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Perylene in surface sediments from the estuarine-inner shelf of the East China Sea: A potential indicator to assess the sediment footprint of large river influence

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ABSTRACT

The large-scale occurrence of perylene in the surface sediment samples from the estuarine-inner shelf of the East China Sea (ECS) were examined, and for the first time by employing the multiproxies of organic geochemistry to explore the possible sources of perylene and its biogeochemical implication in this river-dominated area. The concentrations of perylene in this area ranged from 7.4 to 141.1 ng g⁻¹, displaying an apparent decreased trend in an offshore direction and increased alongshore to the south. In addition to the fluvial input, the hydrodynamic sorted fine sediments and associated organic components could also act on the spatial variability of perylene and its varied relationships with the total organic carbon based proxies and PAHs. Higher proportions of perylene towards the 5-ring PAHs indicated a natural diagenetic input. Together with the reported high perylene abundance outside the sediment compartments, the significant relationships between perylene and the terrigenous organic matter (OM) proxies could suggest a combination of the predepositional fluvial input of perylene and in situ formation from its precursors with land-derived OM origins for its appearance in the coastal ECS. The deposition flux of perylene could be likely served as a geochemical imprint to assess the river input influence on the sedimentary environment of the coastal ECS.

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1. Introduction

Because of the variable river discharge and complex hydrodynamic and oceanic conditions within the coastal margins, the supply and footprint of riverine sediments and organic materials on the sediment environment is highly variable over time and space (McKee et al., 2004; Burone et al., 2013). Therefore, a thorough characterization from the source to sink of the terrigenous sediments and associated organic matter (OM) is essential to understand the mechanism of carbon cycles and human-induced interference on the continental margins (Hedges and Keil, 1995).

Perylene, a 5-ring polycyclic aromatic hydrocarbon (PAHs), has been widely found in the varied sediment environments, such as from the recent marine sediments (Orr and Grady, 1967; Venkatesan, 1988; Slater et al., 2013); the river and freshwater sediments (Ishiwatari et al., 1980; Sicre et al., 1993) and peats (Aizenshtat, 1973). Because of its widespread occurrence and distinctive sedimentary profiles,

perylene is usually thought to be a diagenetic product from its natural biogenic precursors via postdepositional formation under anoxic conditions (Silliman et al., 2001). However, the formation mechanism of perylene and natural sources of its precursor materials remains unclear (Venkatesan, 1988; Jiang et al., 2000; Silliman et al., 2001; Fan et al., 2011). For example, it has been suggested that the sources of perylene could be related to the degradation of autochthonous OM from algal and crinoids' productions (Orr and Grady, 1967); while other viewpoint suggested that the land-based OM input and allochthonous contribution could provide the main precursor materials for perylene (Aizenshtat, 1973; Ishiwatari et al., 1980; Jiang et al., 2000; Grice et al., 2009). On the other hand, the pre-formation of perylene outside the sediment compartment has also been reported (Bertrand et al., 2013 and references therein), for examples, significant amounts of predepositional perylene were also observed in the soil materials with association with the termites activity and/or their wood substrate (Wilcke et al., 2002; Bakhtiari et al., 2009), and/or in dead wood and sub-soil on the land (Krauss et al., 2005; Gocht et al., 2007).

Recently, it has been reported that the formation of perylene was related to the component of wood-degrading fungi (Jiang et

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al., 2000; Grice et al., 2009) and the most likely precursors of perylene could be perylene quinones and their derivatives, which are widely present in modern plants, fungi and insects (e.g. Bertrand et al., 2013 and references therein), supporting a possible link between perylene and terrigenous sedimentary organic matter (SOM) input. These statements have also been evidenced by the compound specific stable carbon isotope compositions ($\delta^{13}\text{C}$) of perylene in the geological samples (Jiang et al., 2000; Grice et al., 2009; Itoh and Hanari, 2010). Furthermore, the direct evidence of a postdepositional formation mechanism of perylene from its parent compounds (4,9-dihydroxyperylene-3,10-quinone, DHPQ) were also elucidated, which was originated from a fungal component (*Cenococcum geophilum*) in the humic acid soils from the catchment (Itoh et al., 2012).

Significant amounts of perylene have been observed in the various geological matrices from the coastal ECS and its surrounding areas, such as the ambient soils (Liu et al., 2008), suspended particles in the rivers (Sicre et al., 1993), estuarine surface sediments (Bouloubassi et al., 2001) and sediment core samples (Guo et al., 2006). High proportions of perylene towards the 5-rings PAHs in these studies indicated a natural diagenetic input of perylene (Baumard et al., 1998; Fan et al., 2011). However, a significant correlation between perylene and anthropogenic PAHs in the ECS inner shelf with few sampling sites was also observed recently, pointing to a possible anthropogenic contribution for perylene through fluvial transport pathway (Liu et al., 2012). Therefore, the exact origin of perylene and its relationships with the land-based organic materials are still unclear in this river-dominated region.

In this study, to our knowledge, the large-scale occurrence of sedimentary perylene and its potential controlling factors in the coastal ECS was firstly examined. The main objectives are to

identify its possible sources with multiproxies approach, and to evaluate its potential as the sediment footprint for the indication of fluvial land-based SOM input and dispersal in the area.

2. Study area

The detailed regional setting of the ECS is available in the [Supplementary materials](#). Briefly, as the largest Asian river and third longest river in the world, the Yangtze River has been usually considered as the dominant supplier of particulate matter to the coastal ECS (Yang et al., 2006; Bianchi and Allison, 2009). The fluvial sediments and their associated materials are temporarily deposited in the Yangtze River estuary (YRE) and later resuspended and transported southward primarily along the inner shelf (DeMaster et al., 1985; Milliman et al., 1985). Approximately 32% of the Yangtze-derived sediments are believed to be accumulated in the inner shelf (Milliman et al., 1985; Liu et al., 2007), while 40% can be accounted for the sediments north of 30°N (DeMaster et al., 1985). The southward dispersal of the resuspended and fine sediments was reported primarily regulated by the hydrodynamic conditions in the coastal ECS (Milliman et al., 1985; Liu et al., 2006, 2007).

3. Material and methods

3.1. Sample collection

The locations of sediment samples were illustrated in Fig. 1. The sediment samples of E1–E20 and S1–S11 were collected by the *R/V Dong Fang Hong 2* of the Ocean University of China in June 2006,

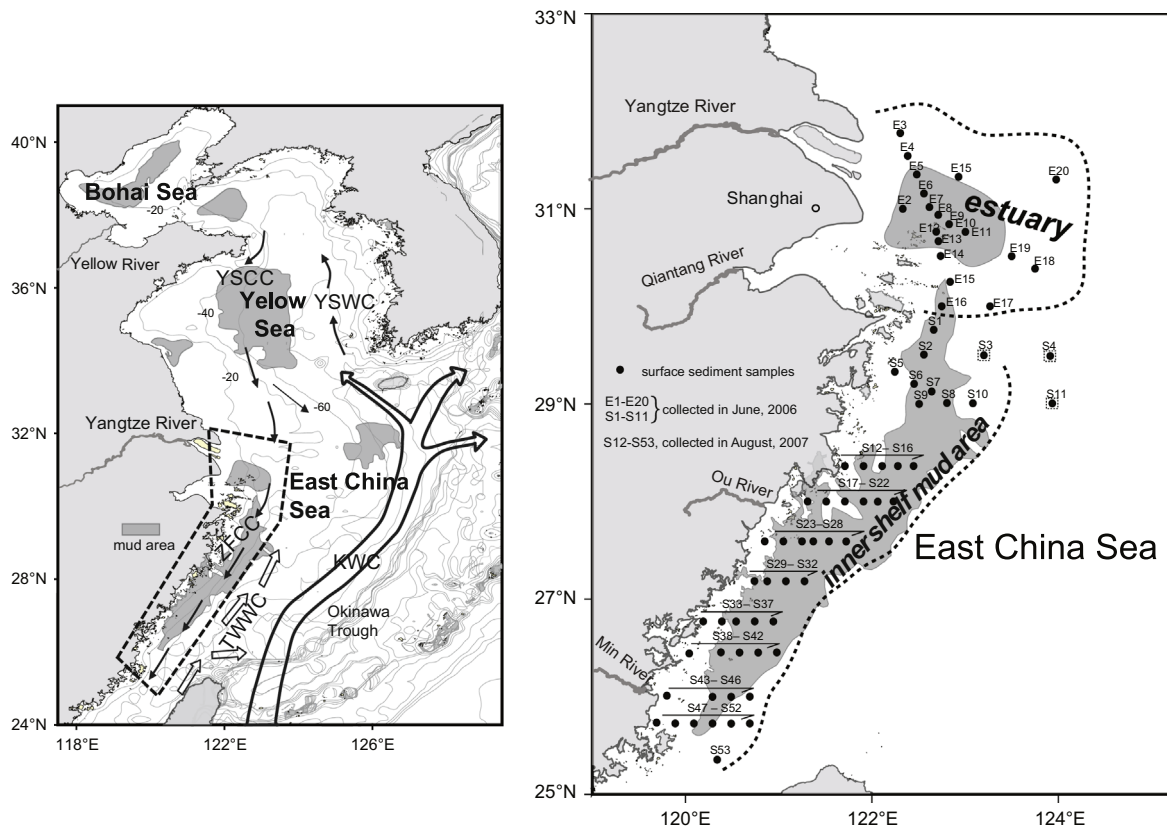


Fig. 1. Locations of the sampling sites and circulation in the ECS (circulation systems and mud areas are modified according to Liu et al. (2007)). The marked sites with rectangle (S3, S4 and S11) in the out sand area were chosen for the grain size normalized perylene abundances as the estuarine samples ($n=22$). KWC: Kuroshio Warm Current; TWWC: Taiwan Warm Current; ZFCC: Zhejiang-Fujian Coastal Current; YSCC: Yellow Sea Coastal Current; YSWC: Yellow Sea Warm Current.

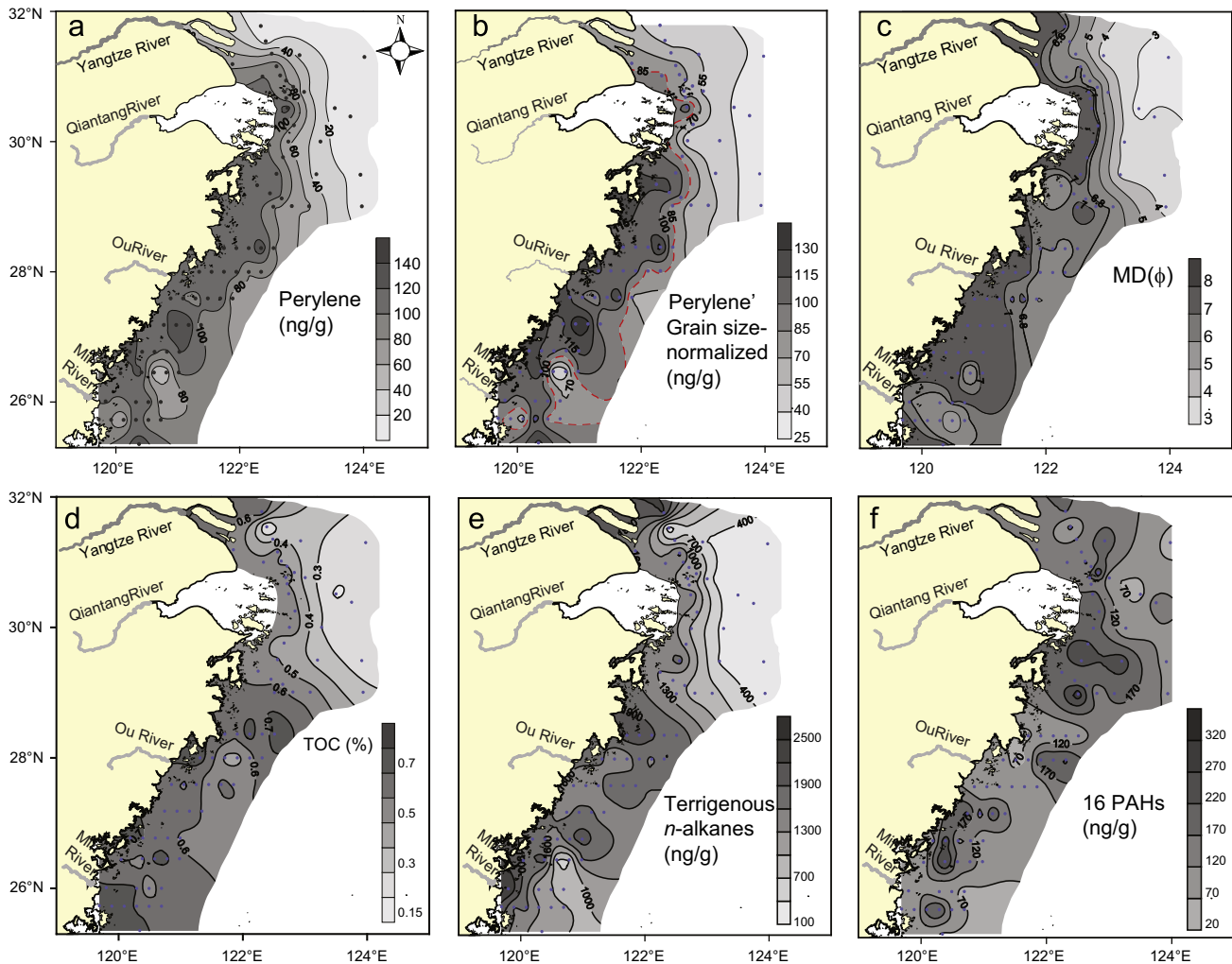


Fig. 2. Spatial distribution of perylene abundance (a), grain size normalized perylene concentration (perylene') (b), median diameters (Md) (c), TOC content (d), concentrations of 16 PAHs (e) and terrigenous *n*-alkanes and (f) in the surface sediment samples (the original datasets of these organic geochemistry proxies were available in the [Supplementary materials](#)).

and the remaining samples (S12–S53) were obtained by the *R/V Kan 407* in August 2007. The selected top layer/surface (0–3 cm) sediments were wrapped in aluminum foil and stored at -20°C until organic analysis.

3.2. Analytical procedure

The detailed analytical methods for TOC-based proxies and sediment grain size were provided elsewhere (Hu et al., 2009). The main analyzed molecular components were the aliphatic and aromatic hydrocarbons, and perylene as a 5-ring PAH compound, is the target compound in this work. The related PAHs and *n*-alkanes analytical procedures were provided in Hu et al. (2011a). Briefly, after extraction and column fractionation, the target fractions were eluted and reduced in volume and added hexamethylbenzene as an internal standard.

The GC/MS analysis was carried out with a 6890/5975 system from Agilent Technologies equipped with a DB-5MS capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). The sample was injected splitless with the injector temperature at 290°C . The MSD was operated in the electron impact (EI) mode at 70 eV and the selected-ion-monitoring (SIM) mode. Authentic standards of individual compounds including U.S. EPA proposed 16 priority PAHs (16 PAHs) and perylene as well as individual *n*-alkanes were used for quantification. The target

biomarker concentrations were calculated on the basis of their individual GC–MS ion responses compared with those of internal standards. Perylene were obtained under the selected ion mode (m/z 252 for perylene and m/z 264 for perylene- d_{12}) for quantification. The average surrogate recoveries were $71.5 \pm 11.2\%$ for naphthalene- d_8 ; $70.0 \pm 9.8\%$ for acenaphthene- d_{10} ; $86.2 \pm 12.3\%$ for phenanthrene- d_{10} and $90.1 \pm 10.5\%$ for perylene- d_{12} , respectively. The relative precision of paired duplicated samples was below 15% ($n=8$), and the targeted compounds were not detected in procedural blank.

4. Results

4.1. Sediment grain size and TOC-based proxies

The original data of the sediment grain size and TOC-based proxies (TOC, TN, $\delta^{13}\text{C}$) were from Hu et al. (2012) and presented in Table S1. Fine sediment was predominant in the YRE and the inner shelf mud, displaying a narrow band that extends southward along the inner-most area of the shelf with a finer grain size (6–7 Φ). The coarse deposits ($< 5 \Phi$) mostly occurred in the outer region off the YRE with a high sand fraction ($> 55\%$) (Fig. 2c). The average TOC content in the samples from the YRE mud areas ($0.55 \pm 0.06\%$) was relatively lower than that from the

Table 1

Occurrence of sedimentary perylene, sediment grain size, TOC-based indices, aliphatic and polyaromatic parameters for surface sediments over the estuarine area and inner shelf of ECS. (the origin detailed datasets of these parameters are available in the [Supplementary materials](#)).

Sediment samples	Perylene (ng g ⁻¹)	Perylene' (ng g ⁻¹)	Depositional flux of perylene' ng/cm ² /yr	16 PAHs (ng g ⁻¹)	2–3 rings PAHs (ng g ⁻¹)	4–6 rings PAHs (ng g ⁻¹)	ALKter% (%)	TOC (%)	C/N	Md (Φ)
Estuarine area										
Range (n=20)	7.4–130.5	26.4–112.9	39.6–277.6	53.1–552.6	34.1–233.1	13.1–568.2	20.4–61.4	0.17–0.70	9.01–13.44	2.51–7.34
Average	60.3 ± 35.6	57.2 ± 20.6	146.7 ± 79.1	161.9 ± 112.5	86.7 ± 51.1	75.2 ± 66.6	46.9 ± 12.9	0.44 ± 0.16	10.9 ± 1.1	5.8 ± 1.7
Southern inner shelf										
Range (n=53)	7.8–141.1	42.7–141.1	32.5–218.0	53.8–308.9	19.9–174.3	24.4–190.8	30.5–67.6	0.25–0.82	4.98–12.12	3.68–7.35
Average	95.2 ± 30.1	99.8 ± 23.4	117.2 ± 47.3	135.0 ± 70.0	58.8 ± 37.8	76.2 ± 42.8	52.8 ± 8.5	0.64 ± 0.12	7.2 ± 1.8	6.7 ± 0.9

ALKter%: the percentage of the “terrigenous *n*-alkanes (C₂₇, C₂₉, C₃₁ and C₃₃)” (Bouloubassi et al., 2001); perylene' is the grain size normalized perylene concentration in the estuarine area (including S3, S4 and S11).

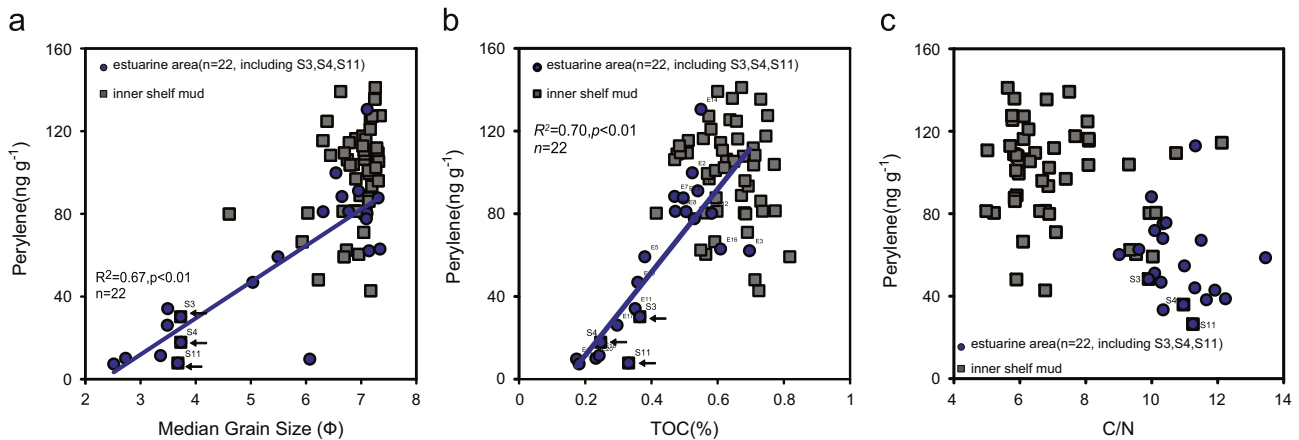


Fig. 3. The scatter plots of perylene abundance and median diameters (a), TOC content (b), and bio-plot of perylene' and C/N (c) in the surface sediment samples.

southern inner shelf ($0.64 \pm 0.09\%$), which corresponded to the increased alongshore trend to the south (Fig. 2d). The $\delta^{13}\text{C}$ in the majority of the estuarine samples in this study ranged from -24.6% to -20.6% , indicating a predominant fluvial terrigenous input of C₃ plants (Hu et al., 2012).

4.2. *n*-alkanes

Normal alkanes (*n*-alkanes), ranging from C₁₄ to C₃₅, occurred in all samples with an almost 10-fold range of concentration levels (Table S2). The sum of these most abundant *n*-alkanes (C₂₇, C₂₉, C₃₁ and C₃₃) related to biogenic terrigenous origins is defined as “terrigenous *n*-alkanes” (ALKter), exhibiting a relatively higher abundance in the fine sediment samples ($> 1000 \text{ ng g}^{-1}$) primarily located at the mud areas along the coastal ECS (Fig. 2e). The presence of high ALKter abundances and corresponding high proportions (ALKter%) could be explained by a predominant fluvial terrigenous OM input (Bouloubassi et al., 2001).

4.3. 16 PAHs

The original dataset of the 16 USEPA priority PAHs (16 PAHs) (Table S3) were reported by Lin et al. (2013). Spatially, the higher 16 PAHs abundance were observed ($> 170 \text{ ng g}^{-1}$) in the stretch between the YRE and the south of Hangzhou Bay (Fig. 2f). The relatively higher 16 PAHs concentration in the north of the inner shelf was inconsistent with the mentioned spatial variability of TOC and median diameter (Md).

4.4. Perylene

In this study, perylene ranged from 7.4 to 141.1 ng g^{-1} , with a mean of $86.3 \pm 34.7 \text{ ng g}^{-1}$ (Table 1), which was comparable to those previously reported in the estuarine area ($4.2\text{--}186.4 \text{ ng g}^{-1}$) (Bouloubassi et al., 2001). As compared to those from outer sand areas, higher perylene concentrations ($> 80 \text{ ng g}^{-1}$) occurred in the mud area in the YRE and extended along the coast of inner shelf to the south (Fig. 2a). Furthermore, accompanied by higher and less varied of TOC and finer grain size, the perylene abundance in the samples from the inner shelf ($95.2 \pm 30.1 \text{ ng g}^{-1}$) were also higher than those from the YRE ($60.3 \pm 35.6 \text{ ng g}^{-1}$) (Table 1), suggesting a direct control of the hydrodynamic forces on the perylene appearance likely due to the sorting process of the transported sediment (Hu et al., 2012).

5. Discussion

5.1. Distribution of perylene and the potential controlling factors

Since there existed a small variation of the perylene and grain size for the samples from the inner shelf mud area, and significant positive correlation between perylene and Md were only observed in the estuarine area (including sites S3, S4 and S11) (Fig. 3a). Thence, the grain size effect on the appearance of perylene within the southern inner shelf mud could be ignored, and only the perylene abundances in the estuarine samples were normalized by the grain size. The grain size-normalized perylene (perylene') concentrations ranged from 26.4 to 112.9 ng g^{-1} (Table 1), which

exhibited a similar spatial variability with its original one (Fig. S1). This result could demonstrate a dominant influence of the source dependent characteristics (*i.e.* the direct river input) on the perylene appearance in the coastal ECS.

Perylene should be usually correlated with TOC in sediments due to its relative low solubility and hydrophobic nature. However, in this study, as shown in Fig. 3b, the relationship between perylene abundance and the TOC content varied, which was significant only in the estuarine area, and by coupling with a separated grouping of the samples for the southern inner shelf, which showed relatively higher perylene abundances and lower C/N ratios (Fig. 3c). The inconsistency between the TOC and the high molecular weight (HMW) PAHs has also been observed before, which could be related to their heterogeneous origins and complicated hydrodynamic depositional process (Lin et al., 2013). The local supply of the algal-derived OM and the presence of the soil-derived and/or microorganism-related OM could change the composition of the SOM in this area (Hu et al., 2012); Furthermore, since the hydrodynamic sorting coupled with the resuspension and alongshore transport process in the coastal ECS is significant, the perylene could also be enriched during this process caused by the similar sorption affinity towards the fine particles due to their large specific surface area. Anyway, in addition to the direct source dependent characteristics, the hydrodynamic forces could also influence the relationships between perylene and the TOC-based proxies in this area.

5.2. Source identification of perylene in the surface sediments

5.2.1. A natural diagenetic origin: perylene versus anthropogenic PAHs

The relationships between perylene and the PAHs have been frequently applied to discriminate the natural diagenetic input of perylene from the anthropogenic combustion process (Silliman et al., 2001; Wu et al., 2001; Liu et al., 2012). In this study, no significant correlation was observed between perylene and the 16 PAHs (Fig. 4a). Similarly, the correlations between the different groups of PAHs (LMW PAHs and HMW PAHs) and perylene varied in the different area. The relationship between perylene and 2+3 ring PAHs was poor; while for the 4–6 ring PAHs and perylene, it was significant only in estuarine area in the north (Fig. 4b and c). As we noted above, insignificant correlation between the hydrophobic chemicals (*e.g.* PAHs, DDTs) and the TOC content could be explained by their heterogeneous origins and the complicated dynamics of the water (Hu et al., 2011b; Lin et al., 2013). Therefore, on the contrary, the observed significant correlation between perylene and HMW PAHs could be explained by either the resemblance of source characteristics or the same input pathway (*e.g.* river input) and migration path caused by the similar high sorption affinity nature (Lin et al., 2002; Zhao et al., 2013). In fact, natural diagenetic formation for perylene could be identified based on its high proportion relative to the 5-ring PAHs (> 70%, see below). Thence, the consistence of perylene and the anthropogenic PAHs indicated that they were more likely to share the same fluvial input pathway and migration path in the coastal ECS rather than the common pyrogenic origin.

The proportion of perylene relative to the total 5-ring PAHs ranged from 40% to 94%, with an average of $73 \pm 11\%$ and $80 \pm 10\%$ for the samples in the estuary and inner shelf, respectively (Fig. 5). This provides a reasonable evidence for the dominance of natural diagenetic input of perylene in the study area (Baumard et al., 1998; Fan et al., 2011). The relatively higher proportion of perylene towards the PAHs in the recent coastal sediments off China has also been observed, such as the Bohai Sea (Hu et al., 2011a), the Yellow Sea (Wu et al., 2001), the Pearl River Estuary and the

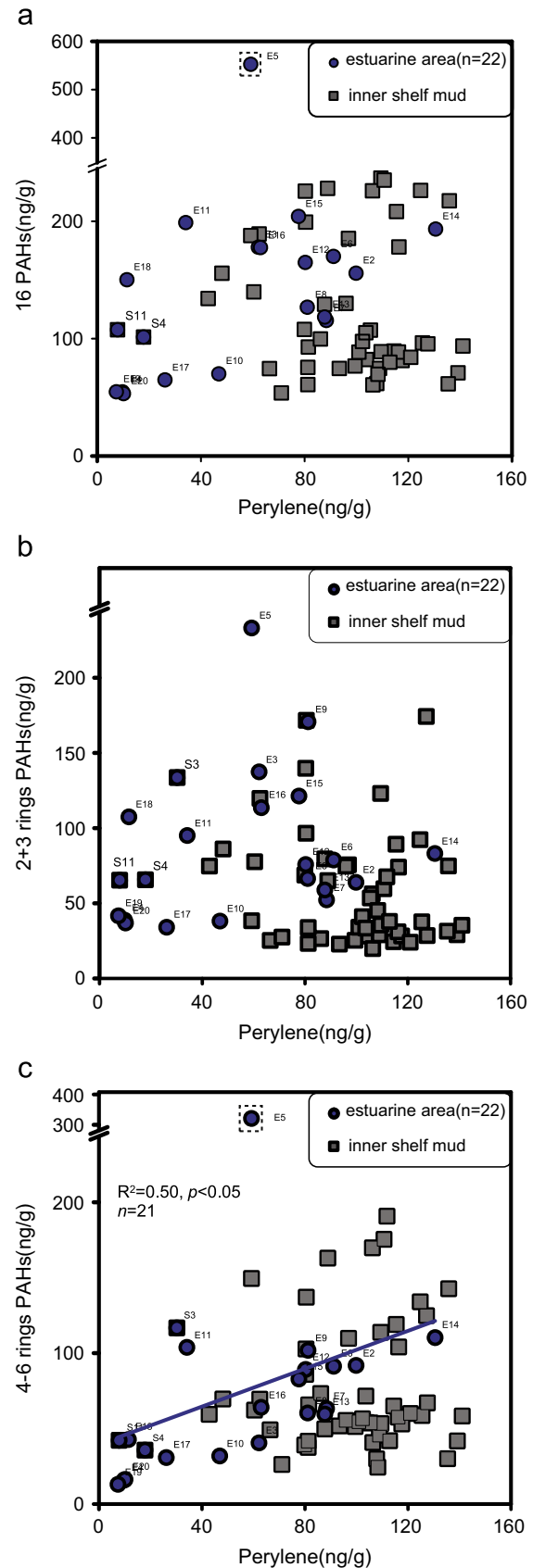


Fig. 4. Correlation between sedimentary perylene and total PAHs (a), LMW PAHs (2–3 rings) (b) and HMW PAHs (4–6 rings) and (c) in the surface sediment samples.

adjacent South China Sea (Mai et al., 2001; Luo et al., 2006), which indicated a widespread natural origins primarily linked to the allochthonous input, and therefore, the presence of perylene were

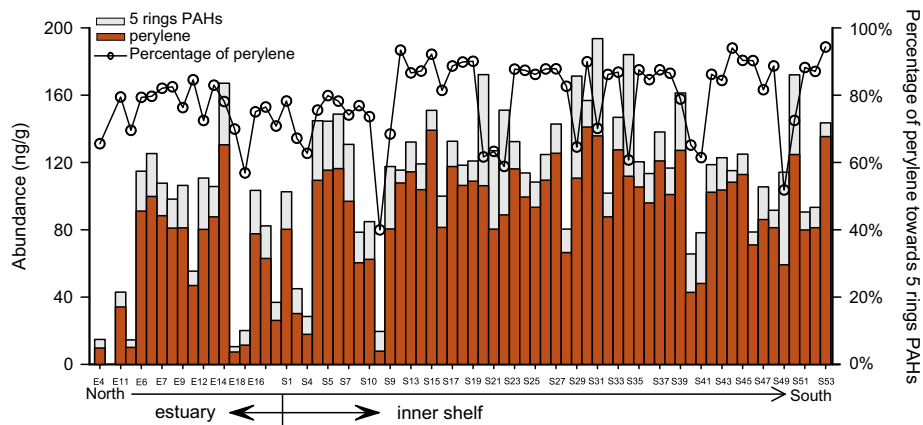


Fig. 5. Stacked histograms and scatter plot showing the abundance of sedimentary perylene, total 5 rings PAHs and the relative percentage of perylene.

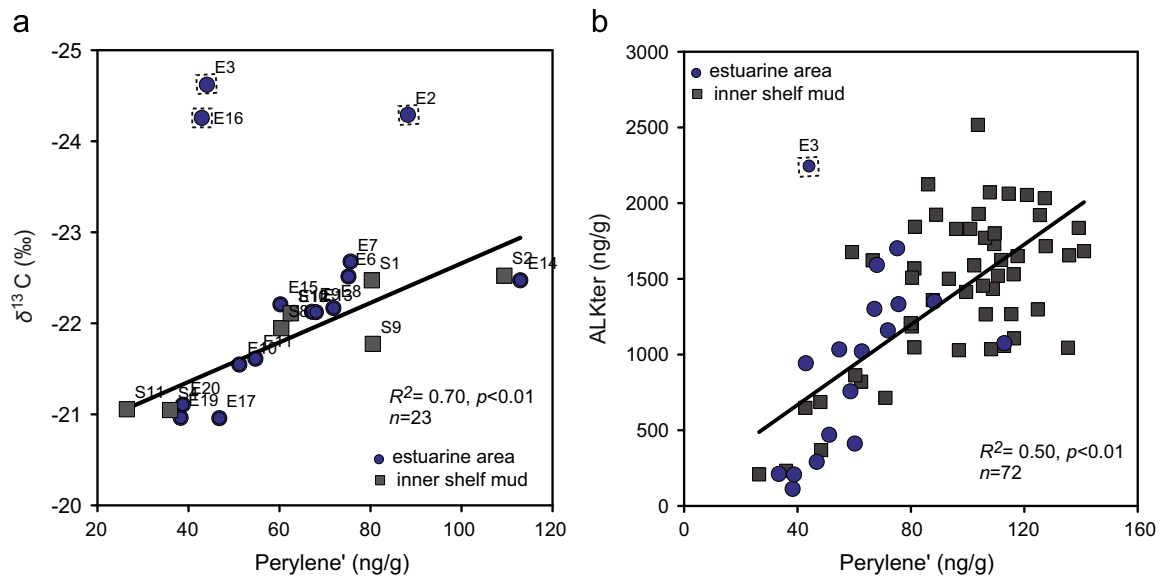


Fig. 6. Correlation of sedimentary perylene with these terrigenous-related indices in the surface sediment samples.

likely to be a potential terrigenous input indicator on these continental margins (Aizenshtat, 1973; Bakhtiari et al., 2009; Itoh et al., 2010).

5.2.2. Terrigenous OM input in relation with the perylene appearance in the surface sediments

Significant correlations were observed between perylene' and the available terrestrial input proxies (Fig. 6), pointing out that the origin of perylene in this work was likely of natural diagenetic process upon the fluvial input of land-based OM. This is consistent with the observed high abundance of sedimentary perylene with significant land-based OM (e.g. soil-derived materials) inputs (Boonyatumanond et al., 2006; Bakhtiari et al., 2009; Itoh et al., 2010). Furthermore, in this area, high perylene abundances were also observed in the surrounding matrices outside the sediment environment, such as the ambient soils (Liu et al., 2008), the suspended particles in the rivers (Sicre et al., 1993; Bouloubassi et al., 2001). This could demonstrate a predepositional fluvial input of perylene in the coastal ECS. In fact, the pre-formation of perylene outside the sediment compartment has also been reported elsewhere (e.g. Bertrand et al., 2013 and references therein). Gocht et al. (2007) elucidated the formation of perylene within a terrigenous sub-soil environment, which suggests that perylene is pre-formed during degradation of wood and/or with woody

debris before deposition. Significant amounts of perylene were detected in termite nest in tropical top soils, indicating a possible association with termites and/or their wood substrate (Wilcke et al., 2002; Bakhtiari et al., 2009). As we know, the termite damage in the southeast China including the drainage basin of the Yangtze River was much more serious than those in North China (Hu et al., 2004), this could be partially responsible for the higher concentrations of perylene in this work as compared to those in the Bohai Sea ($\sim 15 \text{ ng g}^{-1}$, our unpublished data) from the northern China.

On the other hand, based on its distinctive sedimentary depth profile, the common idea for the diagenetic mechanism of perylene in sediments was in situ formation after the deposition through diagenetic alteration of its natural biogenic precursors under reducing conditions (Orr and Grady, 1967; Wakeham et al., 1979; Silliman et al., 1998; 2001; Itoh et al., 2010; Bertrand et al., 2013). Although the exact natural precursor materials for perylene have not been confirmed, one of the leading hypothesis is that its precursor could be attributed to the terrigenous materials (Aizenshtat, 1973; Ishiwatari et al., 1980; Jiang et al., 2000; Grice et al., 2009; Itoh et al., 2012; Bertrand et al., 2013), while other viewpoint suggests that it could be originated from the autochthonous OM from algal and crinoids production (Wakeham et al., 1979; Venkatesan, 1988). Recently, the $\delta^{13}\text{C}$ of perylene provided the evidences that perylene was originated from wood via wood-degrading fungi (Jiang et al., 2000; Grice et al., 2009;

Marynowski et al., 2013), and the degradation of lignin by fungal and bacterial activities in a more oxidizing conditions could also enhance the subsequent formation of perylene (Bertrand et al., 2013). It was also reported that the 4,9-dihydroxyperylene-3,10-quinone (DHPQ) as the parent compound of perylene was observed in the widespread fungal component (*C. geophilum*) that existed in the humic acids soils (Itoh et al., 2012).

In this work, considering the middle-lower reach of Yangtze River basin is characterized by the warm and moist climate especially in rainy season, the significant terrigenous influx of land-based OM (e.g. soil-derived OM) delivered by the fluvial and/or surface runoff were likely related to the introduction of high abundance of perylene and/or its biogenic precursors in the coastal environment (Zhu et al., 2011; Bao et al., 2014). It has been reported that the estuarine-inner shelf of the ECS is a major

depository of the fluvial sediments and their associated terrigenous organic materials (Liu et al., 2007; Hu et al., 2012; Zhao et al., 2013). Therefore, the widespread and significant amount of perylene in the large-scale coastal ECS could reflect a predepositional terrigenous input of perylene and/or its natural precursors with the land-based SOM origins, which could be both tied to the fluvial control on its appearance in this area.

5.3. Provenance of sedimentary perylene in the coastal ECS: a potential indicator to assess the sediment footprint of large river influence

It was reported that soil-derived OM could contribute approximately 50% to the suspended OM within the lower reach of the Yangtze River (Bao et al., 2014). In the coastal ECS, the presence of

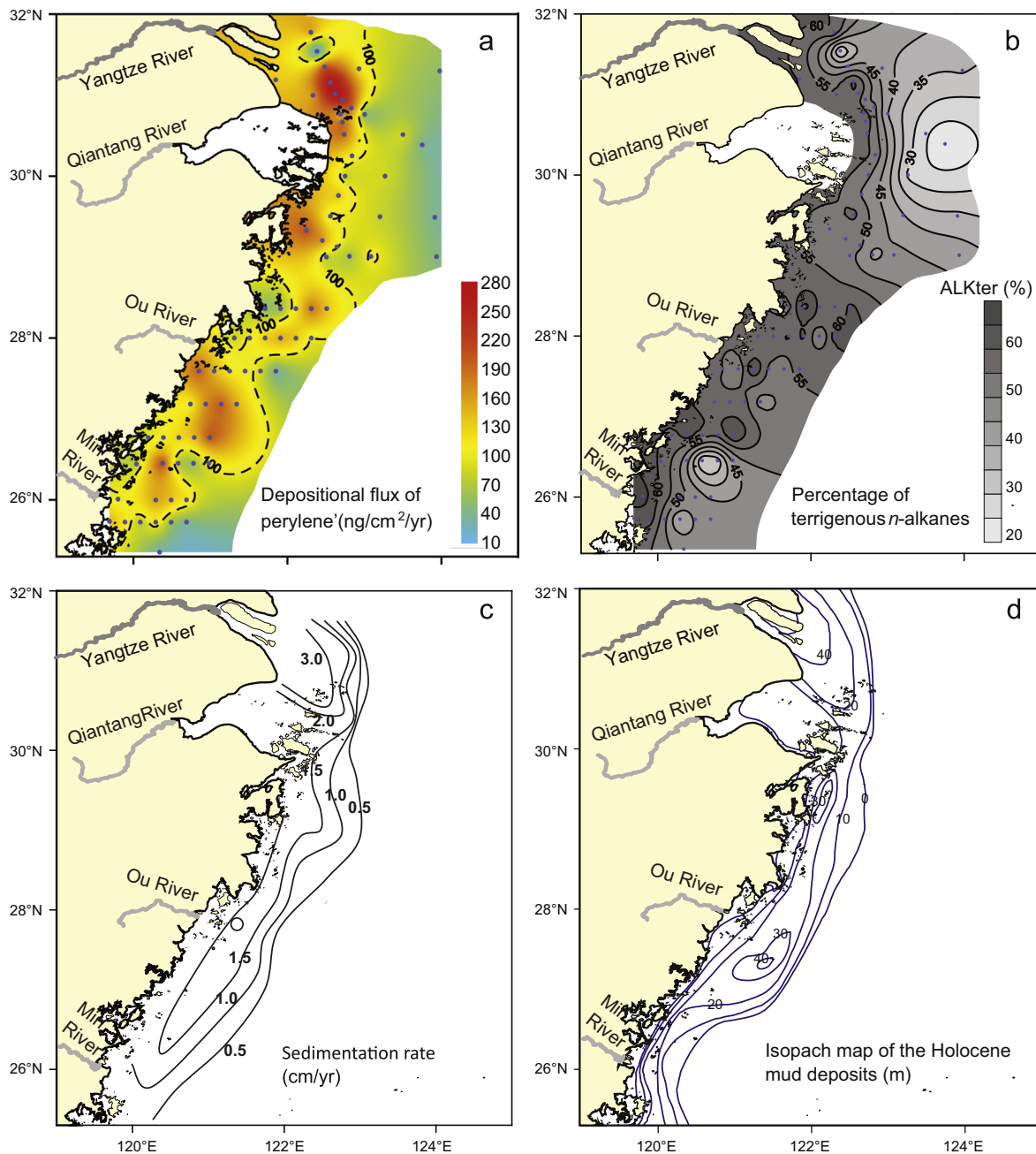


Fig. 7. Deposition flux of perylene' (a) with indication for the fluvial input impact on the benthic environment over the estuarine-inner shelf of ECS by coupling with the spatial distribution of ALKter% (b), modern sedimentation rates (c) and corresponded isopach map of Holocene mud deposits (d) (the spatial variability of sediment rates and the isopach map were referred from Liu et al., 2006, 2007).

the soil-derived OM from the catchment could also be evidenced by the degradation of the riverine branched GDGTs (glycerol dialkyl glycerol tetraether) (Zhu et al., 2011), the appearance of the soil-released pollutants input (Lin et al., 2012) and the elemental signatures of the bulk SOM (Hu et al., 2012). Besides the dominance of direct river input, the speciation of the transported SOM during the migration process could also be associated with the presence of soil-derived OM in the southern inner shelf area (Hu et al., 2012). Furthermore, the high abundance of perylene in the southern inner shelf regime could also be partially attributed to the impacts from the adjacent local rivers (*i.e.* the Qiantang River, the Ou River and the Min River). It was reported that the soil-derived hydrophobic chemicals could be transferred into the coastal ECS through these coastal rivers (Hu et al., 2011b). Although their relatively low sediment load as compared to the Yangtze River discharge, the coastal rivers can contribute to the presence of perylene in the mud deposits, especially during the typhoon storms in the flood season. The water discharge of the Ou River could rise up to 1100 times more than that during the dry season (Qin et al., 1996). Therefore, the impact of these major coastal rivers for the perylene appearance in the coastal ECS could not be ignored. Anyway, the provenance of perylene in the surface sediment samples from the coastal ECS was likely a combination of predepositional fluvial input and introduction of its potential precursors with land-based OM origins, and these two points could both support the clear link with the impact of fluvial input of sediments.

The deposition flux of perylene in the coastal ECS was estimated according to the estimated procedures from Lin et al. (2013) (see Supplementary materials). Spatial variation of the deposition flux of perylene was shown in Fig. 7a, displaying a narrow band type trend along the coast. Higher average flux of perylene was observed in the estuarine area (~ 150 ng/cm²/yr) than that in the inner shelf (~ 117 ng/cm²/yr) due to the riverine sediment input from the Yangtze River, revealing the dominant impact of the proximity to the direct land-based OM inputs on the perylene appearance in the estuarine area. Therefore, the deposition flux of perylene could be potentially as a sediment footprint to indicate a direct fluvial input of sediments and associated materials in this area. As noted above (*e.g.* Tesi et al., 2007; Hu et al., 2012), the coastal rivers' inputs and the relocalization of the more degraded terrestrial OM during the migration process are responsible for the alongshore southward high perylene influx (Fig. 7a), these results provide evidence that the perylene could also be potentially served as imprint not only for the influence of the initial river sediment inputs but also for its subsequent remobilization (Fig. 7a). Coupling with the spatial distribution of plant-derived hydrocarbon, modern sedimentation rates and isopach map of the mud deposits (Fig. 7), the deposition flux of perylene could be applied to assess the sediment footprint of the influence of fluvial input on the coastal ECS, which could also be an indicator to infer the transport pathway and preservation of terrigenous SOM on the river-dominated continental margins. Furthermore, this results could also imply that perylene in sediments will be valuable to provide more information for terrigenous input contribution in the reconstruction of paleoenvironments.

6. Conclusions

In addition to the coastal fluvial input, the high abundance of perylene observed in the southern inner shelf was also controlled by the sorption affinity towards the transported finer sediments under the hydrodynamic conditions. The consistence of perylene and anthropogenic PAHs indicated that they were more likely to share the same fluvial input pathway and migration path in

the coastal ECS with the similar high sorption affinity towards the fine particles rather than the common pyrogenic origin. Higher proportions of perylene towards the total 5-ring PAHs and its significant correlation with terrigenous input proxies were observed in the coastal ECS. These results could link the perylene appearance with a combination of the predepositional fluvial input and the diagenetic production from its natural precursors with land-based SOM origins. The deposition flux of perylene could be served as a potential terrigenous input indicator to assess the sediment footprint of the river input influence in the coastal ECS.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.csr.2014.04.014>.

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