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RESEARCH ARTICLE

Polycyclic aromatic hydrocarbons in the largest deepwater port of East China Sea: impact of port construction and operation

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Abstract PAHs were analyzed for samples of seawater, sediment, and oyster (*Saccostrea cucullata*) collected from Yangshan Port, East China between 2012 and 2013. Concentrations of ∑PAHs in seawater (180–7,700 ng/L) and oyster (1,100–29,000 ng/g dry weight (dw)) fell at the higher end of the global concentration range, while sediment concentrations (120–780 ng/g dw) were generally comparable to or lower than those reported elsewhere. PAHs in the particulate phase accounted for 85 % (52–93 %) of the total PAHs in seawater. Congener profile analysis revealed that PAHs in waters originate mainly from petrogenic sources, while high-temperature combustion processes are the predominant sources for sediment. ∑PAHs in oyster well correlated with ∑PAHs in the particulate phase, suggesting particle ingestion as an important pathway for bioaccumulation of PAHs. Cancer risk assessment of PAHs in oyster indicated high human health risks posed by these chemicals to the coastal population consuming this seafood.

Keywords Polycyclic aromatic hydrocarbon · Suspended particulate matter · Source diagnosis · *Saccostrea cucullata* · Bioaccumulation · Cancer risk

Introduction

Yangshan Port, the largest deep water port in East China Sea, was built to expand the Port of Shanghai limited by shallow water nearshore (Fig. 1). As the shipping center of China (Shanghai) Pilot Free Trade Zone, the port was planned to have had over 30 berths with a handling capacity of 13 million transmission extension units by 2020. With the completion of the Yangshan Port project, the container throughput of the Port of Shanghai ranked first in the world in 2013 (SISC 2013). Yangshan Port was built on the two islands, Dayang and Xiaoyang, and was connected to a supplementary park by 32-km Donghai Bridge. The supplementary park includes the check zone, supplementary operation zone, and operation zone for hazardous goods in the port, covering an area of 610, 000, 450,000, and 60,000 m^2, respectively. The port is also adjacent to the Zhoushan fish ground, which is among the four most important marine fish culture zones of China. Over the past decade since Yangshan Port was operated, hydrodynamics, suspended particulate matter (SPM) settlement, and sediment dredging have been the focus of previous studies to ensure the navigational depth and safety (Zuo et al. 2009, 2012; Wang et al. 2013). With the increase in port handling capacity, intensive human and port activities are likely to introduce a large quantity of chemical pollutants to the port and then pose a threat to the marine system and fishery sources. However, there are few studies on hydrophobic organic contaminants including organochlorine pesticides, polychlorinated biphenyls, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in seafood from Zhoushan fish

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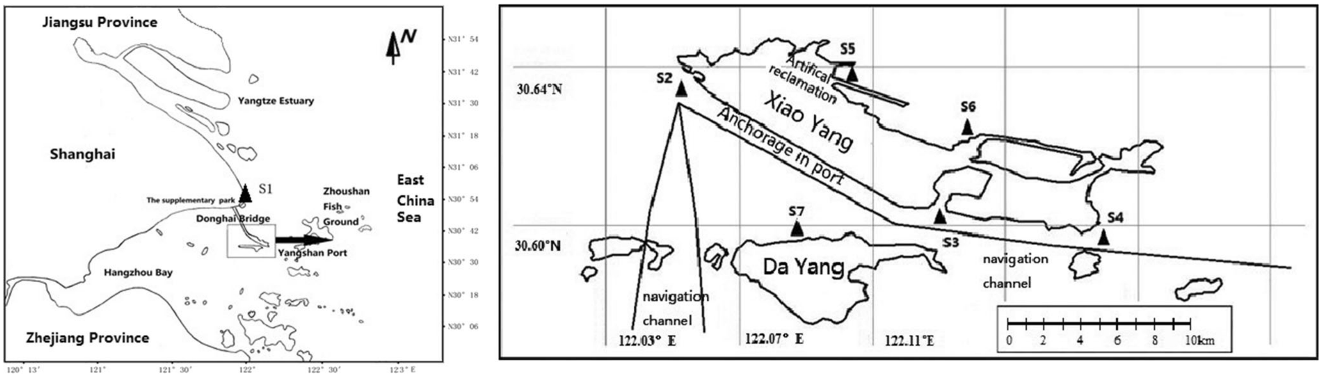

Fig. 1 Position of Yangshan Port in East China and the sampling sites in the Port waters

ground adjacent to the port (Wang et al. 2014, 2015). Little was known about petroleum-associated chemicals, such as polycyclic aromatic hydrocarbons (PAHs), introduced during port construction and operation (Orecchio et al. 2010). These compounds may also pose threats to the marine ecological system, fishery resources, and human health via seafood consumption.

Distribution, transport, and fate of PAHs in port/harbor area were conducted in many studies due to public concerns on their adverse effects (Wang et al. 2001, 2010; Basheer et al. 2003; Sprovieri et al. 2007; Casado-Martínez et al. 2009; Abdollahi et al. 2013). Atmospheric deposition, surface runoff, oil spillage, and leakage are major pathways of PAHs to reach seawater (Wang et al. 2001; Huang et al. 2011; Castro-Jiménez et al. 2012). After entering port water, PAHs tend to bind SPM and settle to sediment due to their low solubility and high hydrophobicity. Sediment-bound contaminants are generally considered as persistent and of low bioavailability. However, under specific hydrodynamic conditions or in the presence of bioturbation, PAHs can be re-suspended or redissolved and become bioavailable (King et al. 2004; Martins et al. 2013). Organisms living in PAH-contaminated environment can uptake these compounds through their body surface and gills or by ingestion of contaminated sediment or SPM, and then transfer PAHs across the aquatic food web (Patrolecco et al. 2010). Benthic organisms, such as bivalves and crustaceans, which typically feed on phytoplankton or organic debris, have a low level of enzyme systems capable of metabolizing hydrophobic organic pollutants such as PAHs (León et al. 2013). As a consequence, a relatively high degree of bioaccumulation and toxicity of these organic compounds would occur after they enter organisms. Therefore, knowledge about the concentration and distribution of contaminants in different compartments and bioaccumulation is crucial in assessing the marine water quality.

To date, no systematic study on PAHs in Yangshan Port has been conducted, thus limiting a comprehensive understanding of the source, distribution, and associated risks of these contaminants in the port waters. Therefore, this study aimed (1) to provide the baseline data of PAH contamination in various environmental media in the waters of Yangshan Port, (2) to benchmark the PAH levels in Yangshan Port via comparisons with those reported in other ports across the world and relevant quality guidelines, (3) to identify potential sources of PAHs to inform decision-making regarding environmental management and quality protection of port waters, (4) to understand the fate of PAHs including accumulation in intertidal organisms and sorption to sediment and SPM, and (5) to evaluate human health risks via consumption of oyster (*Saccostrea cucullata)* from this region.

Materials and methods

Sampling site description

Yangshan Port is characterized by high content of SPM with remarkable seasonal variations (high in winter and spring and low in summer and autumn with annual average concentration of 750±420 mg/L). Seawater temperature ranges from approximately 5.0±0.5 °C in winter to 26±2.9 °C in summer. Seasonal variation in salinity is small (from 15 to 23) (Li and Chen 2002; Zuo et al. 2012).

In the present study, samples of seawater, sediment, and *S. cucullata* were simultaneously collected at low tide at seven locations in June 2012 and 2013 from Yangshan Port waters (Fig. 1). The sampling season coincided with high biomass in summer. The sites were selected to cover areas of different functional and regional characteristics throughout the processes of shipping and construction activities in the ports (Table SI-1), thus allowing for a comprehensive assessment.

Sample collection and preparation

Grab samples of surface seawater (4 L for each site) were collected and placed in pre-cleaned glass bottles. Five grams of NaCl and 10 mL methanol were added to 1-L surface seawater after filtration through 0.45-μm membrane (hybrid fiber membrane). PAHs were extracted by solid phase extraction using C18 cartridge (Supelclean, China) preconditioned with 5 mL methanol and distilled water. The flow rate of the sample through the cartridge was 8 mL/min, and the cartridge was dried under vacuum condition after extraction. PAHs in the cartridge were eluted with 15 mL dichloromethane. Finally, the extracts were reduced to1 mL under a gentle stream of nitrogen gas (Wu et al. 2011).

Intertidal surface sediment samples (about 2 kg wet weight each, approximately 5 cm in depth) were collected underwater at low tide with a stainless steel shovel. At each site, three subsamples were collected within a 200-m range and combined to one composite sample. Samples were fortified with sodium azide (NaN_3, 0.1 % based on sediment dry weight (dw)) and well-homogenized manually using a glass rod. Sediment were freeze-dried after sieving through a 200-mesh and stored at −18 °C, and then analyzed within 3–4 weeks. Sediment extraction and clean-up followed the protocols given in USEPA standard methods and slightly modified as follows (Fang et al. 2003). Briefly, 2 g of freeze-dried sediment was soxhlet extracted in a solvent mix of hexane and acetone (1:1, *v*/*v*) with the addition of activated copper for desulfurization at 65 °C for 24 h. Extract was reduced to approximately 10 mL by rotary evaporation and cleaned up by a silica gel column filled with 8 g of neutral silica, 4 g of alumina, and 4 g of anhydrous sodium from bottom to top. The column was eluted with 45 mL of *n*-hexane/dichloromethane (3:7, *v*/*v*) to retrieve PAHs. Extracts were finally evaporated to1 mL with purified nitrogen gas.

The SPM samples collected on the filter membrane via seawater filtration were extracted and cleaned up using the same procedure as described for intertidal surface sediment.

At each site, oysters of similar size ($n=10-20$) were sampled from rocks using a chisel and hammer, wrapped in aluminum foil, and transported with ice blocks in a cooler box to the laboratory. Soft tissue was picked out with bamboo tweezers and homogenized. The tissue homogenate was mixed with 5 g of anhydrous sodium and 150 mL of dichloromethane. Tissue samples (equivalent to 2 g dw) were extracted at 65 °C on soxhlet for 24 h with a solvent mix of hexane and acetone (1:1, *v*/*v*). Extracts were reduced to approximately 10 mL on a rotary evaporator and purified with activated copper and florisil column (8 g of florisil baked at 600 °C for 4 h in muffle furnace and 2 g of copper powder activated with 1 M HCl to fill in a 30-cm column from bottom to top). The column was eluted with 20 mL of dichloromethane to retrieve the fractions containing PAHs. Extracts were finally reduced to 1 mL under a gentle stream of nitrogen gas (Fang and Wang 2007). *S. cucullata* were selected as a bioindicator of Yangshan Port for two main reasons. The first is high enrichment capability on heavy metals in this area (other studies in our group), and the second is *S. cucullata* is often consumed by coastal residents.

Instrumental analysis

PAH compounds were identified and quantified using Agilent 7890A/5975C ion trap mass spectrometer. The GC is equipped with a 30 m DB-5 column (30 m×0.25 mm×0.25 μm) with a constant flow (1.2 mL/min) of helium as carrier gas. Two microliter sample extract was injected in splitless mode. The oven temperature was programmed from 100 to 190 °C at a rate of 15 °C/min, then to 215 °C at 6 °C/min, further to 280 °C at 20 °C/min and held for 10 min, and finally increased to 310 at 20 °C/min and held for 2 min. The injector temperature was 280 °C. Total PAHs (∑PAHs) was calculated as the sum of 16 priority congeners for each sample type.

QA/QC

All data were subjected to strict quality control procedures. Deuterated internal standards were used to compensate for losses involved in the sample extraction and clean-up. The 16 US-EPA priority PAHs were naphthalene (NAP), acenaphthylene (ANY), fluorene (FLU), acenaphthene (ANA), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), chrysene (CHR), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBA), indeno[*1,2,3-cd*]pyrene (IPY), and benzo[*ghi*]perylene(BPE). Standard solutions of PAHs were run at the beginning of sample analysis to determine the relative response factors and evaluate peak resolution. Each sample was analyzed in triplicate. Instrumental limits of detection (LOD) were determined as three times the background signal. Method detection limits and the recoveries for PAHs in dissolved water, SPM, sediment, and oyster were listed in Table SI-2.

Results and discussion

PAHs in seawater

Levels and spatial distribution

In the dissolved phase, ∑PAHs concentrations ranged from 110 to 860 ng/L (Table SI-3), while ∑PAHs concentrations in SPM were much higher (from 120 to 11,000 ng/g dw) than those in the dissolved phase and varied greatly among neighboring sites (Table SI-4). The lowest total concentrations of PAHs were observed in S1 ($\sum PAHs_{dissolved}+\sum PAHs_{SPM}=180\pm4.2$ ng/L), which is in supplementary park and is approximately 40 km away from the port. The sampling site is 5 km away from the outlet of Dishui Lake (the total area is 5.6 km^2 and storage capacity is 16 million m^3) located in the supplementary park. PAHs carried in lake drainage could be a potential source. Additionally, the development of transport infrastructures and surrounding towns introduced PAHs into seawater (Mei et al. 2013). The concentrations of total PAHs in seawater (∑PAHs$_{\text{dissolved}}$+∑PAHs$_{\text{SPM}}$) at sites located in the north of Xiaoyang island (7,700±890 and 3,800±570 for S5 and S6, respectively) were far higher than those observed in the south of the island (890–1,800 ng/L for S2-4 and S7). The greater contamination in the north can be attributed to the more intensive port activities and associated incidents in this area (e.g., large-scale reclamation works near S5 and fuel leakage from three large oil tanks near S6 in 2010–2012). All these events contributed multiple emission sources of PAHs into the surrounding waters. In addition, reclamation along the northern land border of Xiaoyang significantly modified the hydrodynamic circulation in this intertidal zone, thus attenuating the spread of PAHs and leading to high localized contamination (Zuo et al. 2009).

Composition profile

The composition of PAHs in the dissolved and particulate phase did not vary much in all the sampling sites except S1 (Fig. 2), indicating common sources over the whole port area. The PAH profile was dominated by lower molecular weight (LMW) congeners (two- and three-ring PAHs), and NAP and ANY are the most abundant individuals (Table SI-3 and SI-4). The ratio of high molecular weight (HMW) PAHs such as four-ring congeners were more enriched in the SPM (18–65 %) than in the dissolved phase (0.28–34 %), which is expected because of the relatively low water solubility and tendency of the HMW congeners to sorb on SPM due to their high organic carbon–water partition coefficients (K_{oc}). S1 is approximately 40 km away from the port and thus a different contamination scenario is expected. Different composition profiles of PAHs, i.e., higher abundance of HMW congeners such as four-ring PAHs, are closely related to local point sources including lake drainage and transportation. Ongoing research in our group on PAHs in Dishui Lake showed that ∑PAH concentrations in the lake drainage were in the range of 71–180 ng/L with the dominance of HMW PAHs such as four- and five-ring congeners (unpublished data). Fuel combustion in transportation can be a potential source for HMW PAHs.

PAHs in the particulate phase accounted for approximately 85 % (52–93 %) of the total PAHs in seawater (∑PAHs$_{\text{dissolved}}$+∑PAHs$_{\text{SPM}}$), which is much higher than those observed in other ports/harbors or similar functional areas (Table 1). Yangshan Port is located in the south of Yangtze Estuary and receives a large amount of fine size and silty-clay particles carried by upstream fresh water into the East China Sea (Wang and Lu 2010), thus leading to a particularly high content of SPM in adjacent waters (from 170 to 1300 mg/L, Tables 1 and SI-4). These SPM in seawater hardly settle to sediment due to the hydrodynamic characteristics in the port area (Shi et al. 2003; Feng et al. 2014). Therefore, SPM, instead of intertidal surface sediment, has become the preferential carrier for PAHs discharged in seawater. The results suggest that particle-associated PAHs are in fact the main form of these chemicals present in the seawater, and this form of PAHs are strongly bound and not easily influenced by further partitioning between the particles and water. However, particle–water partitioning of PAHs, including sorption and desorption of PAHs between the dissolved phase and the particulate phase are largely affected by the environmental conditions. Once environmental conditions change, SPM may serve as a secondary source via desorption of PAHs from their surface or directly ingestion by filter-feeding organism.

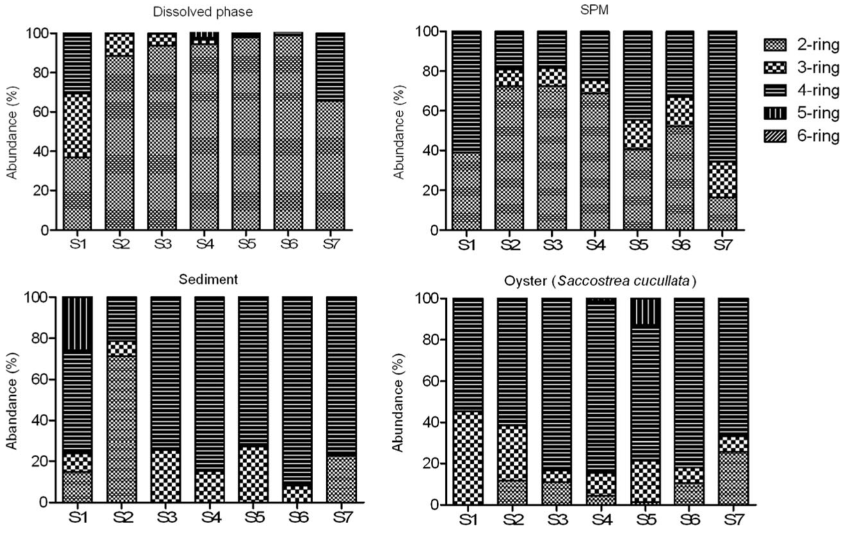

Fig. 2 Composition profiles of PAHs in various environmental media in Yangshan port

Global comparison

PAH concentrations in both dissolved and particulate phases were lower than those previously reported in the adjacent Yangtze estuary (Table 1), in which sampling sites were along the coast and local land-based pollution sources were the main reasons for high levels of PAHs (Wang 2013b). However, ∑PAHs in the dissolved phase and SPM, respectively, were 1–2 orders of magnitude higher than those reported in other regions, such as ports in Italy, France, Spain, and Singapore (Table 1), and PAH concentrations in Yangshan Port were also much higher than those in the Zhoushan fish ground (Fang 2007). These comparisons suggest that current PAH contamination levels in Yangshan Port are relatively high and PAH contamination does exist in the port area. Although Yangshan Port has only 10 years of history, the higher levels of PAHs in the water phase may be associated with the point source emission from ongoing intensive construction projects at certain sites of the port and subsequent rapid diffusion in the seawater. Furthermore, Yangshan Port is located in Shanghai and surrounded by most economically developed provinces, including Jiangsu and Zhejiang in the north and south, respectively, where land-based contaminants are discharged into East China Sea (Fang 2007; Wang 2013b). In our ongoing research, we are working toward a better understanding of the relative contribution of port activities to PAH contamination in the local marine environment.

PAHs in sediment

The PAH concentrations in sediment ranged from 120 to 780 ng/g dw, which were 1–2 orders of magnitude lower than those in SPM (Table SI-4 and SI-6). The spatial pattern of PAHs in intertidal surface sediment was similar to that of water phase, that is, samples from the north of Xiaoyang island have higher PAH concentrations than those from the south. Smaller variability was observed with PAH concentrations in sediment compared to that in SPM, as sediment is believed to be long-term sinks and reflect the long-term equilibrium. The relative abundance of PAH congeners in sediment was different from that in water (Fig. 2). HMW congeners are the dominant compounds due to their hydrophobicity and tendency to sorb on sediment. Four-ringed PAHs were abundant in surface sediment except S2 with BaA being the most. A similar pattern of PAH contamination has been observed in adjacent areas and South China (Fang et al. 2003; Yan et al. 2009).

Yangshan Port falls at the low end of the sediment PAH concentration range reported worldwide (Fig. 3a). Similar to the adjacent Yangtze Estuary and Zhoushan fish ground, PAH levels in sediment from the port are generally 1–2 orders of magnitude lower than those in ports/harbors in developed countries or regions and can be generally classified as moderate pollution level according to the ranking scale proposed by Baumard et al. (1998). As sediment is a long-term sink for hydrophobic chemicals, the lower levels of PAHs in the sediment may reflect the relatively short history of Yangshan Port compared to others worldwide. Meanwhile, the differing concentrations among sampling sites may be related to the local projects, such as sediment dredging and artificial reclamation. We compared the sediment PAH levels with two widely used sediment quality guidelines (SQGs), i.e., effects range low (ERL) and effects range medium (ERM) on the basis of the Biological Effects Database for Sediment (Long et al. 1995) as well as the threshold effect level (TEL) and probable effect level (PEL) used in Canada (Canadian Council of Ministers of the Environment 1999). Most individual PAH congeners occurred at concentrations below the low range SQGs (ERL or PEL) and considered unlikely to cause immediate adverse effects to benthic organisms (Table SI-6). However, combined

Table 1 Reported PAHs concentrations in the dissolved and particulate phase in different areas in the world (nanogram per liter)

Locations	Dissolved phase	Particulate phase	SPM content (mg/L)	Mean percentage[b]	References
YangshanPort (16[a])	110–860	640–2900	170–1300	85 (52–93)	This study
Yangtze estuary, China (16)	478–1188	753–2060	124–980	62	Wang (2013)
Zhoushan fish ground, China (16)	83–226	–	18–124	–	Fang (2007)
Pearl River Estuary, China (16)	11–18	16–28	19–31	52	Li et al. (2014)
Barcelona, Spain (16)	3.6–41	0.76–62	5.7–30	29	Guitart et al. (2007)
Port of Singapore (14)	2.6–46	3.8–31	–	52	Lim et al. (2007)
Western Taiwan Strait, China (15)	12–58	10–45	–	43	Wu et al. (2011)
Vieux-Port, France (17)	25–148	6.0–350	7.2–47	48	Guigue et al. (2014)
Port of Leghorn, Italy (16)	140–187	267–1230	3.9–5.2	57	Cincinelli et al. (2001)

[a] Numbers in the parentheses represent the total number of PAH congeners analyzed

[b] Fraction of PAHs in the particulate phase relative to total PAHs in the water phase

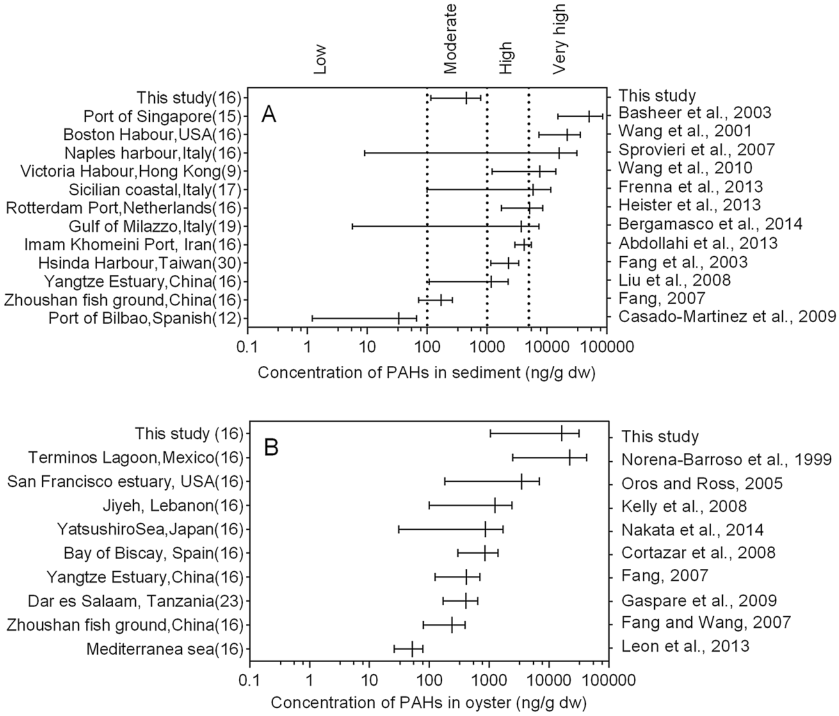

Fig. 3 **a** Global comparison of PAH concentrations in marine sediment. **b** Global comparison of PAH concentrations in oyster. *Numbers in the parentheses* represent the total number of PAH congeners analyzed. The *dashed lines* represent the three benchmark levels of PAHs (100, 1,000, and 5,000 ng/g dw) for sediment contamination ranking from low to very high (Baumard et al. 1999)

effects of these PAH mixtures are warranted in the future along with long-term monitoring and assessment in order to better understand the cumulative risks due to PAHs.

Source diagnosis of PAHs

Identification of PAH sources informs management options in source mitigation and site remediation. PAHs originate mainly from pyrogenic and petrogenic sources. Pyrogenic PAHs produced during incomplete combustion of fossil fuel are characterized by the abundance of four- to six-ringed congeners (also termed HMW PAHs), in contrast, petrogenic PAHs originating from petroleum products are typically dominated by LMW compounds, such as two- to three-ringed congeners (Jiang et al. 2009). The validity of using PAH isomeric ratios in source apportionment has been well established. Pyrogenic and petrogenic sources can be distinguished and cross-validated by several diagnostic ratios (e.g., LMW/ HMW, ANT/(ANT+PHE) and FLA/PYR) (Fang et al. 2003; Tobiszewski and Namieśnik 2012). Samples with LMW/HMW<1, ANT/(ANT+PHE)>0.1, and FLA/(FLA+PYR)>0.4 can be attributed to pyrogenic sources, while those with LMW/HMW>1, ANT/(ANT+PHE)<0.1, and FLA/(FLA+PYR)<0.4 can be attributed to petrogenic sources. Petrogenic sources can be further categorized into coal, grass, and wood combustion and liquid fossil fuel combustion by FLA/(FLA+PYR)>0.5 and in the range of 0.4–0.5, respectively.

The majority of the SPM samples with LMW/HMW ratios greater than one and all with ANT/(ANT+PHE) less than 0.1 and FLA/(FLA+PYR) less than 0.5 (Table 2 and Fig. 4) strongly suggest SPM-associated PAHs in the port waters originated mainly from petrogenic sources. The petrogenic sources inputs may be related to the extensive use of fossil fuels to support the increasing growth of vehicles in YangshanPort. Similar source characteristics were reported for port waters in other regions (Fang et al. 2003; Huang et al. 2011; Li et al. 2012; Miki et al. 2014). For some samples with FLA/(FLA+PYR) higher than 0.4, this indicates that pyrogenic sources may have a minor contribution. Except for S2, sediment from all sampling sites showed characteristic ratios of pyrogenic sources. S2 is situated at the central area of the port and dedicated to ship docking, cargo transportation, and storage and maintenance work. Petrogenic source inputs or crude oil spills from heavy traffic of vessels might account for higher abundance of two- and three-ringed PAHs in sediment samples from S2.

Concentrations of particulate-associated PAHs in the port area are inevitably affected by the input from the Yangtze Estuary. However, PAH contamination in the Yangtze Estuary waters was mainly localized in nearshore sites as demonstrated by previous studies, and was closely related to land-based sources. Levels of PAHs significantly decreased with increasing distance off shore (Li et al. 2012; Wang 2013b). Yangshan port is approximately 40 km away from land sources, therefore PAHs in the port area may be attributed to port activities. This is also supported by the distinct PAH composition profile in SPM collected from the port waters (dominated by two- to three-ring congeners) as compared to that from the Yangtze estuary (dominated by four- to six-ring congeners; Guo et al. 2007; Liu et al. 2008), indicating

Table 2 Ratios of LMW/HMW of PAHs in SPM and sediment from Yangshan Port

	S1	S2	S3	S4	S5	S6	S7
SPM	0.64±0.02	4.2±0.23	4.4±0.08	3.1±0.26	1.3±0.10	2.0±0.02	0.52±0.08
Sediment	0.31±0.07	3.6±0.08	0.33±0.02	0.18±0.007	0.37±0.06	0.09±0.005	0.29±0.01

that pyrogenic sources mainly account for PAH contamination in Yangtze estuary and petrogenic sources for Yangshan Port. Therefore, petroleum-associated chemicals, such PAHs, originating from port activities call for management attention.

Bioaccumulation of PAHs in oyster and health risk assessment

Levels

Similar to SPM, ∑PAHs in *S. cucullata* in this study showed high variations among neighboring sites on a large scale, ranging from 1100 to 29,000 ng/g dw (Table SI-7), which are among the higher end of PAH concentrations in oyster over the world and are generally 1–2 orders of magnitude higher than reported elsewhere, including the adjacent Yangtze Estuary and Zhoushan fish ground (Fig. 3b). PAH congeners with four or more rings dominated the composition profile in *S. cucullata* (Fig. 2 and Table SI-7). Four-ring compounds are highly accumulated in soft tissues and accounted for 54–83 % of total PAHs predominated by BaA, BbF, and BkF. Such a profile is not in agreement with the observations in other studies that aquatic animals are mainly exposed to the water phase and their body burdens reflect and accumulate water-borne compounds such as low molecular weight PAHs (Bandowe et al. 2014; Nakata et al. 2014). Therefore, it can be reasonably speculated that there may be other exposure routes contributing to bioaccumulation in addition to uptake from the dissolved phase.

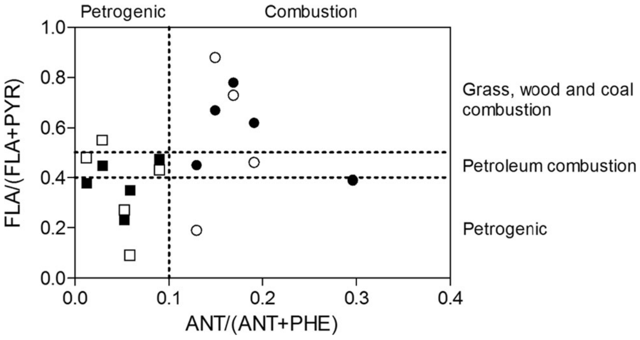

Fig. 4 Cross plot of FLA/(FLA+PYR) ratios versus ANT/(ANT+PHE) ratios for sediment and SPM samples analyzed in this study. *Squares* and *circles* represent SPM and sediment samples, respectively. *Filled* and *empty data points* represent data collected in 2012 and 2013, respectively

Role of SPM in PAHs bioaccumulation

Sediment is believed to be sinks for hydrophobic compounds, including moderate and high molecular weight PAHs, and it is generally believed that benthic organisms and sediment from the same site should be of similar exposure patterns. However, *S. cucullata* are not directly in contact with sediment, and no correlation between concentrations of PAHs in oyster and those in sediment can be found in our samples (Fig. 5).

Correlation between concentrations of PAHs in oyster and in dissolved phase was also statistical insignificant; however, PAH concentrations in oyster are well correlated with those in the seawater phase ($\sum PAHs_{dissolved}+\sum PAHs_{SPM}$) (Spearman $r=0.86$, $p=0.02$, Fig. 5). Therefore, it can be reasoned that SPM plays a major role for the accumulation of these contaminants in oyster. Approximately 85 % (52–93 %) of overall PAHs in the water phase ($\sum PAHs_{dissolved}+\sum PAHs_{SPM}$, Table 1) partitioned in the SPM, and SPM was found to contain 1–2 orders of magnitude higher levels of PAHs than sediment, possibly explaining the high concentrations of PAHs in oyster. Uptake from water (i.e., the freely dissolved fraction of contaminants) is usually the dominant exposure pathway for organic compounds with log $K_{ow}<3$ (Kimmo et al. 2011), while particle can be filtered and ingested by *S. cucullata* contributing substantially to the body residual for organic compounds with $\log K_{ow}>3$, such as PAHs with four or more rings predominant in oyster tissue in the study.

The biota-sediment accumulation factor (BSAF; BSAF= C_{lip}/C_{OC}, C_{lip}, and C_{OC} are lipid normalized concentration in oyster and organic carbon normalized concentration in sediment, respectively) based on SPM were also calculated to further evaluate the importance of SPM in bioaccumulation of PAHs in oyster (Fig. 6). BSAF are less than 10 with a small variation, which is in accordance with the experimental BSAF typically below 5 and often in the range of 1–3 for metabolically inert chemicals and lower for labile ones, such as LMW PAHs, whose parent compounds can be biotransformed in benthic organism (Li et al. 2013).

While freely dissolved concentrations of contaminants are the driving force for bioaccumulation and SPM is generally believed to reduce the contaminant bioavailability, SPM-associated contaminants can become available if they are re-partitioned into water or directly toxicologically relevant to organisms that can collect, ingest or be fouled by particulate PAHs (Li et al. 2014), and the particulate-associated PAHs can serves as a reservoir for freely dissolved fractions and play an

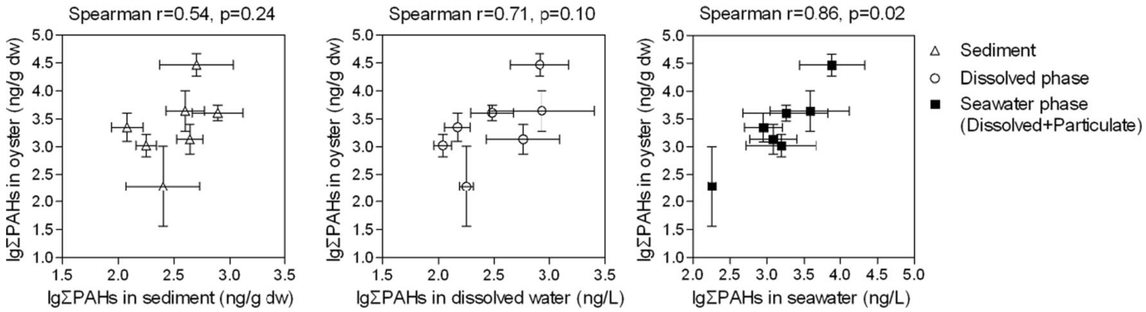

Fig. 5 Correlations between ΣPAHs concentrations in oyster and those in the dissolved phase (*black circle*), the water phase (*white square*) and sediment (*white up-pointing triangle*)

important role in bioaccumulation (Carls et al. 2008). Thus, the feeding mode of marine animals determines the route(s) for bioaccumulation of contaminants. In our case, *S. cucullata* are exposed to PAHs in both digestible SPM and resuspended sediment in the water phase in addition to the freely dissolved fraction.

Continued study on desorption kinetics of particulate-associated PAHs and their bioavailability is recommended for the further risk assessment on marine organisms (Gaspare et al. 2009). Desorption kinetics of particulate-associated PAHs in our ongoing work on SPM from Yangshan Port waters indicated that PAHs in the rapid desorption phase representing the bioavailable fractions exceeds 50 % of the total particulate-bound PAHs (unpublished data). PAH bioaccumulation showed greater correlation to their levels in SPM, confirming the importance of SPM in exposure assessment. As such, it becomes mandatory to monitor organic chemical pollutants in whole water samples, including SPM, in major regulatory bodies, such as Water Framework Directive 2000/60/EC in European legislation.

Health risk assessment of oyster as seafood

Potentially carcinogenic PAHs (including BaA, BbF, BkF, BaP, DBA, and IPY) in *S. cucullata* represent 61–83 % of ∑PAHs concentrations in oyster samples except where no carcinogenic PAHs were detected at S1, and the values ranged from 650 to 19,000 ng/g dw (Table SI-7). We conducted a preliminary cancer risk assessment of PAHs due to human consumption of oysters from the studied area using the toxic equivalent (TEQ) approach according to the USEPA (1993). The concentration of each carcinogenic PAH congener (C_i) was converted to a BaP equivalent concentration (BaP_{eq}) via its consensus toxic equivalency factor (TEF) relative to BaP, and sums up to the total $BaP_{eq}$of the sample (Eq. (1)).

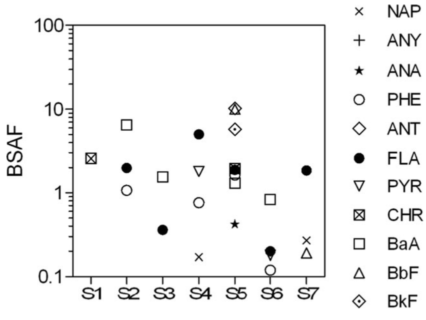

Fig. 6 BSAF based on SPM

$$\mathrm{BaP_{eq}(ng/g_{ww})} = \sum_{i}^{n-1} [\mathrm{C}_i(\mathrm{ng/g_{ww}})\cdot \mathrm{TEF}_i] \quad (1)$$

The incremental lifetime cancer risk (ILCR) based on consumption of oysters in the studied area was then calculated according to Eq. (2) (Yang et al. 2014).

$$\mathrm{ILCR} = \frac{\mathrm{BaP_{eq}}\cdot \mathrm{CSF_{ingestion}}\cdot \sqrt[3]{(\mathrm{BW}/70)}\cdot \mathrm{IR_{oyster}}\cdot \mathrm{EF}\cdot \mathrm{ED}}{\mathrm{BW}\cdot \mathrm{AT}\cdot \mathrm{CF}} \quad (2)$$

Where the carcinogenic slope factor (7.3 mg kg^{-1} $day^{-1})^{-1}$ (CSF) was based on the cancer-causing ability of BaP. BW is body weight (in kilogram), 70 kg; AT is average life span (in year), 70 years; EF is exposure frequency (days per year), 365 days $year^{-1}$; ED is the exposure duration (per year), 30 years; IR is the oyster intake rate (in kilogram per), 0.02 kg day^{-1} (wet weight) (FAO 2007); CF is the conversion factor, 10^6.

The ILCR over a 70-year life span exposure to 16 US-EPA PAHs via consumption of *S. cucullata* from Yangshan Port was also calculated and compared to the acceptable guideline value of 1×10^{-6} set by US-EPA. The ILCR calculated for oyster samples from five out of the seven sampling sites (Table SI-7) were remarkably higher than the acceptable guideline value of 1×10^{-6} (Ding et al. 2012). It is particularly noted that the concentrations of BaP in oyster samples from some sites (e.g., S4 and S5, 52±2.0 and 3,800±400 ng/g dw, respectively) were close to or much higher than the maximum allowed concentration of 10 ng/g ww (converted from 59±4.3 ng/g dw with 83±6 % water content) for seafood set by the EU legislation. Therefore, consumption of *S. cucullata* from these sites may lead to significant health risks. PAH levels in other seafood types are being analyzed in our group in order to further determine the impact of the port construction and operation on the local marine environment and provide a more scientifically sound guidance on seafood consumption.

Conclusions

The construction and operation of Yangshan Port has led to ubiquitous PAH contamination in the port waters. PAH concentrations in surface seawater are higher than those reported in other major ports around the world. Among the lower end of global concentrations, sediment PAH levels fell below the major guideline values, and may therefore not cause significant ecological risks to the marine organisms in the port waters. Remarkable accumulation of PAHs was found in oyster from the port waters at levels higher than those reported worldwide. The incremental life cancer risks due to PAH intake from oyster were close to or higher than the acceptable guideline value of 1×10^{-6}, which calls for risk management strategies concerning human seafood consumption.

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Compliance with ethical standards The authors declare that they have no conflict of interest.

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