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Emission factors and environmental implication of organic pollutants in PM emitted from various vessels in China

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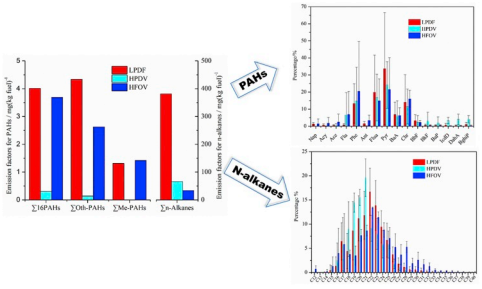
GRAPHICAL ABSTRACT



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ABSTRACT

Organic pollutants from ship exhaust have significant health and air quality impact in coastal areas; their profiles are also in urgent need. Studies on organic pollutants from ships are still rare, especially in China. Therefore, 21 PAHs and 29 n-alkanes in PM emitted from 15 ships with different types and fuels under different operating modes in China were tested in this study. The results showed that: (1) Identified organic matters accounted for 0.15%–23.3% of PM. Fuel-based emission factors (EFs) for Σ16PAHs ranged from 0.095 to 5.80 mg (kg fuel)$^{-1}$, with low-engine-power fishing boats and heavy fuel oil (HFO) training ship had higher values compared with light diesel vessels. EFs for Σn-alkanes ranged from 5.22 to 1589 mg (kg fuel)$^{-1}$, with low-engine-power fishing boats had higher values compared with other vessels. (2) The dominant PAHs were medium molecular weight components of Pyr, Flua, Phe, and Chr. N-alkanes from C15 to C33 accounted for more than 97% of the total n-alkanes. (3) Ratios of typical PAHs and n-alkanes parameters in this study showed typical diagnostic characteristics of oil combustion source. Profiles and diagnostic characteristics of PAHs together with n-alkanes could

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provide a more precise source apportionment result in the future. (4) Besides, PAHs in PM emitted from ships inferred non-ignorable health influence.

1. Introduction

Pollutants emitted from shipping emissions have gained more and more attentions in recent decades due to their significant impact on human health, air quality and climate change (Corbeet, 1997; Diesch et al., 2013; Eyring et al., 2010; Fuglestvedt et al., 2009; Hassellov et al., 2013; Jonson et al., 2009; Lack and Corbett, 2012; Liu et al., 2016; Schreier et al., 2006; Viana et al., 2014; Winebrake et al., 2009). As one of the most watched pollutants, particulate matter (PM), especially fine PM ($PM_{2.5}$) account for non-ignorable proportions to primary $PM_{2.5}$ in harbor or offshore areas, such as 2.4–3.3% in Venice (Gregoris et al., 2016), 3.1% in Tianjin (Chen et al., 2016), 4.23% in Shanghai (Zhao et al., 2013), 5–10% in Bay of Algeciras (Pandolfi et al., 2011), 8.8% in West Long Beach Harbor. If secondary contribution is considered, it can reach very high proportions, such as 20–30% in Shanghai (Liu et al., 2017), 17% in Bay of Algeciras (Pandolfi et al., 2011). Pollutants emitted from land-based sources are gradually decreasing due to the implementation of more advanced emission reduction technologies (e.g., on-road diesel engines) in recent years. The relative impact of shipping emissions is increasing, especially in coastal areas. In comparison to on-road vehicles, the emission characteristics from maritime vehicles are still poorly known. Chemical compositions such as heavy metal elements, OC (organic carbon), BC (black carbon) and other soluble elements of PM from shipping emissions are mainly concerned (Agrawal et al., 2008; Lack and Corbett, 2009; Diesch et al., 2013; Anderson et al., 2015; Celo et al., 2015; Zhang et al., 2016, 2018). Only limited studies have mentioned the organic compounds in PM (Agrawal et al., 2008, 2010; Cooper, 2003; Cooper et al., 1996; Crimmins et al., 2004; Sippula et al., 2014).

Polycyclic aromatic hydrocarbons (PAHs), a typical class of persistent organic pollutants, are ubiquitous in the environment. Due to their characteristics of toxicity, persistence, carcinogenicity, and mutagenicity (Srogi, 2007), the sources and distributions of PAHs have received more attention. The US Environmental Protection Agency (EPA) has promulgated 16 unsubstituted PAHs (EPA-PAH) as priority pollutants in 1970s (U.S. EPA., 1979). Vehicular emission is recognized as one of the most significant sources of PAHs. Moreover, particle-bound PAHs are considered to be a significant hazardous substance to human health through breathing (Srogi, 2007). Diagnostic ratios of PAHs can be used as potential special tracers when contribution of shipping emissions on atmosphere is calculated (Czech et al., 2017). N-alkanes are ubiquitous species that can suit to trace the origin and fate of different samples because of their relatively stable characteristics in the environment (Pietrogrande et al., 2010). The number of terms and the abundance distribution of the odd/even terms in the series are the two particular relevance parameters in describing n-alkane properties, which can determine the biogenic and anthropogenic sources, even fossil fuel source (Bray and Evans, 1961). Besides, Detailed PAHs and alkanes profiles are the basis to give more precise results of source apportionment of ambient PM. Therefore, studies on emission factors and characteristics of PAHs and alkanes from ships are in urgent need.

Shipping emissions in China have gained more and more attentions over the last decade due to the negligible total pollutant emission and their influence on atmosphere. However, most of the studies are focusing on emission inventories but based on data from other countries and areas (Chen et al., 2017; Fan et al., 2016; Fu et al., 2012; Jin et al., 2009; Li et al., 2016a; Song, 2014; Yang et al., 2015a, 2015b; Ye et al., 2014; Zhang et al., 2010); contributions of shipping emissions to harbor cities and areas (Zhang et al., 2014; Zhao et al., 2013). Only several studies have carried out onboard experimental test to give emission factors and characteristics of pollutants from ships in China (Fu et al., 2013; Peng et al., 2016; Song, 2015; Xiao et al., 2018; Zhang et al., 2016, 2018), which is the basis of emission inventory estimation and source apportionment. However, almost all of the studies are focusing on gaseous matters, PM and its main components such as OC, EC, water-soluble ions and elements, but no organic matters. Emission factors and profiles for organic matters emitted from vessels in China are in urgent need, not only for inventory estimation, but also for more precise source apportionment results of ambient PM.

In this study, organic compounds including 21 PAHs, 29 n-alkanes from C12 to C40 in PM were analyzed from 15 offshore vessels in China. (1) Emission factors and profiles of PAHs and alkanes of these vessels were given; (2) Diagnostic characteristics of PAHs and n-alkanes in PM from vessels in this study and other sources were discussed; (3) Potential toxicity risk assessment of PAHs in PM emitted from vessels were estimated, comparison with other sources were investigated.

2. Material and methods

2.1. Test vessels and fuels

PM samples from 15 different kinds of vessels were obtained in this study, including 11 fishing boats, 1 engineering ship, 2 research ships and 1 training ship, whose technical parameters are shown in Table A1. Detailed information of the tested vessels were introduced in previous studies (Zhang et al., 2016, 2018) except for the training vessel (YK), which is a typical HFO-ship. As introduced before, fishing boats, high speed diesel engine power vessels are the most important and negligible ships in offshore area in China. While YK is a typical heavy fuel oil ocean-going vessel, which can give representative emission data of HFO-ship in China. The sampling systems used in this study were two combined on-board emission test systems that were introduced in our previous studies (Zhang et al., 2016, 2018). The sampling system applied for YK was the same diluted system used for the fishing boats (Zhang et al., 2018).

The fuels used for the test vessels were different kinds of diesel fuels and heavy fuel oils. Table A2 presents the quality analysis results of the fuels. Main elements such as carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) were analyzed; other parameters were also analyzed in this study such as calorific values and some important metal elements. Detailed information of the heavy fuel oil used for YK was added in this study, other fuels had been introduced in previous studies (Zhang et al., 2016, 2018).

2.2. Samples

A total of 59 PM samples emitted from the 15 test vessels were chosen in this study, main operating modes of each vessel were included (seen in Table A3). According to actual operating modes, 3–6 PM samples were chosen for each vessel, which could represent the actual emission conditions.

2.3. Chemical analysis and data analysis

Sixteen priority PAHs, as indicated by US EPA, several Methyl substituted PAHs, and N-alkanes from C12 to C40 were detected in this study (seen in Table A4). The detailed chemical analysis method was introduced in section A1 of Supporting Information.

The carbon balance formula was used to calculate the EFs for all exhaust components in this study that was introduced in previous study

(Zhang et al., 2016). Average emission factors for 21 PAHs and 29 n-alkanes in PM of each vessel were calculated according to actual operating condition in this study, which was the same method used in previous studies (Zhang et al., 2016, 2018).

2.4. Quality assurance/quality control

Rigorous quality assurance and control were conducted during the whole experiment. Filter blanks, reagent blanks were analyzed in the same way as mentioned above to determine any background concentration. Duplicate samples as well as standard samples were examined after analyzing a batch of 10 samples to ensure that the error was within 5%. Five PAH surrogates and four n-alkane surrogates were added to each sample to assess the overall analytical procedure and recoveries. The average recoveries of the surrogates ranged from 66.7% to 128% in this study. The results of each sample were subtracted filter blank results. The final data reported in this research were not corrected by the recoveries.

3. Results and discussions

3.1. Particle emissions and their composition

Detailed fuel-based emission factors of PM and their chemical composition, including OC, EC, water-soluble ions, and metal elements, emitted from all the test vessels except the HFO training ship (YK) were introduced and discussed in our previous studies (Zhang et al., 2016, 2018). Combined with the data from YK, a general discussion and comparison of PM EFs and their main chemical compositions from all the vessels were given in this study (seen in Table A5). The test vessels in this study were divided into three categories according to engine power and fuel type, which were low-power-diesel fishing boat (LPDF), high-power-diesel vessel (HPDV), and HFO vessel (HFOV) (seen in Fig. 1). The PM EFs varied between 0.16 and 17.2 g (kg fuel)$^{-1}$ for all the test vessels. Among the different types of vessels, LPDF had much higher PM emission factors of 7.73–17.2 g (kg fuel)$^{-1}$, which might be caused by the high-speed engine used that usually had relatively lower combustion efficiencies (Zhang et al., 2018). The HPDV (DFH and XYH) had much lower PM EFs values of 0.72 and 0.16 g (kg fuel)$^{-1}$, which might be caused by the well-maintained engines and high quality of the fuels used (Zhang et al., 2016). And the HFOV had medium PM emission factors of 3.19–7.48 g (kg fuel)$^{-1}$, which was generally similar to the levels of cargo and passenger ships (Endresen et al., 2003; Moldanova et al., 2009).

Carbonaceous matters of OC and EC were the most abundant component in PM, accounting for almost half for HFOV and HPDV, and more than half for LPDF. The detailed mass fractions of (OC + EC)/PM were between 11.9% and 91.6%, with 2.11%–47.9% of OC and 2.28%–87.5% of EC. OC/EC ratio varied between 0.03 and 21.0. OC was clearly higher than EC in PM for HFOV and other low quality fuel vessels, which was similar to previous study about HFO vessel (Sippula et al., 2014). Water-soluble ions including SO_4^{2-}, NO_3^-, NH_4^+, Cl^- and Na^+ accounted for 1.07%–26.9% of PM for all the test vessels. Much higher proportions of water-soluble ions were accounted for HFOV than HPDV and LPDF, which might be caused by the relative higher sulfur content in fuels that generated more SO_2 and higher combustion temperatures in engine cylinders that produced more NO_x. Metal elements such as Na, Mg, K, Ca, Fe, Zn, Cu, Mn, V and Ni only accounted for very small sections from 0.06% to 5.36%, also showed higher proportions for HFOV that caused by the relative higher contents of heavy metals in fuels used for HFO vessels. More than half of the components can be identified for most of the vessels, with the remainder inferred as materials such as ash and hydrate materials.

Organic matters (OM) in this study were calculated by using OC × 1.2, which could account for 2.53%–57.5% of the PM mass. Of these, sum of the analyzed organic matters, including 16 priority PAHs, 5 methyl substituted PAHs, and 29 n-alkanes are shown in Fig. 1, accounting for 0.14%–23.3% of PM for all the test vessels. The analyzed organic matters for different vessels showed significant variations. Both HPDV and LPDF showed much higher n-alkanes proportions than HFOV, which might be caused by the fuel types that diesel fuels contain more n-alkanes but less PAHs. N-alkanes were the highest content species for all of the vessels, whose sums made up percentages of 0.11%–21.3% in PM. Though the 16 priority PAHs only accounted for very small proportions of 0.005%–0.13%, they played non-ignorable roles in health influence aspect.

3.2. Emission factors of PAHs and alkanes

Fuel-based average EFs for PAHs and n-alkanes in PM in this study are shown in Table 1. EFs for Σ16PAHs of each vessel ranged between 0.095 and 5.80 mg (kg fuel)$^{-1}$, ΣPAHs ranged between 0.095 and 8.68 mg (kg fuel)$^{-1}$, and EFs for Σn-Alkanes of each vessel ranged between 5.22 and 1589 mg (kg fuel)$^{-1}$ in this study. Both EFs for PAHs and n-alkanes varied significantly with the type of the vessels, which were thought to be influenced by the integrated factors of engine parameters, ship tonnage, fuel type and composition (Russell et al., 2000). Fishing boats and the training ship (YK) had relatively higher EFs for PAHs than the light diesel vessels, which had very low values ranged from 95.3 to 477 μg (kg fuel)$^{-1}$. Because incomplete combustion of fuels was one of the major sources of carbonyls compounds (Agrawal et al., 2010; Carlier et al., 1986), smaller vessels such as

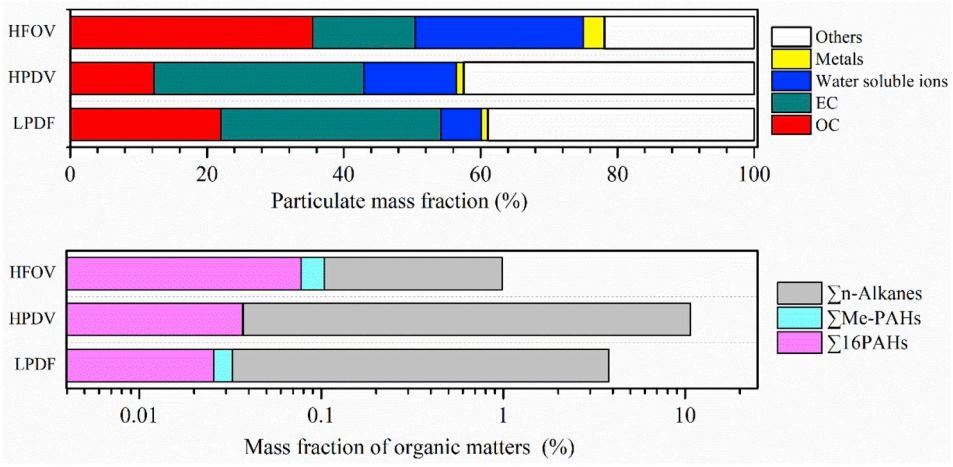

Fig. 1. Chemical composition of PM and the analyzed organic matters (%).

Table 1
Emission factors of PAHs and n-alkanes in PM(μg (kg fuel)$^{-1}$).

	GB1	GB2	AB1	AB2	TB1	TB2	TB3	TB4	TB6	TB7	TB8	HH	DFH	XYH	YK
Nap	21.5	13.5	16.2	21.3	89.6	68.6	72.9	42.3	17.2	7.17	155	0.06	–	–	7.14
Acy	–	17.3	3.82	10.3	95.9	74.3	18.9	17.0	5.07	10.5	185	0.51	–	–	3.76
Ace	8.54	6.31	17.9	5.43	27.5	29.4	78.8	48.2	4.18	6.11	255	4.67	2.16	–	21.2
Flu	24.2	16.3	28.7	15.1	2.56	25.6	62.7	107	7.22	21.1	724	60.7	0.10	0.15	26.2
Phe	41.6	135	1777	438	34.9	583	205	631	73.9	78.9	1755	107	11.7	17.1	438
Ant	186	14.0	87.4	20.2	1.17	142	18.7	62.5	6.88	21.9	201	0.26	0.84	0.10	159
Flua	271	91	793	398	130	742	455	1129	74.8	113	692	83.2	60.1	10.7	847
Pyr	380	200	1770	782	262	1641	1022	1394	111	198	862	61.3	115	44.6	1323
BaA	1117	28.5	276	50.8	25.5	18.6	302	107	43.4	136	174	9.82	45.6	0.63	388
Chr	9.40	129	925	163	44.5	95.8	808	477	195	430	622	43.8	57.7	4.49	729
BbF	402	17.8	28.3	63.0	21.6	39.1	170	57.8	33.1	47.1	92.1	19.4	1.42	1.45	114
BkF	91.7	5.19	2.52	23.0	15.0	9.97	47.7	14.6	8.19	9.64	28.4	25.4	2.27	1.14	25.4
BaP	28.3	3.20	3.44	26.9	9.63	17.6	50.2	3.68	29.9	9.99	22.0	17.0	0.14	0.04	29.9
IcdP	3.74	6.79	11.6	43.1	12.5	9.16	36.6	2.11	5.67	2.47	10.3	13.4	12.9	4.07	13.8
DahA	48.2	2.61	–	7.51	19.0	14.4	16.2	0.99	5.99	4.71	12.1	11.8	20.8	4.24	16.9
BghiP	47.0	7.12	9.31	70.5	3.12	1.12	66.9	4.34	7.26	4.58	14.3	17.8	13.5	6.03	24.6
Σ16PAHs	2681	693	5751	2139	795	3512	3431	4098	629	1101	5803	476	345	94.7	4168
1-MeN	25.5	181	126	294	36.5	34.1	401	430	138	88.1	2286	–	–	0.03	65.2
2-MeN	317	3.63	0.43	3.60	32.6	29.2	9.10	12.1	1.85	39.0	75.7	–	–		2.58
2,6-DiN	10.6	10.1	27.9	18.5	24.5	30.7	21.3	27.7	6.29	20.3	136	–	–		10.2
9-MeA	97.3	–	275	–	23.9	168	9.62	11.4	–	5.83	12.1	0.19	2.38	0.05	43.4
MeFlua	23.3	130	1718	129	23.2	150	627	804	143	95.9	363	1.11	3.89	0.52	1028
ΣMPAHs	474	325	2148	446	141	412	1068	1285	290	249	2873	1.29	6.27	0.60	1150
ΣPAHs	3155	1018	7899	2585	936	3924	4499	5383	919	1350	8676	477	351	95.3	5318
C12	7.96	17.6	–	8.69	–	–	96.8	–	–	25.5	448	–	–	–	–
C13	4.49	–	–	1.27	–	0.53	70.2	21.6	–	–	19.4	–	–	–	–
C14	2.88	23.0	–	16.7	47.9	197	328	4.27	0.54	–	196	–	–	–	–
C15	5.54	94.3	–	62.6	225	1630	3621	94.4	26.9	0.95	1011	–	–	216	–
C16	21.4	432	8616	615	1203	2994	6784	547	228	46.0	2861	–	1615	922	164
C17	296	3159	113,649	5334	11,699	27,395	7324	1758	1933	46.4	3524	23.9	10,343	1564	2250
C18	1753	1722	26,979	4855	25,035	27,749	5224	1041	629	114	913	434	17,388	1927	3955
C19	947	2484	116,186	9315	37,482	36,207	9865	2668	1024	1.16	881	2055	22,853	2332	4955
C20	6187	4260	102,098	12,646	32,616	39,347	10,725	5646	2496	418	1507	2636	22,814	2268	6490
C21	20,131	5076	86,400	13,547	10,530	30,231	8777	6938	3690	463	1801	3742	31,966	2235	7142
C22	28,103	4879	137,520	10,668	20,668	445,844	15,933	7475	3774	706	3574	1637	18,448	846	9150
C23	26,143	4436	106,555	8681	15,662	402,072	10,313	6234	3356	646	2663	1598	15,903	604	8174
C24	18,338	3545	67,057	6450	9812	250,573	6421	4484	2419	520	1843	1296	10,901	380	6607
C25	10,915	2483	39,255	4317	9762	252,197	3561	2389	1692	466	1203	1285	10,841	378	5440
C26	6068	1563	13,591	2897	2168	701,54	2692	2841	1263	414	642	444	2760	112	3725
C27	3628	590	589	1491	945	1394	3414	1474	628	295	388	283	1181	80.7	2729
C28	1662	511	–	855	328	496	1775	1029	465	383	1445	158	427	45.4	2068
C29	1300	159	–	330	157	193	573	718	379	150	198	62.5	138	25.9	1437
C30	615	178	190	163	85.1	83.9	1756	256	403	209	232	39.8	53.3	13.9	2018
C31	360	99.4	209	68.0	61.9	47.3	1421	211	273	140	208	33.2	43.5	19.8	1122
C32	373	27.3	48.4	35.8	54.0	40.5	319	183	190	96.2	129	15.4	34.6	7.65	1065
C33	178	21.8	64.9	14.8	42.0	34.2	451	76.2	83.5	38.3	62.1	3.45	4.65	0.01	382
C34	60.0	68.5	48.2	13.8	65.8	38.6	87.5	23.4	54.4	15.9	57.5	2.52	1.13	0.20	324
C35	37.4	9.72	36.3	3.94	51.0	38.8	149	16.4	30.5	17.2	58.1	2.67	3.08	0.57	310
C36	66.2	8.51	81.3	9.52	54.2	40.6	61.5	30.9	24.7	4.62	124	1.17		0.04	72.4
C37	41.4	18.9	70.0	5.20	43.8	31.0	88.9	8.85	9.52	0.06	74.9	0.66	0.52	0.03	123
C38	33.4	6.24	40.3	–	88.8	65.4	102.4	–	7.66	0.80	53.9	0.77	–	–	35.5
C39	17.3	4.89	47.7	1.49	100	76.1	96.0	0.85	5.14	–	30.9	1.18	–	–	17.2
C40	2.83	–	74.4	–	87.5	68.3	146	0.17	–	–	67.7	1.39	–	–	–
Σn-Alkanes	127,299	35,878	819,405	82,406	179,076	1589,238	102,175	46,170	25,086	5217	26,213	15,757	167,718	13,978	69,754

fishing boats in this study had more incomplete combustion process (Diesch et al., 2013; Zhang et al., 2018), which might lead to the increase of PAHs emissions. Besides, it is confirmed that low-sulfur fuel would considerably reduce emissions of PAHs with respect to the use of high sulfur content fuel (Cooper and Gustafsson, 2004; Donateo et al., 2014; Endresen et al., 2003). However, there was not a perfect linear dependency of sulfur and PAHs emission factors in this study, which might be caused by the different fuel qualities that not only decided by the sulfur contents. As for n-alkanes, fishing boats with lower power engines had relatively higher EFs, and HFO fuel vessels had relatively lower EFs in this study. There was a correlation coefficient of 0.80 between the sulfur content of fuels and the ratios of Σ16PAHs to Σn-alkanes in this study, which means more PAHs than n-alkanes emitted from HFO fuel vessels compared with DF vessels. This was inferred as higher fraction content of polycyclic aromatic compounds in HFO fuel than DF, HFO fuel vessels usually emit substantially higher amounts of various PAHs, O-PAHs and Nitro-PAHs than n-alkanes compared with DF vessels (Sippula et al., 2014). Besides, methylic-PAHs in this study had obviously lower EFs of clean diesel fuel than high-sulfur content fuels, which was also confirmed by previous study (Sippula et al., 2014).

In order to give comparison of ship emissions with other studies, emission factors for the total 15 priority control PAHs (except for Nap, which was influenced significantly by temperature because of its high volatility), total n-alkanes (from Dodecane to Tetracontane), and their proportions in this study and previous studies are given in Figure A1 and Figure A2.

The results showed that emission factors for the Σ_{15}PAHs in this study were in the range of the results from previous studies. HFO ships (from references of R1 (Agrawal et al., 2010), R2 (Murphy et al., 2009),

R3 (Agrawal et al., 2008), R5-10 and R5-11 (Cooper, 2003)) and fishing boats had higher Σ_{15}PAHs emission factors compared with diesel fuel ships, which inferred that HFO fuel ships and fishing boats had more potential health effects, especially in offshore areas. The dominant PAH species were Flu, Phe, Flua and Pyr, but with significant differences in proportion of different ships, which might be caused by the combustion temperature in the cylinder.

As for n-alkanes, diesel fuel vessels showed higher emission factors than HFO vessels, especially for fishing boats with diesel fuel in this study. Because n-alkanes emitted from engines were typically related to the fuel types, diesel fuel generally contain more aliphatic compounds than HFO (Sippula et al., 2014). High EFs for n-alkanes of diesel engine vessels implied a large amount of incomplete combustion fuel might be emitted along with the exhaust, which had been proved in this study that diesel fuel vessels such as fishing boats had relatively lower combustion efficiencies compared with HFO vessels.

3.3. Emission profiles of organic compounds

In order to give PAHs profiles in PM emitted from ships, as the same as before, the test vessels in this study were also divided into three categories of LPDF, HPDV, and HFOV. As seen in Fig. 2, the major compounds were Pyr, Flua, Phe, and Chr for all the test vessels in this study, which had the similar result to previous studies about PAHs emitted from harbor ships (Cooper, 2003) and tested in harbor area (Donateo et al., 2014). Both low and high molecular weight PAHs only accounted for very small proportions in this study. As shown in Figure A3, three- and four-ring PAHs of medium molecular weight were the dominant species that could account for 67%–98% of the total 16 PAHs mass. Among the three categories, the LPDF and the HFOV showed similar PAH distributions that had relatively higher proportions in low molecular weight PAHs but lower proportions in high molecular weight PAHs compared with HPDV. PAHs emitted from other sources showed significant differences, such as high composition in Nap, Pyr, Phe for heavy-duty diesel vehicles (Shah et al., 2005); high composition in Pyr, BghiP, Flua and Phe for road dust (Pengchai et al., 2004); high composition in high molecular weight PAHs of DahA, BghiP, IcdP and medium molecular weight PAHs of Flua, and Pyr for biomass combustion (Oanh et al., 2005); high composition in high molecular weight PAHs of BbF, BghiP, IcdP and also Chr, Phe for coal combustion (Chen et al., 2004, 2005); high composition in low molecular weight PAHs for gasoline-powered motor vehicles (Schauer et al., 2002). Detailed PAH profiles of vessels might provide strong evidence to identify ship emissions from other sources in source apportionment, which could give results that are more precise.

The n-alkane profiles for the three types of vessels in this study are shown in Fig. 2. N-Docosane (C22) was the highest composition for both LPDF and HFO vessel, but n-heneicosane (C21) was the highest composition for HPDV. Diesel fuel vessels had higher proportions in low carbon number n-alkanes (< 21), and HFOV had higher proportions in high carbon number n-alkanes (> 22) with a broader distribution of alkanes, which was in accordance with previous study (Sippula et al., 2014). Because n-alkanes emitted from engines were typically related to the fuel types, high quality light diesel with more low-carbon chains used for the diesel vessels could responsible for the lower carbon number n-alkanes, and vice versa. All the test vessels had very small proportions of n-alkanes with both low carbon number (< 15) and high carbon number (> 33), which only accounted for less than 3% of the total n-alkanes. N-alkanes emitted from different emission sources always showed different profile characteristics, which could be used for source apportionment. Motor vehicles, biomass combustion and coal combustion are the most concerned air pollution sources in China. The results showed that n-alkanes emitted from light-duty vehicles typically had variant maximum carbon numbers from different studies, which could range from C21−C30 (Chellam et al., 2005; Dai et al., 2015; Huang et al., 2016; Perrone et al., 2014), yet typically with C24−C26 as the most possible maximum carbon numbers. N-alkanes emitted from biomass in different studies had very consistent characteristics that n-Nonacosane (C29) was the maximum carbon number and showed obvious odd-carbon advantage (Hays et al., 2005; Vasconcellos et al., 2010; Yan et al., 2008; Zhang et al., 2007). Coal combustion is a large air pollution source in China, especially in winter. The results from previous studies showed that C23 and C21 were the C_{max} in heating season (Duan et al., 2010; Xie et al., 2009), which could be characteristics of coal combustion. Besides, N-Eicosane (C20) was the highest composition for biodiesel exhaust PM, followed by C19, C21, C18 and C22, others only accounted for very small proportions (Kasumba and Holmen, 2016). The results in this study inferred that combined with detailed profiles of both PAHs and n-alkanes, it will be benefit to give more precise source apportionment results.

3.4. Diagnostic characteristics of PAH and n-alkanes in PM

PAH diagnostic ratios have come into common use recently as a tool for the identification and assessment of pollution emission sources, such as diesel and gasoline combustion emission (Ravindra et al., 2008a),

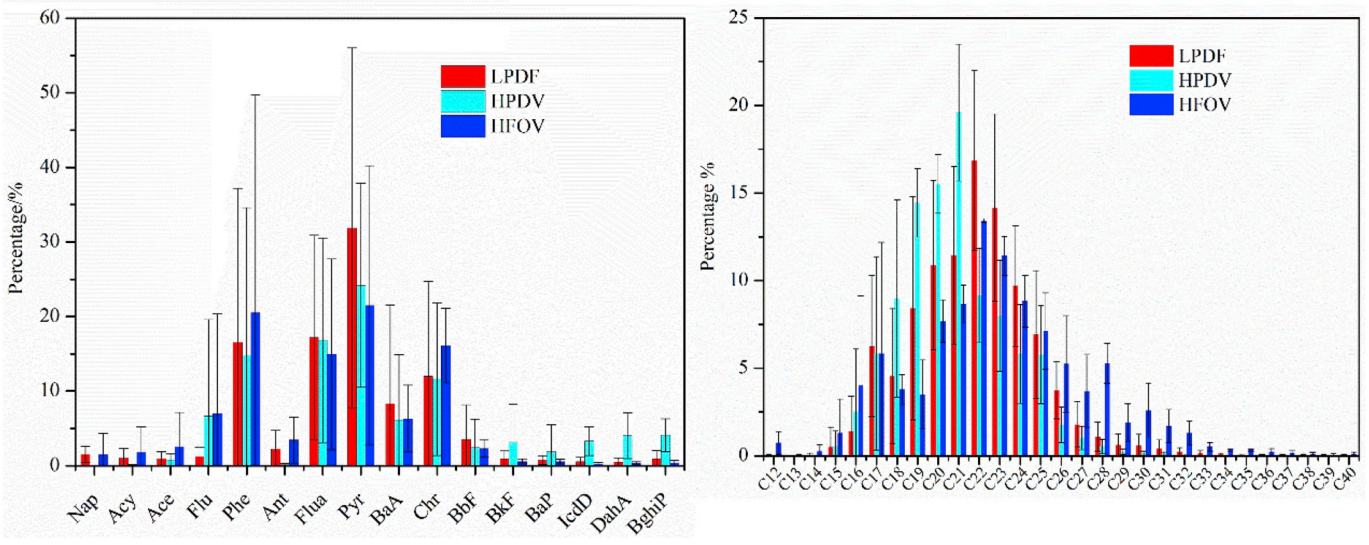

Fig. 2. PAHs and n-alkanes profiles for the test vessels.

different crude oil processing products and biomass burning processes, including bush, savanna and grass fires (Yunker et al., 2002). Table 2 and Figure A4 list the PAH diagnostic ratio ranges from different sources in previous studies and this study. The results showed that the ratios of Ant/(Ant + Phe), Flua/(Flua + Pyr), Flu/(Flu + Pyr), and IcdP/(IcdP + BghiP) in PM emitted from marine fuel combustion indicated obvious petroleum combustion characteristics compared with previous studies. An Ant/(Ant + Phe) ratio of 0.1 is often applied to distinguish petrogenic (< 0.1) from pyrogenic/combustion (> 0.1) sources (Pies et al., 2008). The ratios for most fuels in the present study were lower than 0.1, supporting the petrogenic characteristics. It is generally indicated the petrol emissions when the ratio of Flua/(Flua + Pyr) is less than 0.5 (De La Torre-Roche et al., 2009). This was well supported by the ratios of Flua/(Flua + Pyr) in this study, ranging between 0.31 and 0.42. The ratios of Flu/(Flu + Pyr) ranged between 0.02 and 0.08 in this study, corresponding to the conclusion that it indicated the petrol emissions when the ratio is less than 0.5 (Ravindra et al., 2008b). An IcdP/(IcdP + BghiP) ratio of 0.5 is usually recommended as a criterion separating liquid fossil fuel combustion (< 0.5) and grass/wood/coal combustion (> 0.5) (Yunker et al., 2002). This was also well supported by the ratios calculated in this study, varying narrowly from 0.35 to 0.49. However, other diagnostic ratios were not so well consistent with previous studies, for example, BaA/(BaA + Chr) ratios varied from 0.18 to 0.35 in this study, making it difficult to distinguish from coal combustion with a ratio range of 0.2–0.35 given by a previous study (Yunker et al., 2002). Ratios of BaP/BghiP, Phe/Ant, and BaA/Chr are also given in the present study in Table 2, however, these ratios varied significantly among different studies (Cereceda-Balic et al., 2012; Ravindra et al., 2008a; Tobiszewski and Namiesnik, 2012). It meant they should be used carefully in evaluating sources. In fact, simultaneous application of more than one PAH diagnostic ratio might help to reduce the uncertainty in source apportionment calculation.

As for n-alkanes, diagnostic parameters such as ratio of low molecular weight to high molecular weight (LMW/HMW), the average chain length (ACL), the maximum carbon number (C_{max}), and the carbon preference index (CPI) in this study and previous studies from different sources are shown in Table 3. Ratio of $W(nC23^-)/W(nC23^+)$ was discussed in this study to represent the characteristic of LMW/HMW as it could indicate different sources, especially for anthropogenic source and biogenic source. It showed that almost all the $W(nC23^-)/W(nC23^+)$ ratios of anthropogenic sources had values higher than 0.5, and very low values for biogenic sources of 0.04–0.24. C_{max} is defined as the carbon number of the alkane that has the highest concentration in the n-alkanes. As the same as $W(nC23^-)/W(nC23^+)$ ratio, C_{max} also had very noticeable characteristic for different sources. All the biogenic sources from previous studies had the same C_{max} of 29, as for anthropogenic sources, all the C_{max} values were lower than 25, which was corresponding to previous study that defined 25 as a threshold (Bin Abas and Simoneit, 1996). And in this study, all the n-alkanes in PM emitted from the test vessels had C_{max} values ranged from 19 to 21, a little smaller than motor vehicles (Chellam et al., 2005; Dai et al., 2015). Besides, ACL also can be used to distinguish different sources', for example, all the biogenic sources had ACL values larger than 27.8 in previous studies (Hays et al., 2005; Vasconcellos et al., 2010; Zhang et al., 2007), however, all anthropogenic sources had ACL values

Table 2
Diagnostic ratios of typical PAHs used in source apportionment.

PAH ratio	Value range	Source	Reference
Ant/(Ant + Phe)	0.04–0.20[a]	Marine fuel combustion	This study
	< 0.1	Petroleum	Pies et al. (2008)
	> 0.1	Combustion	
Flua/(Flua + Pyr)	0.31–0.42[a]	Marine fuel combustion	This study
	< 0.4	Petrogenic	De La Torre-Roche et al. (2009)
	< 0.5	Petrol emissions	
	> 0.5	Wood combustion	
BaA/(BaA + Chr)	0.18–0.35[a]	Marine fuel combustion	This study
	0.2–0.35	Coal combustion	Akyuz and Cabuk. (2010)
	> 0.35	Vehicular emission	
	< 0.2	Petroleum	Yunker et al. (2002)
	> 0.35	Combustion	
IcdP/(IcdP + BghiP)	0.35–0.49[a]	Marine fuel combustion	This study
	< 0.2	Petroleum	Yunker et al. (2002)
	0.2–0.5	Liquid fossil fuel combustion	
	> 0.5	Grass, wood/coal combustion	
BaP/BghiP	< 0.01[a]	Marine fuel combustion	This study
	< 0.6	Non-traffic emissions	Katsoyiannis et al. (2007)
	> 0.6	Traffic emissions	
Flu/(Flu + Pyr)	0.02–0.08[a]	Marine fuel combustion	This study
	< 0.5	Petrol emissions	Ravindra et al. (2008b)
	> 0.5	Diesel emissions	
	0.4–0.5	Fuel combustion	Katsoyiannis et al. (2007)
	> 0.5	Grass, wood/coal combustion	
Phe/Ant	4.12–21.7[a]	Marine fuel combustion	This study
	2.7	Vehicles	Simcik et al. (1999)
	8	Street dust	
	3.4–8	Gasoline exhaust	
	3	Firewood fire/coal	
	7.6–8.8	Diesel	
	0.79	Coke oven	
BaA/Chr	0.22–0.53[a]	Marine fuel combustion	This study
	0.63	Vehicles	Simcik et al. (1999)
	0.28–1.2	Gasoline exhaust	
	0.93	Firewood fire	
	1.0–1.2	Coal	
	0.17–0.36	Diesel	
	0.70	Coke oven	

[a] The value ranges given in this study were between 25th and 75th percentile of the total test values.

smaller than 26.36 in this study and previous studies shown in Table 3. Therefore, ACL value of 27 could consider being a divide point for anthropogenic source and biogenic source. Moreover, the CPI is a common indicator to distinguish the contribution of biogenic organic matter and anthropogenic sources to organic aerosol (Simoneit, 1989). The alkane CPI is defined as the sum of the concentrations of odd carbon number alkanes divided by the sum of the concentrations of even carbon number alkanes. A CPI near unity is expected for anthropogenic sources, and larger than one is expected for biogenic sources (Choiseul et al., 1998). It was completely obvious in Table 3 that biogenic sources had higher CPI values (1.48–11.53) than anthropogenic sources with values near unity (0.77–1.36).

Diagnostic parameters of n-alkanes in PM could provide very recognizable evidence to distinguish anthropogenic source and biogenic source. Moreover, PAH diagnostic ratios could be used to identify petrogenic source, different fuel combustion, biomass burning, etc. If possible, these two diagnostic methods, along with n-alkanes and PAHs profiles, should be taken into consideration together, which will be preferred in source apportionment calculation.

3.5. Potential toxicity risk assessment of PAHs in PM emitted from vessels

Widely known parameters, including 2,3,7,8-tetrachlorodibenzodioxin (TCDD)-based toxicity equivalency concentration (TEQ), total carcinogenic PAHs (C-PAHs), and BaP-based equivalency concentration (BaPeq) have been extensively applied to assess PAH risks to humans (Chen et al., 2004; Finardi et al., 2017; Li et al., 2016b, 2018; Liu et al., 2009; Nguyen-Duy and Chang, 2017). The calculated results of potential toxicity risk of PAHs in this study are shown in Table 4. It showed that the three toxicity risk assessment methods indicated the similar results. Therefore, TEQ was discussed only in this study to assess the potential toxicity risk of PAHs in PM emitted from vessels. The results showed that TEQ varied largely for the test vessels in this study, ranging from 5.192 to 241.1 μg (kg fuel)$^{-1}$, with GB1, TB3, and YK having the highest values, and light-diesel engines of DFH and XYH having the lowest values. The dominant compounds were BaA, BbF, Bap, and DahA, with four and five-ring PAHs accounting for 73%–98% of the total TEQ (seen in Figure A5). The sulfur content in the fuels had no obvious relationship with the TEQ. This was consistent with the result that PAHs EFs had no positive correlation with sulfur content in the fuels, which might be caused by the same reason that fuel quality of vessels in China might not only evaluated by the sulfur contents.

Comparison of TEQ in PM from different sources are given in Figure A6, including the vessels in this study and previous studies, biomass combustion, coal combustion, and vehicles with different fuels from previous studies. In order to give the most intuitive comparison, all the TEQ values were unified into μg (g PM)$^{-1}$ in this study. The results showed that the TEQ from marine vessels in this study had a medium level, ranging from 1.76 to 38.8 μg (g PM)$^{-1}$, a little lower than previous studies of HFO vessel exhausts, almost the same level with diesel vehicles (Borras et al., 2009; Riddle et al., 2007; Shah et al., 2005), but lower than gasoline and liquefied petroleum gas vehicles (Yang et al., 2007). Besides, residential coal combustion showed much higher TEQ values (Chen et al., 2005; Liu et al., 2009), which was three to five orders of magnitude higher than that of diesel engines. However, open

Table 3
Characteristics of n-alkanes from different sources in this study and previous studies.

ID	W(nC23$^-$)/W(nC23$^+$)	C_{max}	ACL	CPI	
GB1	1.91	22	23.03	1.01	
GB2	2.86	21	21.71	1.08	
AB1	5.75	22	20.85	1.30	
AB2	3.95	21	21.35	1.10	
TB1	6.49	19	20.52	0.94	
TB2	1.76	22	22.92	0.90	
TB3	3.42	22	21.43	0.95	
TB4	2.36	22	22.36	0.96	
TB6	2.16	22	22.52	1.10	
TB7	0.90	22	24.27	0.77	
TB8	2.85	22	21.16	0.86	
HH	6.73	21	21.79	1.36	
DFH	5.36	21	20.90	1.25	
XYH	12.14	19	19.70	1.14	
YK	1.54	22	23.12	0.96	
Motor vehicle		25	25.74–26.36	1.21–1.27	Chellam et al. (2005)
Heavy-duty diesel buses	0.66	21	24.91	1.15	Huang et al. (2016)
On-road vehicle	0.55	24	24.71	0.93	Dai et al. (2015)
Light-duty vehicles		21	21.87–23.06	0.80–0.87	Perrone et al. (2014)
Crop residues	0.04–0.13	29	28.13–28.81	1.93–11.53	Hays et al. (2005)
Forest	0.04	29	29.24	1.48	Vasconcellos et al. (2010)
Cereal straw	0.24	29	27.77	4.05	Zhang et al. (2007)
Oceanic aerosols (Atlantic)		27, 29, 31		5–10	Gagosion et al. (1981, 1982)
Oceanic aerosols (Pacific)		27, 29, 31, 33		2–4	
Western United States (rural)		27, 29		1.6–8.4	Simoneit, (1989)
Western United States (urban)		29		1.8–2.8	
Central Africa (rural)		29, 31		3.0–7.8	
Central Africa (urban)		29, 31		1.7–3.3	
Southeastern Australia (rural)		17, 18, 29		2.0–2.4	
South America remote (Punta Arenas)		29		2.1	
South America remote (Amazonia)		29		2–4	
Vascular plant waxes		27, 29, 31, 33		6–10	
Smoke (natural fires)		29, 31		1.2–10	
Vehicular exhaust (auto)		22		0.93	
Vehicular exhaust (diesel)		21		1.02	

$W(nC20^-)/W(nC20^+) = \frac{\sum_1^{20} c(C_n)}{\sum_{21}^{40} c(C_n)}$; $W(nC23^-)/W(nC23^+) = \frac{\sum_1^{23} c(C_n)}{\sum_{24}^{40} c(C_n)}$; C_{max}, the carbon number maximum; CPI, the carbon preference index, $CPI = \frac{\sum concentrations\ of\ odd\ carbon\ number\ homologs}{\sum concentrations\ of\ even\ carbon\ number\ homologs}$; ACL, the average chain length, $ACL = \frac{\sum\{n \times c(C_n)\}}{\sum c(C_n)}$, $c(C_n)$, concentration of n-alkane with carbon number of n.

Table 4
Toxic equivalents of the 16 priority control PAHs (μg (kg fuel)$^{-1}$).

	GB1	GB2	AB1	AB2	TB1	TB2	TB3	TB4	TB6	TB7	TB8	HH	DFH	XYH	YK
Nap	0.021	0.014	0.016	0.021	0.090	0.069	0.073	0.042	0.017	0.007	0.155	0.000	0.000	0.000	0.007
Acy	0.000	0.017	0.004	0.010	0.096	0.074	0.019	0.017	0.005	0.010	0.185	0.001	0.000	0.000	0.004
Ace	0.009	0.006	0.018	0.005	0.028	0.029	0.079	0.048	0.004	0.006	0.255	0.005	0.002	0.000	0.021
Flu	0.024	0.016	0.029	0.015	0.003	0.026	0.063	0.107	0.007	0.021	0.724	0.061	0.000	0.000	0.026
Phe	0.042	0.135	1.777	0.438	0.035	0.583	0.205	0.631	0.074	0.079	1.755	0.107	0.012	0.017	0.438
Ant	1.862	0.140	0.874	0.202	0.012	1.416	0.187	0.625	0.069	0.219	2.008	0.003	0.008	0.001	1.593
Flua	0.271	0.091	0.793	0.398	0.130	0.742	0.455	1.129	0.075	0.113	0.692	0.083	0.060	0.011	0.847
Pyr	0.380	0.200	1.771	0.782	0.262	1.641	1.022	1.394	0.111	0.198	0.862	0.061	0.115	0.045	1.323
BaA	112	2.849	27.61	5.084	2.550	1.860	30.20	10.72	4.335	13.64	17.37	0.982	4.557	0.063	38.79
Chr	0.094	1.288	9.252	1.634	0.445	0.958	8.080	4.767	1.950	4.296	6.217	0.438	0.578	0.045	7.295
BbF	40.20	1.775	2.833	6.300	2.162	3.910	17.05	5.777	3.311	4.714	9.214	1.938	0.141	0.145	11.44
BkF	9.175	0.519	0.252	2.296	1.501	0.997	4.707	1.406	0.819	0.964	2.837	2.541	0.227	0.114	2.541
BaP	28.26	3.198	3.439	26.90	9.634	17.62	50.25	3.680	29.89	9.991	22.03	17.022	0.137	0.044	29.88
IcdP	0.374	0.679	1.161	4.309	1.250	0.916	3.664	0.211	0.567	0.247	1.029	1.336	1.285	0.407	1.382
DahA	48.24	2.607	0.000	7.509	19.03	14.42	16.16	0.988	5.994	4.712	12.11	11.80	20.84	4.241	16.95
BghiP	0.470	0.071	0.093	0.705	0.031	0.011	0.669	0.043	0.073	0.046	0.143	0.178	0.135	0.060	0.246
ΣTEQ	241.1	13.61	49.92	56.61	37.26	45.27	132.9	31.58	47.30	39.27	77.59	36.56	28.10	5.192	112.8
C-PAHs[a]	1700	192.9	1247	377.8	147.8	204.7	1430	662.5	321.2	640.0	960.4	140.6	140.8	16.05	1318
BaPE[b]	159.1	8.621	23.09	43.92	26.14	31.56	96.22	15.90	39.43	25.17	48.98	28.90	16.66	3.133	74.20

[a] C-PAHs, Sum of seven carcinogenic PAHs (marked by bold font) (μg (kg fuel)$^{-1}$).
[b] The BaP-equivalent carcinogenic power (BaPE) for the total PAHs (μg (kg fuel)$^{-1}$): BaPE = BaA × 0.06 + B[b,k]F × 0.07 + BaP + DahA × 0.6 + IcdP × 0.08 ((Liu et al., 2009)).

fire had the lowest TEQ values (Gullett et al., 2012), a little lower than cookstove with different fuels (Oanh et al., 2005). Biomass TEQ varied largely in previous studies, which might be caused by the different combustion conditions. Although the TEQ from marine vessels were not so high, the health effect still cannot be neglected considering of the high emission factors of PM and the large amount of total PM emitted from vessels, especially in coastal areas (Chen et al., 2017; Zhang et al., 2018). Besides, a large amount of heavy metal elements are always emitted from ship exhausts, which could enhance the healthy influence further.

4. Conclusions

(1) Identified organic pollutants including 16 priority PAHs, 5 methyl substituted PAHs, and 29 n-alkanes in this study accounted for 0.14%–23.3% of PM for all the test vessels, with significant variations for different vessels. N-alkanes were the highest content species, whose sums made up percentages of 0.11%–21.3%. The 16 priority PAHs only accounted for very small proportions of 0.005%–0.13%.
(2) Fuel-based average EFs for Σ16PAHs and Σn-alkanes of each vessel ranged between 0.095 and 5.80 mg (kg fuel)$^{-1}$, 5.22 and 1589 mg (kg fuel)$^{-1}$ in this study, respectively. Fishing boats and the HFO training ship had relatively higher EFs for PAHs compared with light diesel vessels. However, as for n-alkanes, fishing boats with lower power engines and HFO vessels had relatively higher EFs levels compared with other vessels.
(3) Three- and four-ring PAHs of medium molecular weight accounted for 67%–98% of the total 16 PAHs, with Pyr, Flua, Phe, and Chr were the major compounds for all the test vessels in this study. N-alkanes from C15 to C33 accounted for more than 97% of the total n-alkanes. Both PAHs and n-alkanes profiles in PM emitted from ships showed significant differences compared with other sources. Besides, the ratios of Ant/(Ant + Phe), Flua/(Flua + Pyr), Flu/(Flu + Pyr), and IcdP/(IcdP + BghiP) in PM in this study indicated obvious petroleum combustion characteristics. Moreover, it was proved that diagnostic characteristics of W(nC23$^-$)/W(nC23$^+$), C_{max}, ACL, and CPI of n-alkanes in PM also can be used to distinguish ship emissions from other sources. Therefore, if possible, profiles of both PAHs and n-alkanes, along with their diagnostic characteristics should be taken into consideration together, which could provide possible approach to identify ship emissions from other sources in source apportionment.
(4) Potential toxicity risk of PAHs in PM from different emission sources were assessed, the results showed that the TEQ from marine vessels in this study had a medium level compared with other sources. However, the health influence still cannot be ignored due to the large amount of total PM emitted from ships in offshore areas.

This study fills a research gap by providing detailed EFs, profiles and diagnostic characteristics of organic pollutants in PM emitted from various vessels in China. In doing so, this study helps to estimate emission inventories of organic pollutants emitted from vessels and improve the accuracies of ship emission source identification and source apportionment.

Notes

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Appendix A. Supplementary data

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