Final Draft
of the original manuscript


First published online by Elsevier: 05.11.2019

https://dx.doi.org/10.1016/j.scitotenv.2019.134763
PAEs and PAHs in the surface sediments of the East China Sea:

Occurrence, distribution and influence factors

Xiangai Zhao¹, Haiyan Jin¹,²*, Zhongqiang Ji¹, Donghao Li³, Han Yeong Kaw ³,
Jianfang Chen¹,², Zhiyong Xie⁴, Tianzhen Zhang¹

¹ Key Laboratory of Marine Ecosystem and Biogeochemistry, State Oceanic
Administration & Second Institute of Oceanography, Ministry of Natural Resources, P.
R. China, Baochubei Road 36, Hangzhou, 310012, China
² State Key Laboratory of Satellite Ocean Environment Dynamics, Second Institute of
Oceanography, Ministry of Natural Resources, Baochubei Road 36, Hangzhou 310012, China
³ Department of Chemistry, MOE Key Laboratory of Natural Resources of the
Changbai Mountain and Functional Molecules, Yanbian University, Park Road 977,
Yanji City, Jilin Province 133002, China
⁴ Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute
of Coastal Research, Max-Planck-Strasse 1, Geesthacht 21502, Germany

Author Contact Information:
* To whom correspondence should be addressed
* Haiyan Jin, Ph.D. (corresponding author)
Phone: +86-89988092
Fax: +86-88071539
E-mail: jinhaiyan@sio.org.cn

Abstract
A total of 29 sediment samples were collected from the East China Sea (ECS),
with the Yangtze River estuary and the Zhejiang coastal area. These sediment samples were analyzed for 6 phthalate esters (PAEs) and 16 polycyclic aromatic hydrocarbons (PAHs): the \( \Sigma \)PAEs and \( \Sigma \)PAHs concentrations ranged between 1649.5–8451.5 ng g\(^{-1}\) (mean = 3446.3 ng g\(^{-1}\)) and 57.5–364.5 ng g\(^{-1}\) (mean = 166.2 ng g\(^{-1}\)), respectively. Overall, the PAEs and PAHs concentrations gradually decreasing in the offshore and southward directions: their compositions and distributions suggest they could have mainly derived from the Yangtze River. In particular, their distribution was influenced by the sources’ proximity, hydrodynamics, and sediment geochemistry (i.e., TOC content and grain size). A classical two-end member model was utilized to estimate the fraction of terrestrial organic carbon in the sediments of the ECS. When the sediment was dominated by terrestrial-derived organic matter (OM), the concentrations of PAEs and PAHs were significantly correlated to the TOC content and gran size of the sediments. In contrast, the poor correlation of TOC content and grain size with PAEs in those sediments dominated by marine-derived OM, implied that the distribution of PAEs in the ECS was mainly related to land-based inputs, (especially to that of the Yangtze River). Regardless of the origin of most of the OM contained in the sediments, we observed positive correlations between the TOC content, and grain size of those containing PAHs. These results suggest that the distribution of PAHs in the ECS was not only related to the Yangtze River input, but also to the geochemical characteristics of the sediments.

Keywords: PAEs; PAHs; distribution characteristics; sediment; ECS

1. Introduction

Organic contaminants enter the marine ecosystems through various pathways,
including wastewater and riverine inputs, overland flows, atmospheric transport and
deposition, or via adsorption onto particles and finally end up in the sediment (Zhang
et al., 2018a; Montuori et al., 2016). The relative importance of these pathways depends
largely on the distance from the input sources and on the characteristics of the emitted
particles; due to sedimentation dynamics, the contributions from lateral transport may
decrease with increasing distance (Liu et al., 2012). Marine sediments are important
sources of information, which can elucidates the fate of organic compounds over long
periods of time. The factors controlling the fate of organic contaminants in sediments
include, among others, the sediments’ characteristics, the pollutants’ geochemical
characteristics, and the environmental conditions (Louvado et al., 2015).

Phthalate esters (PAEs) are a group of chemical compounds that are widely used
in the manufacturing and processing of plastics products (e.g., plasticizers), which are
employed for a broad range of industrial and consumer products (Zhang et al., 2018a;
Chen et al., 2017). Previous studies have shown that PAEs are endocrine-disrupting
chemicals that pose potential health risks to humans and other organisms; for example,
they can disrupt the hormonal balance of mammalian species (Wang et al., 2016). PAEs
are easily degraded by light, as well as by degraded bacteria and actinomycetes;
therefore, they are not considered as persistent chemicals (Wezel et al., 2000). After
PAEs enter an aquatic system, given their low solubility, they are easily adsorbed onto
particles and eventually accumulate in the bottom sediments (Liu et al., 2014).

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with two or
more fused aromatic rings produced during the incomplete combustion of organic
matter (OM). PAHs are lipophilic, non-biodegradable, environmentally persistent, toxic
and a few of individual PAHs are categorized as carcinogen (Pérezfernández et al.,
2018). Sources of PAHs included, among others, motor vehicle exhausts, industrial
emissions, coal burning for commercial and household heating, forest fires and the 
combustion of other biomass fuels. Consequently, PAH pollution mainly occurs in 
densely populated areas, major manufacturing districts, intensive agricultural basins, 
and other industrial centers (Han et al., 2017). Due to their low solubility and high 
hydrophobic-lipophilic characteristics, in marine ecosystem PAHs tend to bound to 
suspended particles and be subsequently deposited within sediments (Sun et al., 2018). 
The East China Sea (ECS) is a typical marginal sea located in the western part of the 
northwest Pacific Ocean, which receives large amounts of fresh water and sediment 
discharges from the Yangtze River (Changjiang). This river, the third longest river in 
the world, is heavily contaminated by industrial-agricultural discharges and by the 
runoff of big cities along the river (Adeleye et al., 2016). Moreover, the ECS receives 
a large amount of pollutants from the Yangtze River Delta, which is one of the most 
urbanized and industrialized regions of China (Zhou et al., 2014). Due to the importance 
of ECS in Chinese coastal, the levels, compositions, sources and ecological risk of 
PAHs in ECS surface sediment have been studied. For example, Hung et al. (2011) 
reported the distribution and levels of PAHs in sediments from ECS. Deng et al. (2013) 
investigated the source apportionment of PAHs in mud areas of ECS. Li et al. (2017a) 
studied the distribution, sources and ecological risk of PAHs in the estuarine-coastal 
sediments of ECS. However, few PAE-related studies in ECS surface sediment have 
been conducted, and these studies only focused on the levels and distribution. Yang et 
al. (2011) reported the occurrence and distribution of PAEs in sediments from ECS, and 
Zhang et al. (2018a) reported the occurrence and distribution of PAEs in sediments of 
Changjiang River Estuary and its adjacent area.

Marginal seas play an important role in the transport and storage of terrestrial input 
organic materials, since they represent transition zones between the continent and the
open sea (Hung et al., 2011). Thus, the ECS can act as an important sinks of pollutants that originate from land-based pollution sources, and affect the transportation of pollutants into the open sea. In addition, the Zhejiang-Fujian Coastal Current (ZFCC), the Jiangsu Coastal Current (JCC), and the Taiwan Warm Current (TWC) also significantly affect the study area (Zhang et al., 2015). ECS as one of an active interface between terrestrial and oceanic environments have complex biogeochemical processes. In order to reveal the fate of organic pollutants in the ECS, a few studies have been conducted. Still, local controls on distribution of organic pollutants in the sediments (e.g., different OM sources or geochemical characteristics of sediment) remain unclear.

In this study, we analyzed the occurrence of sixteen PAHs and six PAEs in sediment samples collected from the ECS. The main objectives of this work were to investigate the contamination status and to compare the distribution characteristics of PAHs and PAEs in the surface sediments, as well as to identify the potential factors influencing their distribution.

2. Experimental

2.1. Sample collection and preparation

A total of 29 representative surface sediment samples (0–2 cm) were collected using a box sampler from 29 sampling locations in the ECS between May–June 2017 (Table S1). After homogenization, the sediment samples were enclosed in a pre-cleaned aluminum foil and immediately stored frozen until analysis. Before extraction, the samples were freeze-dried, grinded, and sieved.

Approximately 0.5 g of grated sediment sample were placed in a glass vial, mixed with dichloromethane and ultrasonic-extracted. The extract was evaporated with a stream of nitrogen until reaching a volume of ~100 μL; then, they were further purified
through gas purge microsyringe extraction (GP-MSE) (Yang et al., 2011). Details about
the GP-MSE are presented in the Supplementary material. All samples were spiked
prior to extraction with a mixture of isotopically labeled compounds, which were used
as internal standards (\(^{2}\text{H}_{10}\)-acenaphthene, \(^{2}\text{H}_{10}\)-fluoranthene and \(^{2}\text{H}_{10}\)-perylene,
(Accustandard, New Haven, CT, USA).

2.2. Total organic carbon (TOC) and grain size of sediments

The freeze-dried and grated sediment samples were treated with 4 N HCl to
remove any carbonate, were rinsed with deionized water, and subsequently dried at
60 °C for 12 h. The resulting carbonate-free samples were analyzed for the TOC content
using a Vario EL- III Elemental Analyzer. A stable carbon isotope analysis of the
organic carbon was also performed on these samples using a Thermo Deltaplus XL
mass spectrometer operating in a continuous flow mode.

The grain size of the sediment samples was determined using a laser particle size
analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, Worcestershire, UK).

2.3. Classical two-end member model of the OM \(\delta^{13}\text{C}\) signatures

The \(\delta^{13}\text{C}\) values change depending on the carbon sources; hence, they can be used
effectively to distinguish different sources (marine or terrestrial) of the bulk
sedimentary OM. The terrestrial OM fraction (\(F_t\)) in a sample is given by:

\[
F_t = \frac{(\delta^{13}\text{C}_s - \delta^{13}\text{C}_m)}{(\delta^{13}\text{C}_t - \delta^{13}\text{C}_m)} \times 100\% \quad (1)
\]

Where \(\delta^{13}\text{C}_m\) and \(\delta^{13}\text{C}_t\) are the \(\delta^{13}\text{C}\) values of the marine and terrestrial end members,
and \(\delta^{13}\text{C}_s\) is that of the sediment sample. We assumed that the OM sample was
composed exclusively of terrestrial OM delivered by the Yangtze River (\(\delta^{13}\text{C}_t =
-25.6\%\)) and of marine OM derived from local sources (\(\delta^{13}\text{C}_m = -20.0\%\)) (Wu et al.,
2007; Wang et al., 2018). The fraction of marine OM (\(F_m\)) was given by \(F_m = 1 - F_t\).

2.4. Chemicals and materials
Six PAEs and 16 PAHs standard mixtures were purchased from AMP (USA) and Accustandard (New Haven, CT, USA), respectively. The purity of all standards was higher than 99%. A mixture standard solution of PAEs was prepared in hexane at a concentration of 1000 mg L\(^{-1}\), while a mixture standard solution of PAHs was prepared in acetone at a concentration of 100 mg L\(^{-1}\). Detail information about the PAHs and PAEs standards are provided in Table S2. The standard solutions were stored in the dark at 4°C until use. HPLC grade organic solvents (e.g., dichloromethane and hexane) were purchased from Caledon (Georgetown, Canada).

### 2.5. Instrumental analysis

The analysis and detection of the PAEs and PAHs were conducted using a gas chromatography coupled to a quadrupole mass spectrometer with electron impact ionization (Shimadzu GC 2010 System connected with a Shimadzu QPMS 2010 MS). The separation was achieved within a DB5 fused-silica capillary column (30 m × 0.25 mm × 0.25 mm). Details about the GC-MS analysis are presented in the Supplementary material.

### 2.6. Quality control and quality assurance (QA/QC)

All the analyses were performed according to the quality assurance and quality control measures. The quantification was done following an internal standard method, and the correlation coefficients (r\(^2\)) of all the PAEs and PAHs calibration curves were higher than 0.99. The recoveries of the three internal standards for the sediment samples were in the range of 59.8–104.8%, 62.0–89.2%, and 51.1–80.2%, respectively. The analyses were simultaneously carried out for every set of blank, laboratory blank spiked, laboratory duplicate, and matrix spiked samples. The recoveries for the laboratory blank spiked samples ranged between 67.8–111.9%, while those of the matrix spiked samples between 62.3–124.9%. The in-lab reproducibility was in the range of 2.6–
3. Results

3.1. PAEs in ECS sediments

Five out of the 6 target PAE compounds (except di-n-octyl phthalate (DnOP)) were detected in the 29 sediment samples collected from the ECS. Table S3 summarizes the concentration of the individual and $\sum$ PAEs in the surface sediments; the $\sum$ PAEs concentrations in the sediments oscillated between 1550.4–7381.5 ng g$^{-1}$ (mean = 3873.9 ng g$^{-1}$). The highest concentration was found at site B1 (in the southeastern area of the Yangtze River estuary), while the lowest concentration was recorded at site H3 (in the southern part of the Zhejiang Coastal area) (Figure 1). Among the individual PAEs, di-(2-ethylhexyl)-phthalate (DEHP) was the most abundant (1100.6–5643.4 ng g$^{-1}$; mean = 2916.8 ng g$^{-1}$), followed by diisobutyl phthalate (DIBP) (202.3–822.6 ng g$^{-1}$; mean = 466.2 ng g$^{-1}$) and dibutyl phthalate (DBP) (205.5–714.1 ng g$^{-1}$; mean = 380.1 ng g$^{-1}$). These compounds account on average for 73.5% (59.1–81.7%), 12.8% (9.0%–20.8%) and 10.6% (7.6%–15.6%) of the total PAEs concentration, respectively (Figure S1). Such results are consistent with the commonly accepted notion that DBP, DIBP and DEHP are the dominant PAE components in sediments (Li et al., 2016a; Li et al., 2017b; Zhang et al., 2018a). In addition, we noted higher concentrations of PAEs in the sediment samples collected from the Yangtze River estuary and a decrease of these concentrations northward, in the direction of the outer shelf.
3.2. PAHs in ECS sediments

Sixteen target PAH compounds were detected in the 25 sediment samples collected from the ECS. Among them Naphthalene (Nap) did not satisfy the criteria of QA/QC considered in this study: the blank values were three times higher than those of the method detection limit. Thus, the concentration of Nap was not determined and this compound was not considered in further discussions.

Table S4 summarizes the concentration of individual and total PAHs in the sediment; the $\sum$PAHs concentrations in the sediments were comprised between 70.7–383.6 ng g$^{-1}$ (mean = 179.9 ng g$^{-1}$). The highest concentration was recorded at site B1 (in southeastern area of the Yangtze River estuary), while the lowest in the lowest longitude-sampling site (C4) (Figure 1). Phenanthrene (Phe) (14.8–65.2 ng g$^{-1}$; mean = 32.6 ng g$^{-1}$), pyrene (Pyr) (15.1–56.8 ng g$^{-1}$; mean = 31.8 ng g$^{-1}$) and fluoranthene (Fluo) (10.5–52.1 ng g$^{-1}$; mean = 26.8 ng g$^{-1}$) were the most abundant PAHs detected, followed by benzo[a]pyrene (BaP) (4.6–41.7 ng g$^{-1}$; mean = 17.0 ng g$^{-1}$), benzo[b]fluoranthene (BbF) (3.7–34.8 ng g$^{-1}$; mean = 16.1 ng g$^{-1}$), and benzo[a]anthracene (BaA) (3.7–26.0 ng g$^{-1}$; mean = 12.8 ng g$^{-1}$). As shown in Figure
S2, 4-ring PAHs (41.2%–56.3%; mean = 47.4%) were the most abundant type of PAHs, followed by 3- and 5-ring PAHs (3-ring: 20.5%–33.1%; mean = 25.6%; 5-ring: 16.9%–28.7%; mean = 22.4%) in most of the sampling stations. Generally, higher concentrations of PAHs with relatively high molecular weights are observed in marine sediments (Huang et al., 2012). Moreover, relatively high concentrations of PAHs were found in the sediment samples collected from the Yangtze River estuary (sampling sites A1, B1 and B2) and the Zhejiang Coastal area (sampling sites E1, F1 and H1); the PAHs concentrations decreased similarly toward the outer shelf.

4. Discussion

4.1. Concentration levels of PAEs and PAHs in the ECS and other areas

The $\Sigma$PAEs and $\Sigma$PAHs concentrations in the ECS sediments were compared with those previously reported in other parts of China and abroad. The results are shown in Table 1. Generally, the $\Sigma$PAEs concentrations in the sediments were found to be slightly lower in the ECS (1550.4–7381.5 ng g$^{-1}$) than in other seas, such as the Bohai and Yellow Sea in northern China (1.24–15.8 μg g$^{-1}$), the Pearl River estuary in southern China (0.88–13.6 μg g$^{-1}$), the Kaohsiung Harbor in Taiwan (1.27 ±0.76–51.94 ±29.21 μg g$^{-1}$) and the coastal areas of Kuwait (2.15 to 15.72 μg g$^{-1}$); however, they are similar to those observed in the Southern Yellow Sea (311.4–6156.5 ng g$^{-1}$). Moreover, the $\Sigma$PAEs concentrations in the ECS sediments were 2–7 times lower than those in the sediments of the Pu River in northeastern China (3.71–46.9 μg g$^{-1}$) and of the Pearl River Delta (PRD) region (0.567–47.3 μg g$^{-1}$), but comparable to those in the sediments of the Qiantang River in eastern China (0.59 to 6.74 μg g$^{-1}$).

The $\Sigma$PAHs concentrations observed during our study (58.6–351.6 ng g$^{-1}$) were similar to those detected in the Liaodong Bay in China (88.5–347.1 ng g$^{-1}$), Daya Bay
in China (140.0–491.0 ng g\(^{-1}\)), the Libyan coastal area in the Mediterranean Sea (41.8–
388 ng g\(^{-1}\)) and in the Tiber River estuary in Italy (36.2–545.6 ng g\(^{-1}\)). Moreover, the
\(\sum\)PAHs concentrations in the sediments of the ECS were 2–4 times lower than those in
the Bohai Sea in China (149.2–1211.8 ng g\(^{-1}\)), Rizhao coastal area in China (79.3–853.0
ng g\(^{-1}\)), the northern part of the Yellow Sea in China (148.3–907.5 ng g\(^{-1}\)) and the Pearl
River estuary in southern China (144.0–1289.0 ng g\(^{-1}\)). Finally, the \(\sum\)PAHs
concentrations observed in the ECS were slightly higher than those on the Chinese
continental shelf (e.g., the inner Yellow Sea (53–224 ng g\(^{-1}\)) and the South China Sea
(27–110 ng g\(^{-1}\)).

Table 1 Concentration levels of PAEs and PAHs in ECS and other different areas

<table>
<thead>
<tr>
<th>Location</th>
<th>Research area</th>
<th>Sample</th>
<th>Concentration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAEs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>North China</td>
<td>Bohai and Yellow Sea</td>
<td>Sediment</td>
<td>1.24–15.8 (16)</td>
<td>Zhang et al. (2018a)</td>
</tr>
<tr>
<td>Yellow Sea, China</td>
<td>Southern yellow sea</td>
<td>Sediment</td>
<td>0.31–6.15 (4)</td>
<td>Li et al. (2014)</td>
</tr>
<tr>
<td>South China Sea</td>
<td>Pearl River Estuary</td>
<td>Sediment</td>
<td>0.88–13.6 (6)</td>
<td>Li et al. (2016a)</td>
</tr>
<tr>
<td>Taiwan, China</td>
<td>Kaohsiung Harbor</td>
<td>Sediment</td>
<td>1.27 ±0.76–51.94 ±29.21 (10)</td>
<td>Chen al. (2017)</td>
</tr>
<tr>
<td>Kuwait</td>
<td>Kuwait's coastal areas</td>
<td>Sediment</td>
<td>2.15–15.72 (6)</td>
<td>Saeedet al. (2017)</td>
</tr>
<tr>
<td>Northeast China</td>
<td>Pu River</td>
<td>Sediment</td>
<td>3.71–46.9 (6)</td>
<td>Li et al. (2016b)</td>
</tr>
<tr>
<td>South China</td>
<td>Pearl River Delta (PRD) region</td>
<td>Sediment</td>
<td>0.567–47.3 (16)</td>
<td>Liu et al. (2014)</td>
</tr>
<tr>
<td>East China</td>
<td>Qiantang River</td>
<td>Sediment</td>
<td>0.59–6.74 (16)</td>
<td>Sun et al. (2013)</td>
</tr>
<tr>
<td>East China</td>
<td>East China Sea</td>
<td>Sediment</td>
<td>1.55–7.38 (6)</td>
<td>This Study</td>
</tr>
</tbody>
</table>

| PAHs              |                                      |                 |                   |                           |
| Bohai Sea, China  | Bohai sea                            | Sediment        | 149.24–1211.81 (16) | Li et al. (2016c)        |
|                   | Liaodong Bay                         | Sediment        | 88.5–347.1 (16)    | Zhang et al. (2018b)     |
| Yellow Sea, China | Rizhao coastal area                  | Sediment        | 79.3–853 (16)      | Chen et al. (2012)       |
|                   | Northern part of the Yellow Sea      | Sediment        | 148.28–907.47 (16) | Li et al. (2015)         |
| South China Sea   | Pearl River Estuary                  | Sediment        | 144–1289 (16)      | Yuan et al. (2015)       |
|                   | Daya Bay                             | Sediment        | 140–491 (16)       |                           |
| Mediterranean Sea | Libyan coastal area                  | Sediment        | 41.8–388 (16)      | Bonsignore et al. (2018) |
| Italy             | Tiber River estuary                  | Sediment        | 36.2–545.6 (16)    | Montuori et al. (2016)   |
| East China        | East China Sea                       | Sediment        | 70.7–383.6 (16)    | This Study                |

The numbers in brackets indicate the number of PAEs and PAH compounds studied.
The unit of PAEs in sediment is µg g⁻¹; The unit of PAHs in sediment is ng g⁻¹.

4.2. Spatial distribution of PAEs and PAHs

As shown in Figure 1, the PAEs and PAHs concentrations decreased with increasing longitude, indicating lower pollution levels in the offshore rather than in the inshore areas. This result illustrates that the potential source (e.g., terrestrial emissions) of pollution might have been located closed to the inshore sites; therefore, the concentration of ∑PAEs and ∑PAHs was higher than that in offshore sites. Moreover, PAEs and PAHs were detected in all of the surface sediment samples, suggesting their widespread distribution in the marine sediments of the ECS region.

A Principal Component Analysis (PCA) was conducted to analyze the spatial distribution of PAEs and PAHs in the sediments. The PCA was based on the individual and total PAEs and PAHs concentrations, on the TOC content and on the grain size data obtained from the 29 sediment sampling sites in the ECS. The loading and factor score plots of the PAEs and PAHs in the ECS sediments are presented in Figure 2. The PCA resulted in the extraction of two principal components (PCs) with eigenvalues >1, which explained 89.9% of the total variation in the analyzed data. The individual and
total PAHs, PAEs, as well as the TOC and grain size values were mainly associated with PC1, which explained 77.9% of the variation. Half of the sampling sites plotted in the PCA corresponded to positive values of the PC1 axis, and were consistent with the PAHs, PEAs, TOC and grain size vectors. The samples corresponding to the positive section of the PC1 axis were characterized by fine-grained sediments, high TOC levels and high concentrations of PAEs and PAHs. As shown in Figure 2, the higher PC1 scores (larger than 0.5) were recorded in the Yangtze River estuary (sampling sites A1, B1, B2, B3 and C1) and in the inshore zone of the Zhejiang coastal area (sampling sites E1, E2 and F1). Relatively high concentrations of PAEs, PAHs and TOC, as well as fine grain sizes were also observed at these sampling sites: they represent significant deposition centers of Yangtze-derived fine-grained sediments in the ECS (Liu et al., 2006). Organic pollutants, especially high molecular weight ones with high $K_{ow}$ values, can easily adsorb to particles due to their high hydrophobicity (Duan et al., 2013; Zheng et al., 2014). Given this characteristic, organic pollutants can be rapidly and abundantly transported downward by sinking particles, once they are discharged into water bodies (Liu et al., 2014). The PAEs and PAHs discharged into the ECS should have been quickly incorporated into the sediments and preferentially deposited near the coast, justifying their relatively high concentrations at the inshore sites, especially those in the Yangtze River estuary.

PC 2 explained 11.9% of the total variation. The sampling sites plotted in the PCA in correspondence of the positive PC 2 axis were consistent with the PAEs and 3-ring PAH vectors, but opposite to the PAHs, TOC and grain size vectors. The negative part of the PC 2 axis showed that the distribution of the PAHs was influenced by sediment geochemistry (i.e., TOC content and grain size). When PC1 was plotted against PC2, we noticed that the sediment samples from the inshore sites formed different groups...
These groupings reflected the PAEs and PAHs loadings of sediments collected from inshore locations, the PAHs loadings of sediments collected from the Zhejiang Costal sites, and the PAEs loadings of sediments collected from the Yangtze River estuary sites (Figure 2b).

4.3. Effect of sediment geochemistry (TOC content and grain size) on distribution of PAEs and PAHs

A previous study has inferred that the TOC and grain size (Mz) of sediments are two important factors controlling the spatial distribution of persistent organic pollutants (POPs) in aquatic environment (Zheng et al., 2014). Like POPs, PAEs and PAHs can adsorb onto particulate matters due to their high hydrophobicity. The concentrations of TOC, PAEs and PAHs in sediments of the ECS were examined through Spearman's correlations (Table 2). The concentration of $\Sigma$PAHs presented significant positive correlations with the TOC content ($p < 0.01$, $r^2 = 0.73$) and the grain size ($p < 0.01$, $r^2 = 0.69$); on the contrary, the concentration of PAEs showed no significant correlations with neither the TOC content or the grain size. These results indicated that the distribution of PAHs in the ECS sediments was controlled by the sediment geochemistry; moreover, a unique distributional pattern of the PAEs could be observed within specific regions of the ECS.

Table 2 Spearman correlation for sediment geochemistry and target compound in surface sediments

<table>
<thead>
<tr>
<th></th>
<th>TOC</th>
<th>OC-T</th>
<th>OC-M</th>
<th>Grain size</th>
<th>PAEs</th>
<th>PAHs</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC-T</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OC-M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain size</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAEs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PAEs</td>
<td>PAHs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td><strong>All site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.38*</td>
<td>-0.04</td>
<td>0.21</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.73**</td>
<td>0.92**</td>
<td>0.01</td>
<td>0.69**</td>
<td>0.39*</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Inshore site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.62**</td>
<td>0.86**</td>
<td>-0.03</td>
<td>0.43*</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.76**</td>
<td>0.97**</td>
<td>0.12</td>
<td>0.68**</td>
<td>0.84**</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Offshore site</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.24</td>
<td>-0.41</td>
<td>0</td>
<td>-0.05</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.88**</td>
<td>0.78**</td>
<td>0.89**</td>
<td>0.82**</td>
<td>0.01</td>
<td>1.00</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

Most of the OM that reaches the ECS marginal sea is brought by the Yangtze River. The terrestrial inputs were expected to dominate over the marine inputs in both the suspended and surface sediments of the inner estuary (Wu et al., 2007; Wang et al., 2018). The two primary end-members of the OM in the ECS sediments were terrestrial matter (mainly transported from the Yangtze River) and marine autochthonous matter (Wu et al., 2007). A classical two-end member model of the OM δ¹³C signatures was used to estimate the fractions of terrestrial (Fₜ) and marine organic carbon (Fₘ) in the ECS surface sediments (Eq. (1)); the corresponding results are presented in Table S1. According to these data, the terrestrial-derived organic carbon (OC-T) generally occurred in the inshore zones of the Yangtze River estuary and of the Zhejiang coastal area, while the marine-derived organic carbon (OC-M) was occurred in the offshore zones of the Yangtze River estuary and of the Zhejiang Costal area (Figure 3).
Although no significant relationship was found between the TOC and the PAEs concentration in the ECS surface sediments, we discovered that the $\sum$PAEs concentrations were positively correlated ($p < 0.05$, $r^2 = 0.38$) with the OC-T, especially in the terrestrial OM-dominated area ($p < 0.01$, $r^2 = 0.86$). Another positive correlation ($p < 0.05$, $r^2 = 0.43$) was also observed between the $\sum$PAEs concentration and the grain size in the terrestrial OM-dominated area. However, no significant correlation was found between the $\sum$PAEs concentration and the OC-M. One of the possibilities is that the pollutants adsorbed onto sediment particles did not reach the adsorption-desorption equilibrium during particle settling, due to the high sedimentation rates characterizing the inshore and estuary areas (Duan et al., 2013). These statistical results indicated that the PAEs and OC-T should have had similar sources, or that they were subjected to the same transport processes. Hence, the distribution of PAEs in the ECS surface sediments may be more prominently influenced by direct and continuous regional inputs, rather than by the natural sorption process on particulate organic carbon. This suggests that the Yangtze River has a great impact on the input of PAEs in these areas. Likewise, the $\sum$PAHs concentrations were significantly and positively correlated with OC-T in the
terrestrial OM-dominated area ($p < 0.01, r^2 = 0.97$), but had no relationship with OC-M in this same area. Additionally, the $\sum$PAHs concentrations showed significant positive correlations ($p < 0.01, r^2 = 0.88$) with the TOC content in the marine OM-dominated area; this can be attributed to the correlation between $\sum$PAHs and OC-M ($p < 0.01, r^2 = 0.89$) and that between $\sum$PAHs and OC-T ($p < 0.01, r^2 = 0.78$). Moreover, a significant positive correlation was found between $\sum$PAHs and grain size in both the marine ($p < 0.01, r^2 = 0.82$), and terrestrial ($p < 0.01, r^2 = 0.68$) OM-dominated areas. In comparison to the distribution of PAEs, that of PAHs in the ECS surface sediments was influenced by the continuous regional input of PAHs from the Yangtze River (especially in the inshore region, which is a terrestrial OM-dominated area) and by the sediment geochemistry (particularly in the offshore region, which is a marine OM-dominated area). Previous soil studies have demonstrated that strong relationships between contaminant and organic carbon concentrations in the soil could occur under a number of scenarios; one of these scenarios consists in a stable chemistry that does not allow degradation (Sweetman et al., 2005). Similarly, relatively persistent PAHs could have achieved steady-state conditions between seawater and sediment on a timescale, strengthening the correlation between PAH and sediment organic carbon concentrations.

### 4.4. Identification of the PAE and PAH sources

As shown in Figure S1, the dominant PAE species was DEHP, followed by DIBP and DBP. These results are consistent with those reported in previous studies, in which DBP, DIBP and DEHP were the dominant PAEs components of the sediment (Li et al., 2017; Zhang et al., 2018a). According to previous reports, DEHP, DIBP, and DBP are the most widely used PAE plasticizers (Sun et al., 2013). Furthermore, DEHP and DBP are the two main PAEs used in the manufacturing of mulch film, which is commonly used in agricultural production (Xu and Liu, 2013). DMP, DEP, DIBP and DBP are also
used in cosmetics and personal care products; moreover, DIBP and DBP are used in epoxy resins, cellulose esters and special adhesive formulations (Zeng et al., 2008). The DEHP constituents represent about 50–60% of the total commercial PAEs being produced (Zeng et al., 2008). Consequently, the high DEHP values reported in the marine sediments of this study are not surprising.

Generally, high molecular weight PAHs are found in higher concentrations than low molecular weight PAHs in marine sediments (Huang et al., 2012). As shown in Figure S2, 4-ring PAHs were the most abundant compounds, followed by 3- or 5-ring PAHs in most of the ECS stations. Based on the characteristics of PAH composition, diagnostic ratios of PAHs isomers can be used to distinguish the probable sources of the PAHs in the marine environment. The isomeric ratios of the selected compounds have been considered good indicators of PAHs source. For example, Ant/(Ant + Phe) < 0.10 primarily indicates petroleum contamination, while Ant/(Ant + Phe) > 0.10 indicates that the contaminants come from a combustion source, Flu/(Flu + Pyr) < 0.40 primarily indicates petroleum contamination, while values between 0.40–0.50 and < 0.50 indicate mixed and combustion sources, respectively (Yunker et al., 2002). When BaA/(BaA+Chr) > 0.35, it implies combustion sources, while values between 0.20–0.35 and < 0.20 indicate mixed and petroleum sources, respectively (Yunker et al., 2002). As shown in Table 3, the ratios of Ant/(Ant + Phe) in the ECS sediments ranged between 0.00–0.15; moreover, the sampling sites located inshore (value < 0.10) and offshore (value > 0.10) indicated two distinct PAH source: petrogenic and combustion sources, respectively. The ratios of Flu/(Flu+Pyr) in the ECS surface sediments ranged between 0.31–0.53; indicating mostly a combustion source. The ratios of BaA/(BaA+Chr) fall between 0.45–0.70, indicating a combustion source for all the sampling sites. Overall, these results suggest that pyrogenic PAHs can be important
sources of PAH pollution in the ECS.

<table>
<thead>
<tr>
<th>Site</th>
<th>Ant/(Ant + Phe)</th>
<th>Flu/(Flu+Pyr)</th>
<th>BaA/(BaA + Chr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.14</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>B1</td>
<td>0.15</td>
<td>0.48</td>
<td>0.50</td>
</tr>
<tr>
<td>B2</td>
<td>0.14</td>
<td>0.48</td>
<td>0.50</td>
</tr>
<tr>
<td>B3</td>
<td>0.14</td>
<td>0.49</td>
<td>0.48</td>
</tr>
<tr>
<td>B4</td>
<td>0.06</td>
<td>0.35</td>
<td>0.57</td>
</tr>
<tr>
<td>B5</td>
<td>0.08</td>
<td>0.32</td>
<td>0.57</td>
</tr>
<tr>
<td>C1</td>
<td>0.15</td>
<td>0.47</td>
<td>0.51</td>
</tr>
<tr>
<td>C2</td>
<td>0.07</td>
<td>0.45</td>
<td>0.60</td>
</tr>
<tr>
<td>C3</td>
<td>0.08</td>
<td>0.45</td>
<td>0.59</td>
</tr>
<tr>
<td>C4</td>
<td>0.07</td>
<td>0.45</td>
<td>0.62</td>
</tr>
<tr>
<td>D1</td>
<td>0.07</td>
<td>0.46</td>
<td>0.56</td>
</tr>
<tr>
<td>D2</td>
<td>0.07</td>
<td>0.46</td>
<td>0.56</td>
</tr>
<tr>
<td>D3</td>
<td>0.06</td>
<td>0.48</td>
<td>0.56</td>
</tr>
<tr>
<td>D4</td>
<td>0.17</td>
<td>0.45</td>
<td>0.59</td>
</tr>
<tr>
<td>E1</td>
<td>0.20</td>
<td>0.48</td>
<td>0.45</td>
</tr>
<tr>
<td>E2</td>
<td>0.18</td>
<td>0.48</td>
<td>0.45</td>
</tr>
<tr>
<td>F1</td>
<td>0.10</td>
<td>0.39</td>
<td>0.51</td>
</tr>
<tr>
<td>F2</td>
<td>0.10</td>
<td>0.39</td>
<td>0.50</td>
</tr>
<tr>
<td>F3</td>
<td>0.08</td>
<td>0.38</td>
<td>0.51</td>
</tr>
<tr>
<td>H1</td>
<td>0.13</td>
<td>0.45</td>
<td>0.57</td>
</tr>
<tr>
<td>H2</td>
<td>0.14</td>
<td>0.48</td>
<td>0.56</td>
</tr>
<tr>
<td>H3</td>
<td>0.15</td>
<td>0.48</td>
<td>0.59</td>
</tr>
<tr>
<td>N1</td>
<td>0.00</td>
<td>0.44</td>
<td>0.70</td>
</tr>
<tr>
<td>N2</td>
<td>0.00</td>
<td>0.44</td>
<td>0.69</td>
</tr>
<tr>
<td>N3</td>
<td>0.00</td>
<td>0.44</td>
<td>0.57</td>
</tr>
<tr>
<td>Q1</td>
<td>0.10</td>
<td>0.52</td>
<td>0.53</td>
</tr>
<tr>
<td>Q2</td>
<td>0.11</td>
<td>0.52</td>
<td>0.50</td>
</tr>
<tr>
<td>Q3</td>
<td>0.12</td>
<td>0.48</td>
<td>0.55</td>
</tr>
<tr>
<td>Q4</td>
<td>0.14</td>
<td>0.50</td>
<td>0.55</td>
</tr>
</tbody>
</table>

5. Conclusion

In this work, we analyzed the concentrations and compositions of 6 PAEs and 16 PAHs contained in surface sediments collected from the ECS. The Yangtze River input is an important factor affecting the distribution of PAEs and PAHs in the sediments of the ECS. The $\sum$PAEs and $\sum$PAHs concentrations decreased gradually from inshore to offshore and from north to south; their maximum values were registered in the
southeastern part of the Yangtze River estuary, indicating that source proximity is another factor influencing the distribution of PAEs and PAHs within the ECS. Sedimentary geochemistry also affected to the distribution PAHs in the ECS sediments, but not that of the PAEs. Finally, DEHP was found to be the major source of PAEs, while pyrogenic PAHs may be an important source of PAHs in the ECS.

Acknowledgements

This study was supported by a grant from the China-German co-joint project: “Anthropogenic fingerprint in Chinese eastern marginal seas: Investigation of pollutant fingerprints and dispersal in Bohai and Yellow Sea”, and the Long Term Observation and Research Plan in the Changjiang Estuary and the Adjacent East China Sea Project (LORCE).

References


Khaled-Khodja, S., Rouibah, K., 2018. Selected organic pollutants (PAHs, PCBs) in


interpreting and modelling field data. Chemosphere. 60, 959–972.


