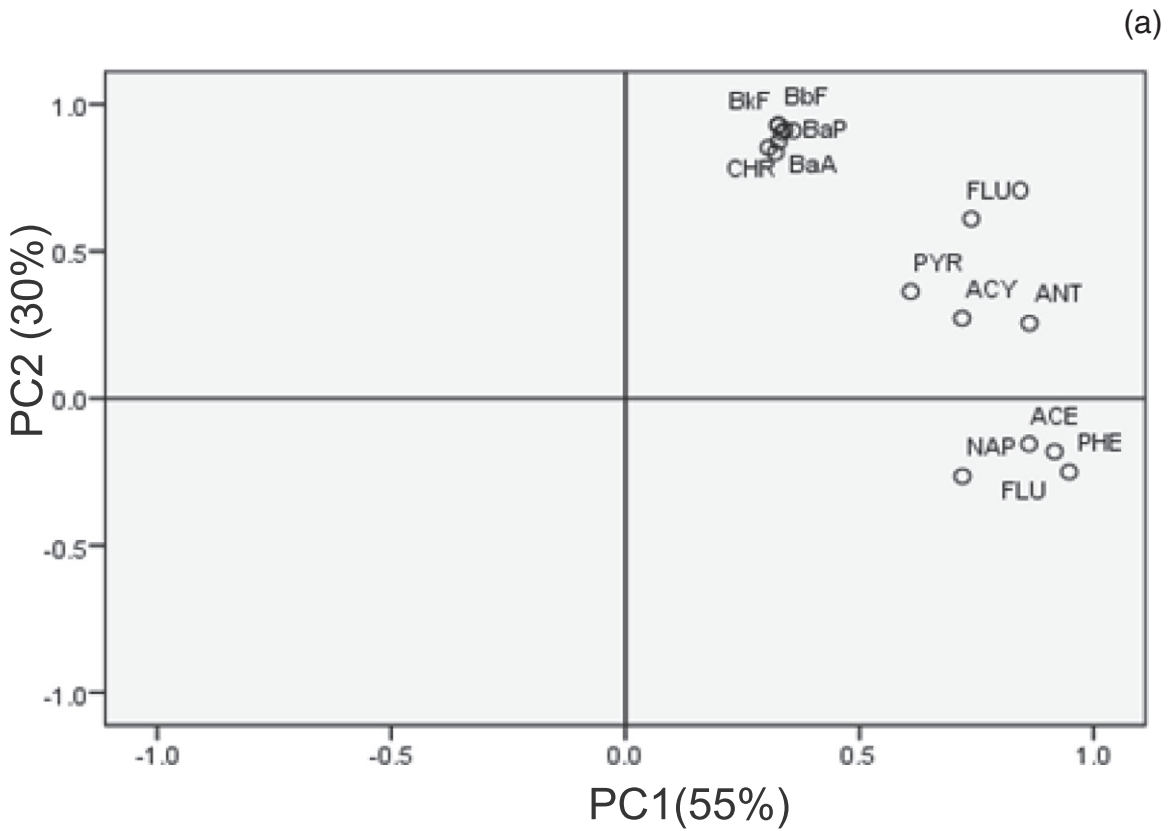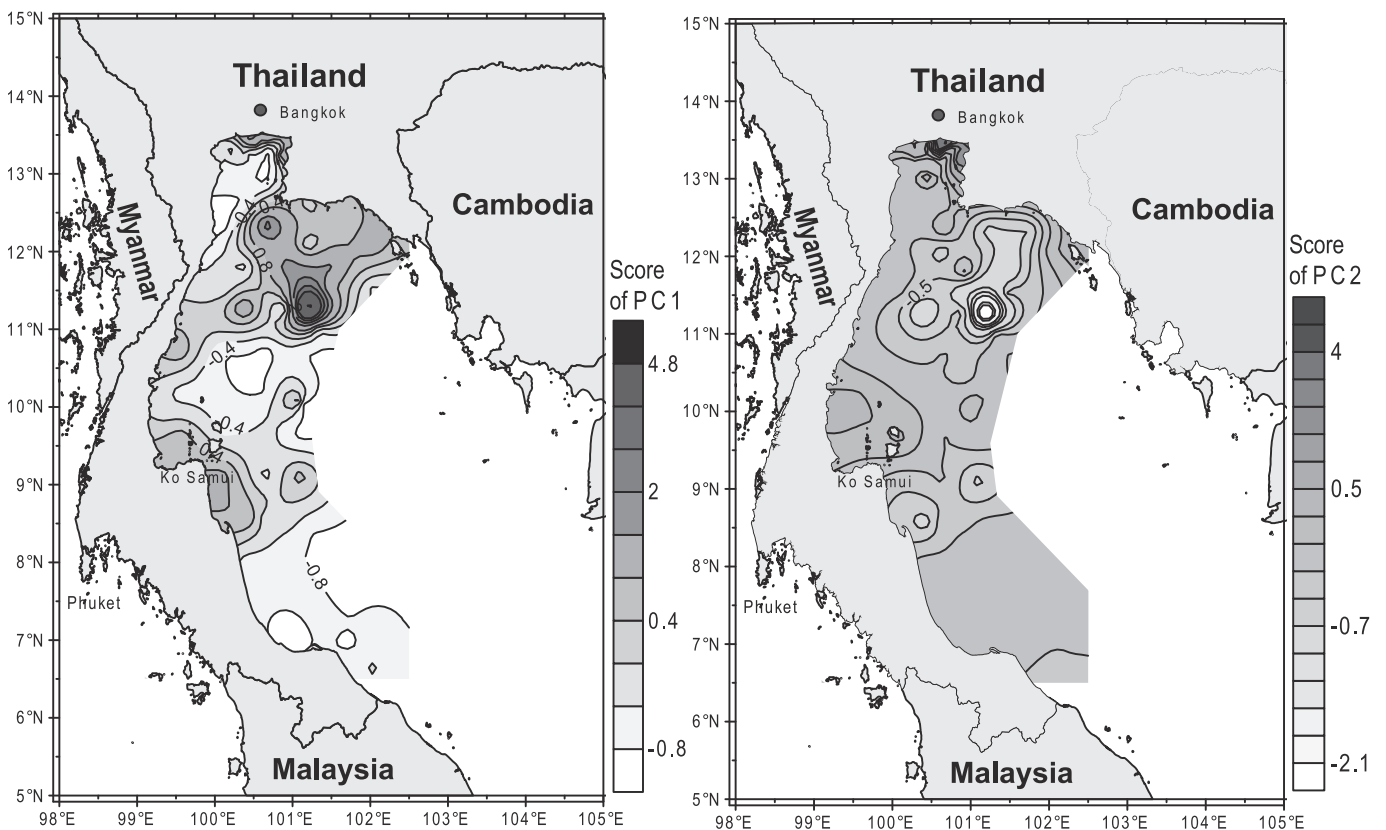
Fig. 5. Loading plot (a) of PCA model of the 16 PAHs and the corresponding sample scores (b) of the first two principal components (PC1, PC2).

(Zakaria et al., 2002; Saha et al., 2009). Factor 2 is composed predominately of Fluo and Pyr, with moderate loadings of BbF, BkF, BaP, Chr, and BghiP (Fig. 6b). It is suggested that Flu, BbF, and BkF are three of the most abundant species in biomass burning, along with moderate emissions of BaA, IP, BghiP, and some others (Rajput et al., 2011), and this source profile in sediments may be derived mainly from biomass burning (Freeman and Cattell, 1990). Recent studies have indicated that the local biomass burning and forest fires are significant in SE Asia (Bond et al., 2004) and serve as predominant sources for the carbonaceous materials in regional aerosol samples, especially during the hot season (Sahu et al., 2011). Factor 3 is identified as vehicular emissions based on the high loadings of Inp and BghiP and moderate contributions of Phe and Fluo (Fig. 6c). A similar profile of high loadings of Inp and BghiP has been observed in the potential source materials, such as automobile gasoline soot in tropical Asia (Saha et al., 2009), and this profile is also consistent with those observed in worldwide urban environments (Lim et al., 1999; Zakaria et al., 2002; Boonyatumanond et al., 2006; Saha et al., 2009; Wang et al., 2009) and coastal systems of the East China Seas (Lin et al., 2011). Moderate molecular weight PAH compounds, such as Fluo and Pyr, were highly weighted in Factor 4, with moderate contributions of BaA, Chr, Inp, and BghiP (Fig. 6d). Fluo and Pyr have been identified as markers of coal combustion (Khalili et al., 1995; Harrison et al., 1996; Yang et al., 2002), whereas high fractions of Inp and BghiP have been observed in source profiles of coal (cook

soot) in tropical Asia (Saha et al., 2009). Therefore, Factor 4 can be identified as the contribution from coal combustion. Factor 5, composed primarily of Flu, Phe, Fluo, and Pyr (Fig. 6e), is different from the usual source profiles; however, this specific profile is similar to the gas phase PAHs that have been reported widely in the atmosphere (Fig. 6e), consisting of a dominant proportion of volatile and/or LMW PAH species (e.g., Flu and Phe) (Marty et al., 1967; Nelson et al., 1998; Gigliotti et al., 2002; Tsapakis et al., 2003; Lee et al., 2004). It has been reported that air–sea exchange can be an important non-point source of PAHs to marine sediments in remote areas (Tsapakis et al., 2003), and gas absorption of PAHs through the air–sea exchange process may be the major contributor of PAHs to the pristine open marine system (Nelson et al., 1998; Arzayus et al., 2001; Gigliotti et al., 2002). Therefore, Factor 5, explaining 25% of the total variance, is identified as a potential net source of LMW PAHs into the GOT through the air–sea exchange process, and gas absorption may be a significant external contributor of these volatile PAHs into the GOT. Furthermore, it has also been reported that a significant presence of Phe, Fluo, and Pyr are associated with natural gas combustion, with a major gas-phase nature of PAHs (Rogge et al., 1993; Simcik et al., 1999; Lee et al., 2004). Therefore, the specific "source" of PAHs described by this process in the present study may be the usage of natural gas, which is the second largest contributor (~42%) in the total energy consumption in Thailand (see below).
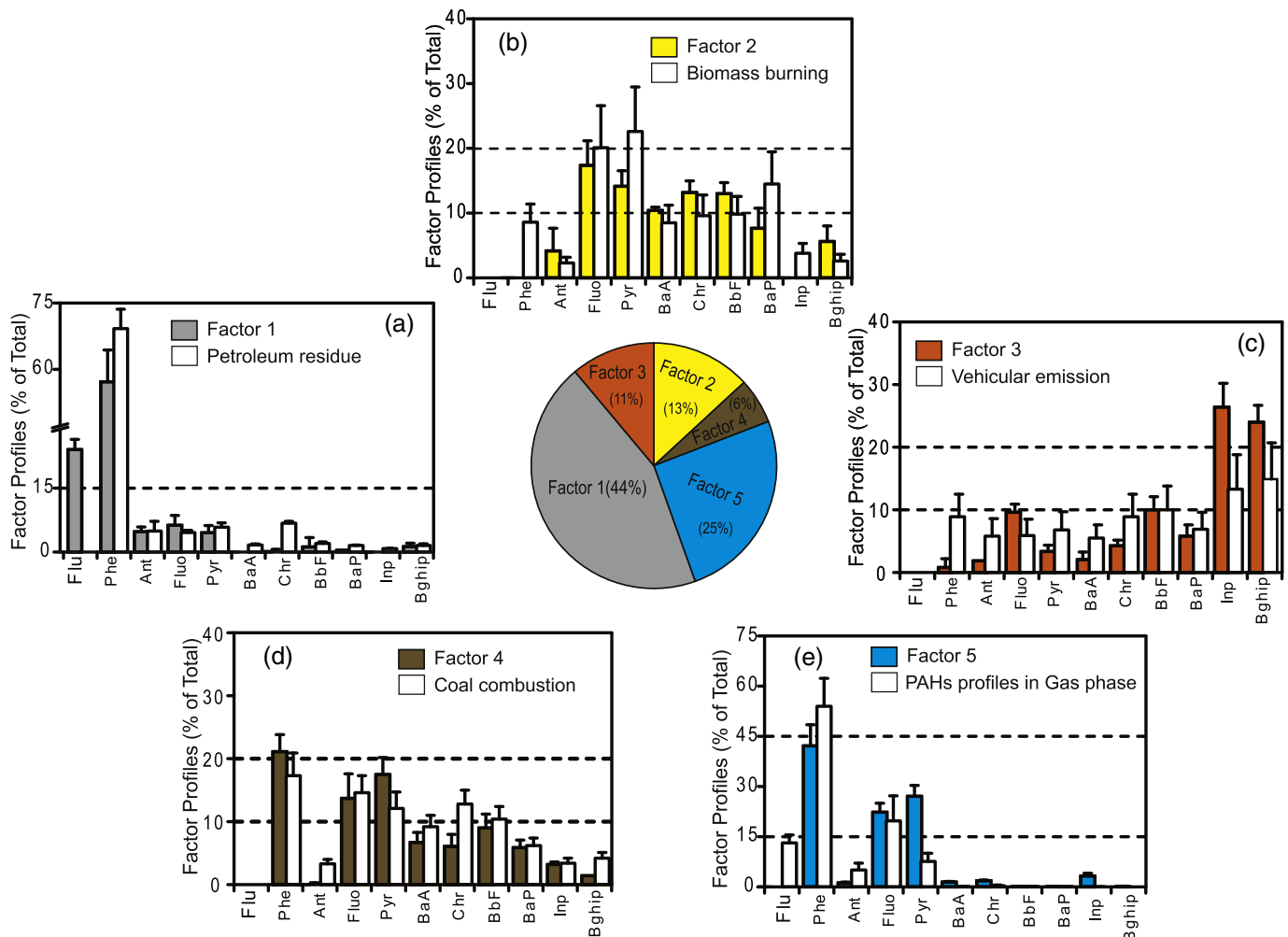

Fig. 6. The five-factor profiles resolved from the PMF model and the percentage of each factor contributing to the sediment PAHs in the GOT. The referenced source profiles are cited from acknowledged references (Zakaria et al., 2002; Saha et al., 2009; Li et al., 2003; Bzdusek et al., 2004; Christensen and Arora, 2007).

3.3. Source apportionment and implications for input pathways of PAHs

The average relative contribution of PAHs from petroleum residue in the study area was estimated to be ~44% (Fig. 7a), indicating a significant petrogenic contribution. This is consistent with the observed oil-contaminated signature in the urban sedimentary environment in tropical Asia (Boonyatumanond et al., 2006; Saha et al., 2009). As noted above, the land-based contribution through fluvial inputs and surface runoff due to the inherent frequent heavy rainfall in the low-latitude area could support the quick transfer and rapid deposition of petrogenic PAHs into the coastal region. Despite this circumstance, some of the samples from the open lower GOT were also characterized by a relatively higher contribution from petroleum residues, and the area harboring these samples were geographically adjacent to areas at high risk for oil spills (Fig. S2) (Singkran, 2013). In actuality, oil spills in the offshore GOT have been observed in navigation areas along the main shipping routes and in these coastal areas at high risk for oil spills (Lu, 2003; Ivanov and Zatyagalova, 2008; Singkran, 2013), indicating an obvious petroleum-derived PAH contribution in the open area.
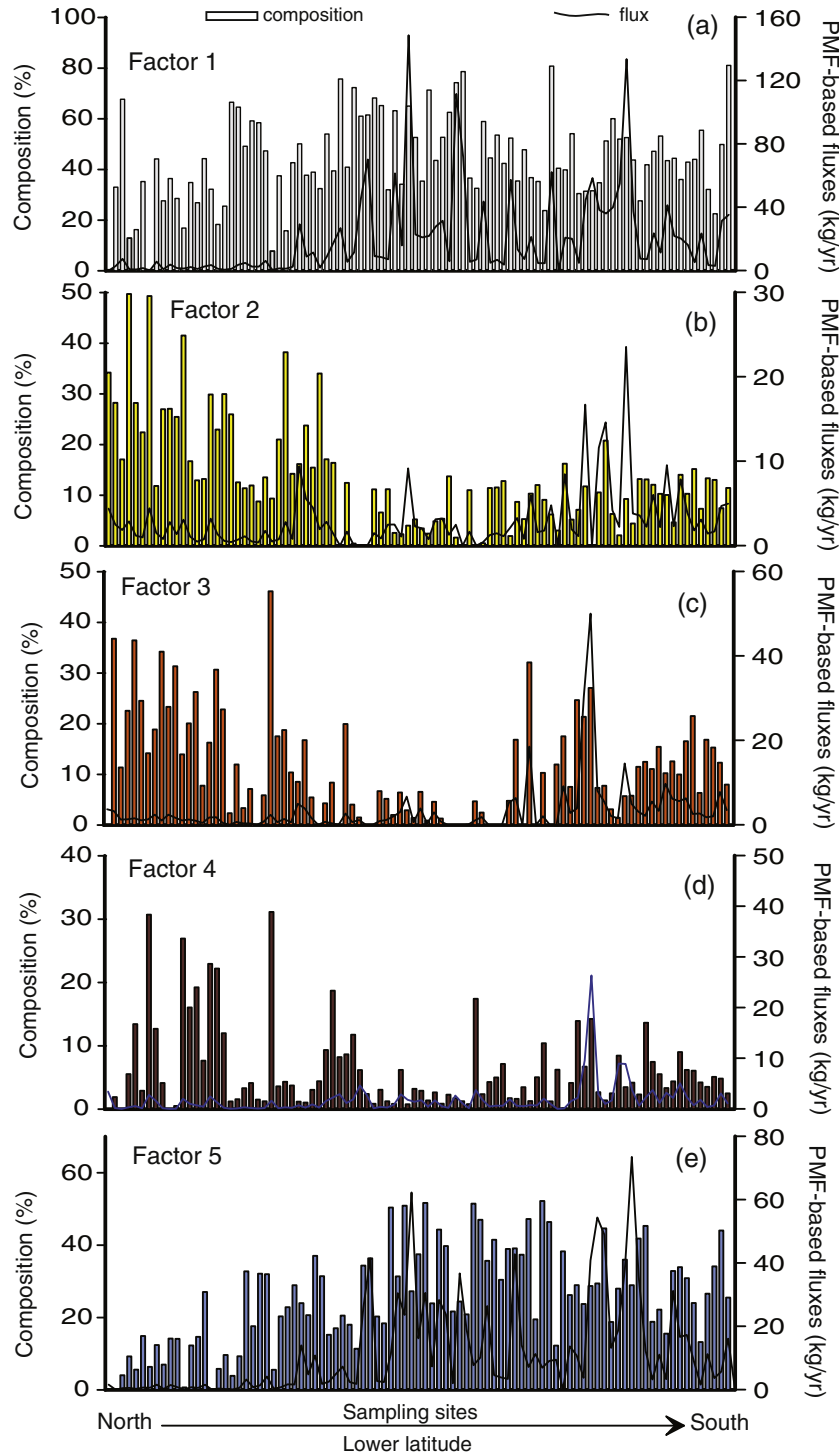

Fig. 7. Source patterns and contributions of five PMF resolved factors to the sedimentary flux of 16 PAHs of each sediment samples in the GOT.

The contribution of biomass burning and vehicle emissions showed similar spatial variability (Fig. 7b and c), which is consistent with the reported decreasing trend of the depositional flux of PAHs into the estuary of the Chao Phraya River (Boonyatumanond et al., 2006, 2007b). It has been suggested that pyrogenic PAHs and char derived from the biomass burning in SE Asia are more easily incorporated into local soils and then discharged into the aquatic environment through rivers and surface runoff (Knicker et al., 2008; Hu et al., 2016). The vehicular emission-derived PAHs are generally composed of less volatile PAHs with six rings, resulting in rapid deposition near their sources (Wania and Mackay, 1996). Street dust, which usually consists primarily of larger or heavier particles, along with the vehicle-emitted PAHs can be deposited readily in the nearshore region of the upper GOT (Boonyatumanond et al., 2006). However, for the open lower Gulf, the atmospheric input pathway of PAHs is likely not negligible because of the observed relatively low but constant contribution of the two pyrogenic sources in the open area (each ~8%) (Fig. 7b and c). This result is also supported by the input of soot black carbon into the lower GOT through atmospheric loading (Hu et al., 2016).

It was obviously noticeable that factor 5 had a relatively significant contribution in the open area (Fig. 7e). Tsapakis et al. (2003) found that gas-phase PAHs, as a predominant component in the atmosphere, were significant contributors to LMW PAHs in sediments through air–sea exchange. It was reported that an increase in atmospheric gas-phase PAHs can induce to an increased absorption flux into the adjacent water (e.g., Nelson et al., 1998; Simcik et al., 1999; Gigliotti et al., 2002). More recently, the high atmosphere-ocean exchange of these semivolatile aromatic hydrocarbons through diffusive process has been represented as a significant source of pollutants into the tropical and subtropical ocean (González-Gaya et al., 2016).Therefore, in this study, the spatial variability of Factor 5 suggests a significant atmospheric loading and diffusive input of volatile LMW PAHs to the open GOT. Moreover, a more significant relationship between the 2–3 ring and 4–6 ring PAHs was also found in the samples collected 50 km off the coast (Fig. 8). This evidence further implies that the atmospheric loading may be an important PAH input pathway to the open GOT, both for the volatile and particulate-phase PAHs.

3.4. Comparison of PAH mass inventories and implications of energy structure along Asia margins

Differentiating the individual contributions and mass inventory of regional PAHs accumulated on the continental margins is of great interest to examine the development strategies and socioeconomic impacts of the Asia marginal regions in the context of different energy consumption structures. The depositional flux of PAHs in the GOT was estimated to be 4.2 ng/cm^2/yr, and a total area-integrated mass budget of 4.1 t/yr (~150,000 km^2) was obtained for the most well investigated region (Fig. 9). This result was much lower than those reported in our previous works around the coastal Chinese seas and other marginal seas in the context of anthropogenic impact (Table 1). The significant gap in PAH

mass budgets between SE Asia and China may be generally consistent with the different amounts of fossil fuel consumption in these regions. For example, in 2003, the total consumption of fossil fuels (coal, gas, and oil) in China was ~2430 million tons of oil equivalent (Mtoe), compared with only ~110 Mtoe in Thailand (data obtained from http://www.tsp-data-portal.org/Energy-Consumption-Statistics). Moreover, the sedimentary PAHs of pyrogenic origin (coal and biomass combustion and vehicular emissions) and the petrogenic contribution were 73% and 27% in the Bohai Sea, 82% and 18% in the Yellow Sea, and 61% and 39% in the coastal northern South China Sea, respectively (Fig. 9, data from Luo et al. (2008), Lin et al. (2011)), whereas in the GOT, the combined contribution from petrogenic and natural gas emission PAHs was ~70%, compared with only ~30% for pyrogenic origin PAHs (Fig. 9). The main energy source in China is still coal (~70% of total energy consumption in 2013), especially in North China for space heating in winter (Xu et al., 2006; Liu et al., 2007; Guo et al., 2009), and the contribution of coal and biomass burning is evidenced as the dominant source of the pyrogenic PAHs in sediments (Mai et al., 2003; Chen et al., 2006; Hu et al., 2011; Lin et al., 2011; Liu et al., 2012). In contrast, for SE Asia, the source profiles of energy consumption are much different, with crude oil (including petroleum products) serving as the main fossil fuel of the total energy consumption (e.g., Philippines, 41%; Malaysia, 49%; Indonesia, 35%; Thailand, 54%, data from World Resources Institute) (Saha et al., 2009). In Thailand, crude oil and natural gas, the main energy sources, accounted for ~89% of total energy consumption.

For the tropical margin of Asia, in addition to the petrogenic signature of deposited PAHs in SE Asia (e.g., Malaysia and Thailand) as mentioned above, there was also a significant presence of pyrogenic PAHs in the various matrices in India of South Asia (e.g., atmosphere, sediments) (Saha et al., 2009; Liu et al., 2014). This result could be related to the different energy source profiles between SE Asia and South Asia. For example, the main energy structure of India in South Asia was coal, coal products, and wood (74% of total energy consumption) (Saha et al., 2009), and the pyrogenic signature of atmospheric PAHs over the North India Ocean, which has been observed, is believed to be derived from continental outflow from South Asia contributed by the combustion of biomass and fossil fuels in India (Lelieveld et al., 2001; Wisthaler et al., 2002; Crimmins et al., 2004; Xu et al., 2012; Liu et al., 2014). It has also been reported that the land-based PAH emissions in these tropical and temperate regions differs regionally in Asia due to differences in energy structure, degree of social development (industrialization and urbanization), and regional climatic conditions (Panther et al., 1999). Above all, these results of the present study are not only consistent with the results of previous works on PAH emission inventories and atmospheric PAH occurrences over the marginal seas of Asia (e.g., Xu et al., 2006; Zhang and Tao, 2009), but they also highlight the potential impacts of regionally varied energy structure and the relationships between the land-emitted PAH contributions and their deposited mass budgets along the Asia continental margins.
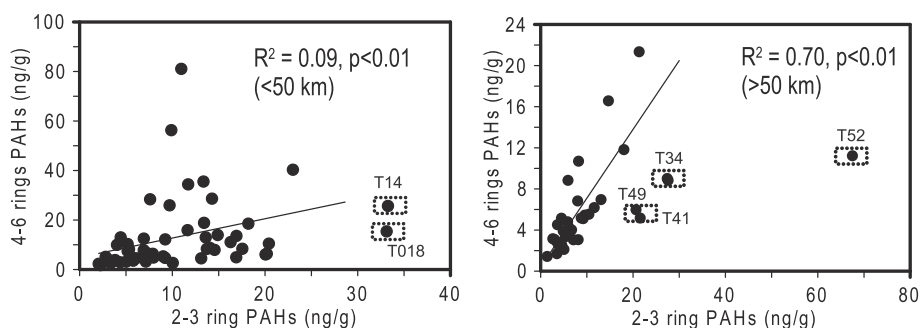

Fig. 8. Scatter plots of the correlation between 2 + 3 ring PAHs and 4–6 ring PAHs in the sediment samples with offshore distance within 50 km (a) and beyond 50 km (b), respectively.
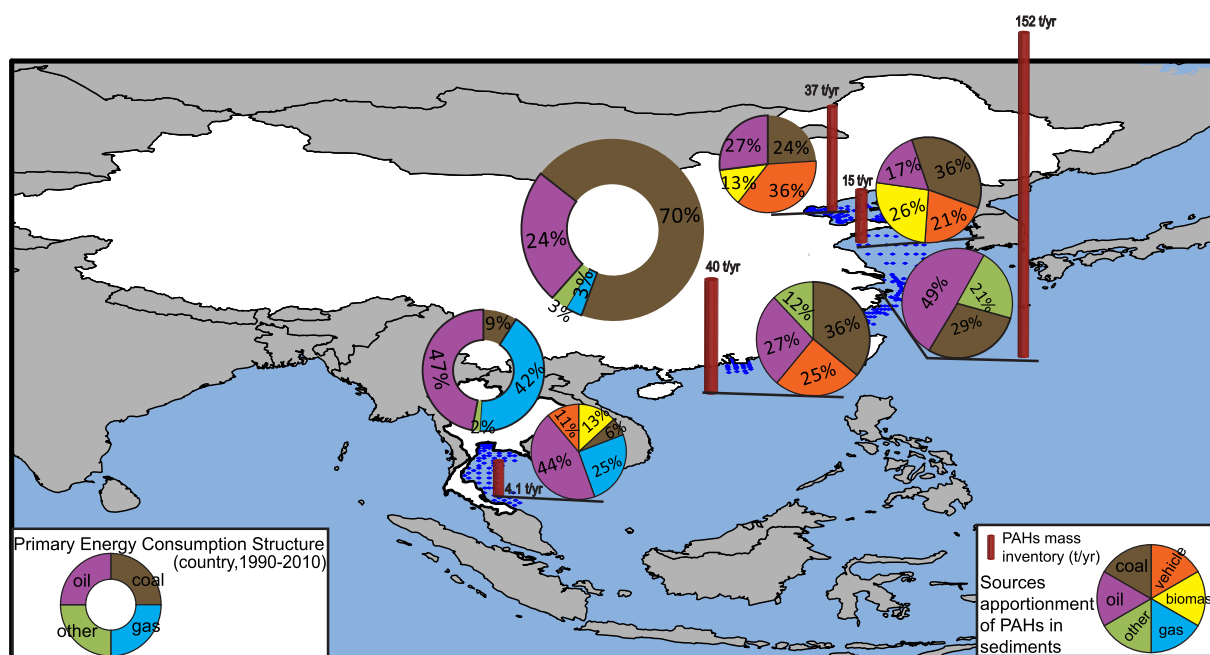
Fig. 9. Source profiles of energy consumption in Thailand and China and the corresponded deposited flux of PAHs with the proportions of each contributed factors in the Gulf of Thailand and Chinese marginal seas.
(Data from Luo et al. (2008), Lin et al. (2011).)

Additionally, the significant gap in the mass budget of PAHs on the continental shelves could also be constrained by the different particle dispersal mechanisms under the regional depositional settings. The coastal East China Seas are characterized as one of the largest river-dominated margins with massive sediment discharge, long-distance (hundreds of kilometers) dispersal systems, and convergent hydrodynamic conditions (Milliman et al., 1985; Liu et al., 2006; Yang and Liu, 2007), they have rapid deposition, subsequent resuspension, and remobilization of the sedimentary organic components (Hu et al., 2013; Lin et al., 2013). Additionally, under the influence of the East Asia Monsoon, the coastal margins of the East China Seas are downwind of the East Asia continental outflow, with its large amount of dust and particulate pollutant deposition, in spring and winter (Lin et al., 2011; Xu et al., 2012). This coupled process could facilitate the sequestration of PAHs in the shelf sediments in the East China Seas (Lin et al., 2011, 2013). In contrast, the offshore sediment dispersion in the GOT is rather limited due to the small fluvial discharge and frequent washout by surface run-off. Although atmospheric loading serves as an important contributor for those land-emitted combustion-derived substances, as noted above, the relatively low PAH emission flux from the continent as well as the lower particulate mass in tropical Asia air may also trigger the regional disparity in PAH sequestration along the East and SE Asia continental margins.

4. Conclusions

The extensive land-based input through fluvial inputs and surface runoff could be responsible for the high LMW PAH levels in the coastal upper Gulf. A PMF model was explored to apportion a factor associated with air–sea exchange containing LMW PAHs, and this diffusive input pathway could imply that atmospheric loading may be an important PAH input pathway to the open GOT. Vehicle emissions and biomass burning were the predominant contributors to particulate-phase PAHs. The depositional flux of PAHs in the GOT was estimated to be 4.2 ng/cm^2/yr, and the area–extrapolated mass budget was 4.1 t/yr. Source profile of each PAH contributor and the mass budget of the sedimentary PAHs highlight the impacts of the varied energy structures and the response of the PAH deposition on a regional scale. Overall, the discrepancy in land-emitted PAH flux and the different sediment dispersal patterns could both be responsible for the regional disparity in PAH sequestration along the Asia continental margins.

Table 1
Annual accumulation flux of PAHs in the Gulf of Thailand and comparison with those from Chinese coastal margins and other regions in the world.

Locations	Surface area (km^2)	Mass inventory of PAHs (t/y)	References
Bohai Sea	43,000	37	Qin et al. (2011)
Yellow Sea	70,000	15	Unpublished data
Inner shelf of East China Sea	100,000	154	Lin et al. (2013)
Pearl River estuary and Northern South China Sea	23,000	40	Chen et al. (2006)
The Gulf of Mexico	1,600,000	3.4	Mitra and Bianchi (2003)
The Gulf of Lions	13,000	15.3	Bouloubassi et al. (2012)
Northwestern Mediterranean	280,000	60	Tolosa et al. (1996)
Mediterranean Sea	850,000	182	Lipiatou et al. (1997)
Beibu Gulf, South China Sea	400	1.57–2.62	Li et al. (2015)
Gulf of Thailand	150,000	4.1	This study

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.09.158.

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