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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.

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 (δ^{13}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,

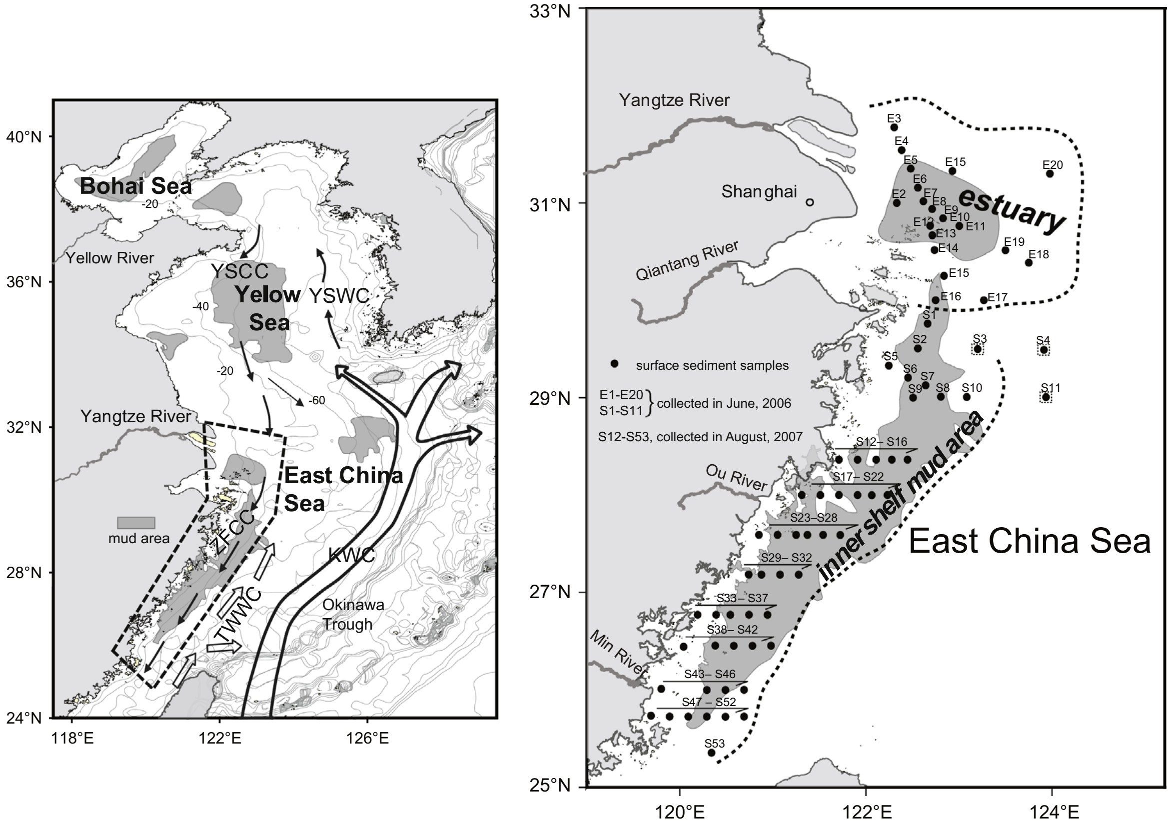

Fig. 1. Locations of the sampling sites and circulation in the ECS (circulation systems and mud areas are modified according to Liu et al. (2007)). The marked sites with rectangle (S3, S4 and S11) in the out sand area were chosen for the grain size normalized perylene abundances as the estuarine samples (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.