

Identification of the sources of polycyclic aromatic hydrocarbons based on molecular and isotopic characterization from the Yangtze estuarine and nearby coastal areas

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Abstract: Samples of suspended particulate matters (SPMs), surface sediment and road dust were collected from the Yangtze estuarine and nearby coastal areas, coastal rivers, and central Shanghai. The samples were analyzed for the presence of 16 polycyclic aromatic hydrocarbons (PAHs) in the USEPA priority-controlled list by GC-MS. The compound-specific stable carbon isotopes of the individual PAHs were also analyzed by GC-C-IRMS. The sources of PAHs in the SPMs and surface sediments in the Yangtze estuarine and nearby coastal areas were then identified using multiple source identification techniques that integrated molecular mass indices with organic compound-specific stable isotopes. The results revealed that 3-ring and 4-ring PAH compounds were dominant in the SPMs and surface sediments, which are similar to the PAH compounds found in samples from the Wusong sewage discharge outlet, Shidongkou sewage disposal plant, Huangpu River, coastal rivers and central Shanghai. Principal component analysis (PCA) integrated with molecular mass indices indicated that gasoline, diesel, coal and wood combustion and petroleum-derived residues were the main sources of PAHs in the Yangtze Estuary. The use of PAH compound-specific stable isotopes also enabled identification of the PAHs input pathways. PAHs derived from wood and coal combustion and petroleum-derived residues were input into the Yangtze Estuary and nearby coastal areas by coastal rivers, sewage discharge outlets during the dry season and urban storm water runoff during the flood season. PAHs derived from vehicle emissions primarily accumulated in road dust from urban traffic lines and the commercial district and then entered the coastal area via the northwest prevailing winds in the dry season and storm water runoff during flood season.

Keywords: PAHs; source identification; compound-specific stable isotope; molecular mass index; the Yangtze Estuary

Received: 2009-03-01 **Accepted:** 2009-07-02

Foundation: National Natural Science Foundation of China, No.40801201; No.40730526; Special grade of the financial support from China Postdoctoral Science Foundation, No.200902224; China Postdoctoral Science Foundation, No.20080440605; Shanghai Postdoctoral Foundation, No.07R214120

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1 Introduction

Estuarine and nearby coastal areas are transitional zones between oceans and land that have various environmental functions and ecological values and play an important role in the economic development of coastal areas. Because they function as interactive zones between two different ecosystems, estuarine and nearby coastal areas are vulnerable to anthropogenic activities. Polycyclic aromatic hydrocarbons (PAHs) are a kind of persistent organic pollutants (POPs) that are hydrophobic, lipophilic and carcinogenic. PAHs can be introduced into the environment by multiple anthropogenic activities, which are generally considered to be the major sources of these compounds. Common sources of PAHs include incomplete combustion of fossil fuels, wood, biomass and other materials containing hydrocarbons (Bau-mard *et al.*, 1998; Oros *et al.*, 2004). In previous studies, the PAH molecular fingerprint, specific compounds molecular markers and organic chemical parameters were used to infer possible sources of PAHs (Yunker *et al.*, 2002; Yim *et al.*, 2005). However estuarine and coastal zones act as sinks for a wide variety of pollutants that originate on land as well as for organic matters generated by in situ organisms. As a result, the source signatures of PAHs in such systems are complex. Moreover, PAHs are subjected to physical, chemical, and biological weathering or transport influences that may alter the molecular signature of their original source (Currie *et al.*, 1999). Because there is no clear fractionation of stable carbon isotopes of organic compounds in response to surface geological processes, the characteristics of the composition of the isotopes of different sources materials cannot be interrupted. Therefore, compound-specific stable carbon isotope ratios have been used widely to identify the sources of PAHs in various environmental media including air, soil and sediment (O'Malley *et al.*, 1996; Smirnov *et al.*, 1998; Mcrae *et al.*, 1999; Reddy *et al.*, 2002; Stark *et al.*, 2003). In addition, the advent of compound-specific stable isotope analytical technology has facilitated PAH source identification (Walker *et al.*, 2005; Kim *et al.*, 2005).

The Yangtze River, which is one of the largest rivers in the world, is a major shipping route in China. As such, the Yangtze River is characterized by intense industrial and urban activity, especially in its lower reaches and estuary. The rapid economic development that has occurred along the Yangtze River has resulted in an increased influx of city industrial wastewater and sanitary waste, especially around the coastal areas of the river. Much of this wastewater has been untreated or insufficiently treated, which has led to a serious coastal water pollution problem in the Yangtze Estuary (Liu *et al.*, 2006). Additionally, the level of PAHs with the potential to damage estuarine ecological systems has increased in the Yangtze Estuary; therefore, evaluation of such compounds in this system has become urgent (Liu *et al.*, 1998). However, to date, identification of the sources of PAHs in the Yangtze estuarine and nearby coastal areas have been dependant on single indices, such as PAH isomer ratios or PAH ring numbers (Liu *et al.*, 1998; Liu *et al.*, 2000; Ou *et al.*, 2007), which has made the results of identification of the sources of PAHs ambiguous. Moreover, the use of a single index only enables petrogenic or pyrogenic sources to be distinguished. In the present study, a combination of multiple indices, including PAH rings, molecular weight ratios and compound specific stable carbon isotopes, was used to track the potential input sources of PAHs and elucidate their transport pathways. It is expected that the method described here will reduce the uncertainty associated with single index source identification.

2 Materials and methods

2.1 Sample collection

Ten sites in the Yangtze estuarine and nearby coastal areas were selected for the collection of overlying water and surface sediment (top 2 cm) based on the characteristics of the estuarine tidal ecosystem and human activities. Samples were collected in February (dry season) and August (flood season) of 2006. In addition, overlying water samples in the coastal rivers (Liuhe, C1; Dazhihe, C2; Jinhuigang, C3) and sewage samples from the Shidongkou sewage disposal plant (SD) and Wusong sewage discharge outlet (WS) were also collected. Additionally, surface sediment samples (top 2 cm) were collected in the Huangpu River (S1–S5) in August 2005 (flood season) and February 2006 (dry season). Surface sediment samples were collected using a stainless steel grab sampler and placed in pre-cleaned glass jars. Overlying water samples and sewage samples were collected into individual 10 L pre-cleaned glass bottles using a stainless-steel submersible pump. The samples were returned to the laboratory, where the SPMs were collected by filtering the water samples through 0.7 μm nominal pore size Whatman GF/F glass fiber filters (combusted for 5 h at 450°C prior to filtration). Next, the filters were placed in pre-cleaned glass dishes, wrapped with aluminum foil and stored at -20°C until analysis. Road dust samples were also collected from traffic lines, industrial areas, cultural and educational districts and a commercial center located in Shanghai using a straw brush in February and August of 2005 and August of 2006 (Figure 1). The road dust samples were stored in solvent-rinsed tightly-sealed amber vials at -20°C until analysis.

2.2 PAH compounds analysis

Approximately 20 g of freeze-dried sample were used for PAH analysis. Activated copper powder and deuterated surrogate recovery standards (d_8 -naphthalene, d_{10} -anthracene, d_{12} -phenanthrene, d_{12} -chrysene and d_{12} -perylene) were added to all samples prior to solvent extraction. The samples were then extracted with a solvent mixture of acetone: dichloromethane (v:v 1:1) for 48 h using a Soxhlet apparatus. The extracts were then concentrated, solvent-exchanged to hexane, and further purified using a silica:alumina (v:v 2:1) chromatographic column filled with anhydrous sodium sulfate. The first fraction, which contained the aliphatic hydrocarbons, was eluted with 15 mL hexane. The second fraction, which contained the target PAHs, was collected by eluting 70 mL of a mixture of dichloromethane:hexane (v:v 3:7). Subsequently, the PAH fraction was concentrated to 2 mL by rotary evaporation and then further reduced to 0.5 mL with nitrogen gas. The samples were then evaluated for the presence of the target PAHs by gas chromatography coupled with mass spectrometry (GC-MS, Finnigan TRACE DSQ), which was performed in the selected ion monitoring mode. For GC-MS, a fused-silica CP SIL CB8-MS capillary column (30 m \times 0.25 mm \times 0.25 μm , Varian) was used with helium as the carrier gas. The temperature program of the oven consisted of 80°C for 2 min, followed by an increase of 6°C/min to 290°C, which was held for 20 min. The mass spectrometer was operated in the electron im-

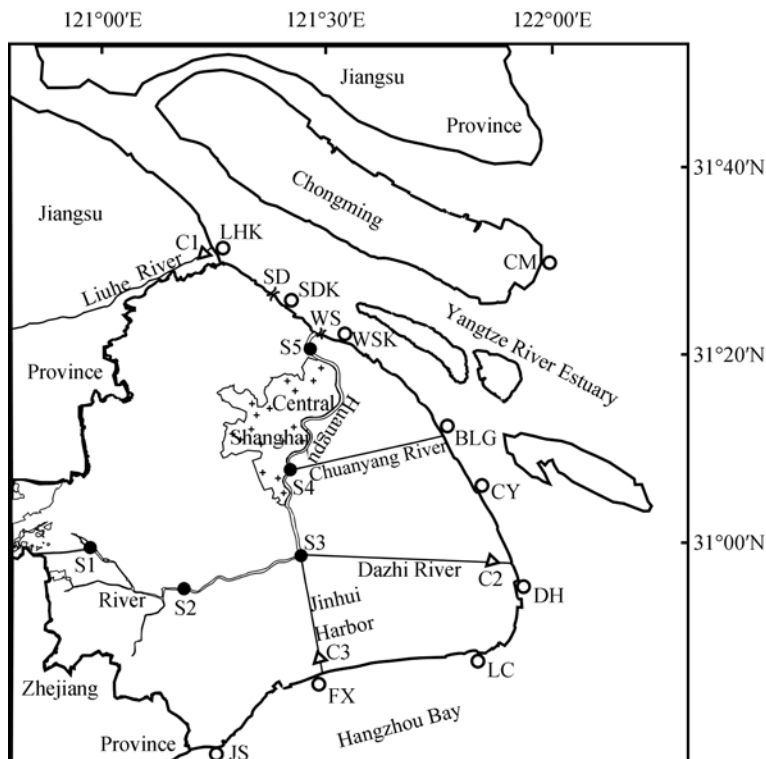


Figure 1 Sampling locations for the identification of sources of PAHs in the Yangtze Estuary

(○: Sampling sites around the Yangtze estuarine and nearby coastal areas; △: Sampling sites in coastal rivers; ≈: Sampling sites in sewage discharge outlets; ●: Sampling sites in Huangpu River; +: Sampling sites in central Shanghai)

pact (EI) mode, with an ion source at 270°C and an electron voltage of 70 eV.

The clean sample extracts and blanks were spiked with deuterated surrogate recovery standards prior to solvent extraction. Recoveries of surrogates generally ranged from 50% to 120% of the spiked concentration. The final PAH concentrations were corrected for surrogate recoveries. A deuterated internal standard was used to calculate all concentrations. Prior to GC-MS analysis, the extracts were spiked with a deuterated internal standard mixture consisting of d_{10} -fluorene and d_{12} -benzo[a]pyrene. To evaluate the accuracy of the analysis, a National Institute of Standards and Technology (NIST) standard reference material (SRM 1941) was analyzed. The concentrations of the target analytes in the NIST SRM 1941 were within 80–120% of the certified values. The target compounds included the following 16 PAH compounds: naphthalene (Na), acenaphthylene (Acey), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IP), dibenzo[*a,h*]anthracene (DA), and benzo[*ghi*]perylene (BP).

The surrogate recoveries were 46%–65% for naphthalene- d_8 , 84%–86% for acenaphthene- d_{10} , 80%–108% for phenanthrene- d_{10} , 88%–92% for chrysene- d_{12} and 89%–99% for perylene- d_{12} .

2.3 Compound-specific stable isotope analysis

The samples for CSIA were Soxhlet-extracted using dichloromethane and acetone. However, deuterated surrogate recovery standards were not added to the samples because they may co-elute with the target PAHs and cannot be resolved by gas chromatography-isotope ratio mass spectrometry (GC-C-IRMS) (Walker *et al.*, 2005). After undergoing purification as described above, additional cleanup was conducted using gel permeation chromatography and thin layer chromatography (Kim *et al.*, 2005) to avoid interference by unresolved complex mixture.

The purified samples were analyzed using a GC-C-IRMS system that employed an Agilent 6890N GC interfaced with a modified Finnigan GC Combustion III unit followed by GV Isoprime isotope mass spectrometry. Compounds were separated on a HP-5MS fused silica capillary column (60 m×0.32 mm×0.25 μm, J&W Scientific). Helium was used as the carrier gas and the flow rate was maintained at 1.0 mL/min. The GC column temperature was programmed to be initially held at 80°C for 2 min, followed by an increase to 160°C at a rate of 10°C/min, where it was held for 2 min, and then another increase to 290°C at a rate of 3°C, where it was held for 20 min.

During each analysis, pulses of a reference CO₂ and *n*-dodecane ($\delta^{13}\text{C}$ value, -28.9‰) were co-injected into the mass spectrometer to monitor the performance of the instrument. The $\delta^{13}\text{C}$ values for each sample were determined by comparing the ¹³C/¹²C ratios of the sample relative to Vienna Pee Dee Belemnite (VPDB) (Eq.(1)). Each sample was injected in duplicate, and samples exceeding 0.6‰ standard deviation were not used in the data analysis.

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000 (\text{‰}, \text{VPDB}) \quad (1)$$

3 Results and discussion

3.1 Evaluation of petrogenic versus pyrogenic sources

The composition characteristics of PAHs in the Yangtze estuarine and nearby coastal areas as well as other potential environmental sources are shown in Figure 2. The PAH compounds in the SPMs and surface sediments from the Yangtze Estuary were dominated by 3-ring and 4-ring PAHs, such as Phe, An, Fl, Py, BaA and Chry. Principal component analysis of the 16 PAH compounds in the SPMs and surface sediments demonstrated that those PAH compounds could be divided into two principal components (Figure 3). Principal Component 1 (PC1) was composed of the following high molecular weight PAHs (HMW): Phe, An, Fl, Py, BaA, Chry, BbF, BkF, BaP, InP and BghiP. Principal Component 2 (PC2) was composed of the following low molecular weight (LMW) and volatile PAHs: Na, Acy, Ace and Fluo. Previous studies demonstrated that parent PAHs were primarily produced by uncompleted combustion of fossil fuels and plant materials or natural diagenesis (Laflamme *et al.*, 1978; Lake *et al.*, 1979; Yunker *et al.*, 1996). Of the combustion-derived PAHs, LMW PAHs (178–202) are primarily produced at low to moderate temperatures (Lake *et al.*, 1979; Yunker *et al.*, 1996), while HMW PAHs (228–276) are generated at high temperatures (Muel *et al.*, 1985). It should be noted that petroleum-derived residues also contain relatively high abundances of 2-ring and 3-ring PAHs (Tolosa *et al.*, 1996; Mai *et al.*, 2003). Therefore, the

results indicate that the two major sources of PAHs in the Yangtze estuarine and nearby coastal areas are incomplete combustion of fossil fuels (PC1) and petroleum-derived residues (PC2) (Figures 2 and 3). In addition, the results shown demonstrate that the PAH composition of different environmental media were similar to the composition of samples collected from the Yangtze Estuary (Figure 2). These findings indicate that the Wusong sewage discharge outlet, Shidongkou sewage disposal plant, Huangpu River, coastal rivers and central urban area contributed PAHs to the Yangtze Estuary (Takada *et al.*, 1990).

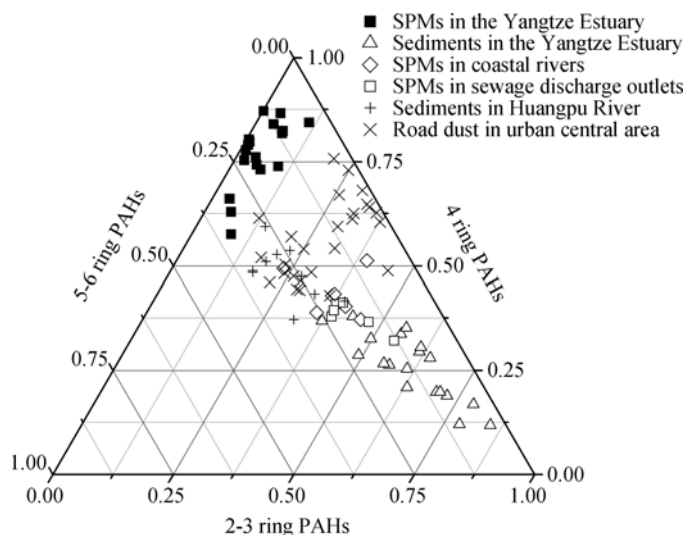


Figure 2 PAH compositions of SPMs (■), surface sediments (△) from the Yangtze Estuary, SPMs from coastal rivers (◇), SPMs from sewage discharge outlets (□), sediments from Huangpu River (+), and road dust samples from central Shanghai (×)

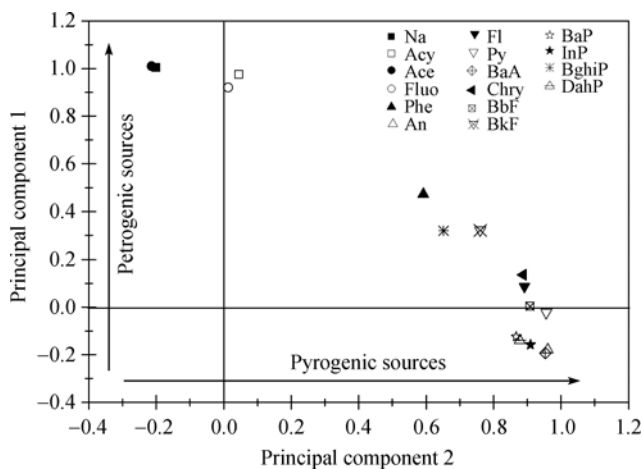


Figure 3 The relationship between Principal Component 1 and Principal Component 2 as determined by principal component analysis of the PAH composition of the SPMs and surface sediments

3.2 Differentiation of pyrogenic PAH sources

Parent PAH isomers have similar physical-chemical properties, thus they have similar dilu-

tion and distribution characteristics after entering the environment. As a result, certain specific PAH isomers can be applied as distinct chemical tracers to further infer pyrogenic PAH sources (Yunker *et al.*, 1996). In general, the following four PAH isomer pair ratios are used: An/178 (An/(Phe+An)), Fl/202 (Fl/(Fl+Py)), BaA/228 (BaA/(BaA+Chry)) and InP/276 (InP/(InP+BghiP)) (Yunker *et al.*, 2002; Yunker *et al.*, 1996; Wise *et al.*, 1988; Grimmer *et al.*, 1981; Budzinski *et al.*, 1997). The An/178 isomer pair ratios for the SPMs from the Yangtze Estuary ranged from 0.09 to 0.34, while the Fl/202 isomer pair ratios ranged from 0.51 to 0.60, the BaA/228 isomer pair ratios ranged from 0.33 to 0.61, and the InP/276 isomer pair ratios ranged from 0.09 to 0.75. When the surface sediments in the Yangtze Estuary were evaluated, the An/178 isomer pair ratios were found to range from 0.05 to 0.12, while the Fl/202 isomer pair ratios ranged from 0.34 to 0.71, the BaA/228 isomer pair ratios ranged from 0.24 to 0.55, and the InP/276 isomer pair ratios ranged from 0.35 to 0.66 (Figure 4). A comparison of the molecular ratios determined for all samples collected in this study with the ratios reported in previously conducted studies (Yunker *et al.*, 2002; Yunker *et al.*, 1996; Wise *et al.*, 1988; Grimmer *et al.*, 1981; Budzinski *et al.*, 1997) (Tables 1–2 and Figure 4) revealed that the PAH compounds in the Yangtze Estuary were from a wide variety of pyrogenic sources, even though they were similar to the ratios of the standard materials from PAH pyrogenic sources. Moreover, it is difficult to identify pyrogenic sources because the isomer pair ratios of PAHs from these sources are very similar. Taken together, these results reflect the complex nature of the effects of anthropogenic activities and the large volume of pollutants impacting the Yangtze estuarine and nearby coastal areas. In addition, these results show the limitation of the use of PAH isomer pair ratios or molecular ratios for source identification.

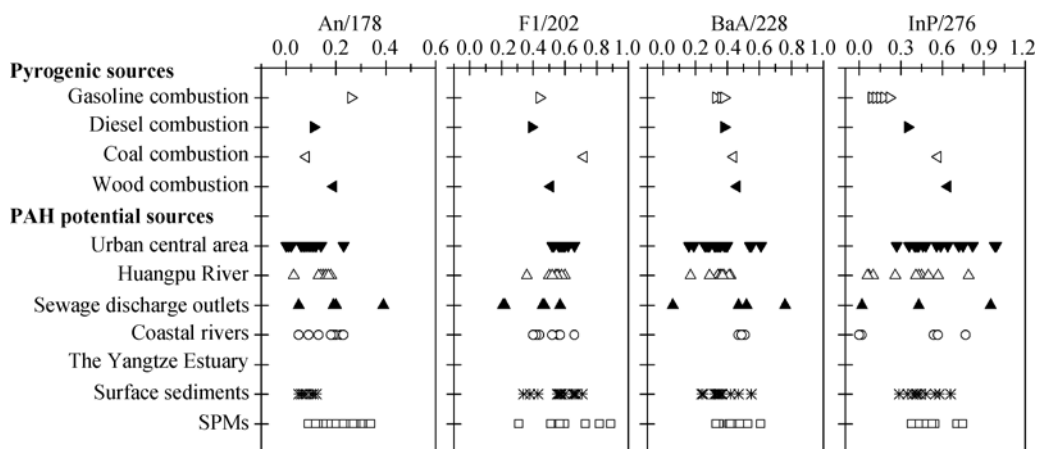


Figure 4 Comparison of molecular ratios determined in all samples from this study with published data for known PAH sources

3.3 Distributions of PAH $\delta^{13}\text{C}$ values

3.3.1 The Yangtze estuarine and nearby coastal areas

The compound-specific $\delta^{13}\text{C}$ values of the SPMs in the Yangtze estuarine and nearby coastal areas had some fractionation. As the molecular weight increased, the $\delta^{13}\text{C}$ values had no

regular changes, with the exception of isotope compositions of Fl being comparatively light. In general, the $\delta^{13}\text{C}$ values of the SPMs in the study area primarily ranged from -27.81‰ to -20.87‰ . The $\delta^{13}\text{C}$ mean values for Phe and An in the dry season were -23.94‰ and -21.72‰ , respectively, while they were -25.56‰ and -26.22‰ , respectively, during the flood season. The mean $\delta^{13}\text{C}$ values for Fl and Py were -26.39‰ and -24.47‰ during the dry season, respectively, and -26.12‰ and -23.98‰ during the flood season, respectively (Figure 5 and Table 3). The compound-specific PAH $\delta^{13}\text{C}$ values were close to the PAH origins and generation type (Walker *et al.*, 2005; O'Malley *et al.*, 1994). Car soot was reported to have the heaviest PAH $\delta^{13}\text{C}$ values, ranging from -24.2‰ to -22.5‰ (Mcrae *et al.*, 1999; Glaser *et al.*, 2005). This was followed by the PAH $\delta^{13}\text{C}$ values of coal soot (-26.1‰ to -24.8‰) (Mcrae *et al.*, 1999; Glaser *et al.*, 2005), petroleum (-27.0‰ to -28.0‰) (Glaser *et al.*, 2005) and wood combustion (-28.8‰ to -28.0‰) (O'Malley *et al.*, 1997). In this study, these isotope patterns indicate that automotive exhausts (gasoline, diesel), coal combustion and petroleum were the sources of the majority of PAHs in the SPMs from the study area.

The compound-specific $\delta^{13}\text{C}$ values in surface sediments were relatively light, ranging from -31.49‰ to -21.10‰ . Only the $\delta^{13}\text{C}$ mean values for Fl were higher in the dry season, while all other mean values were higher during the flood season. The mean values of Phe, An, Fl and Py during the dry and flood seasons were -25.06‰ and -25.66‰ , -24.92‰ and -26.53‰ , -29.35‰ and -26.81‰ and -24.04‰ and -24.51‰ , respectively (Figure 5 and

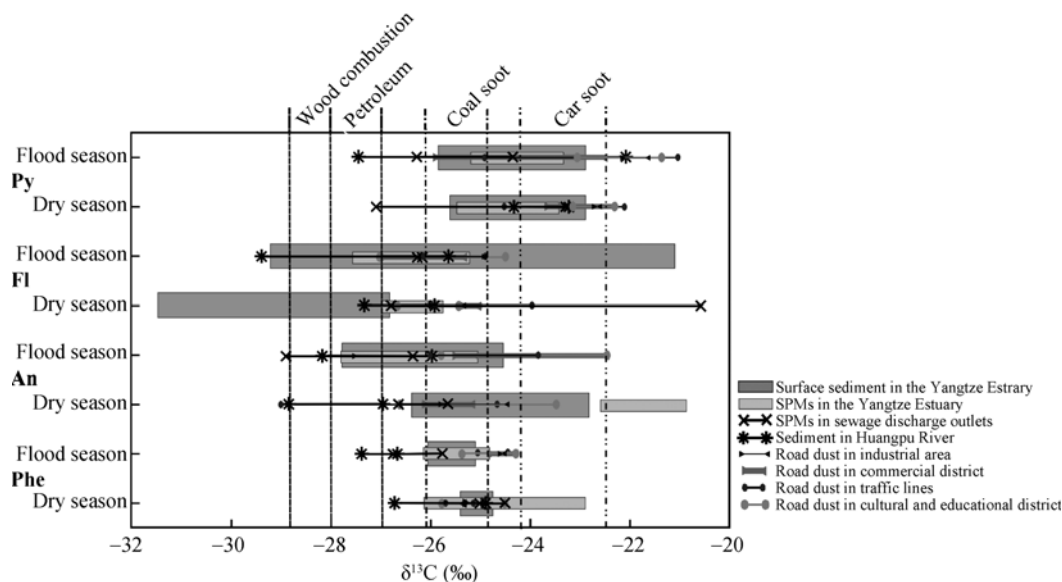


Figure 5 PAH compound-specific stable isotopes of SPMs and surface sediments from the Yangtze Estuary and targeted sources

Table 1 Molecular ratios of standard materials from PAH pyrogenic sources

	An/178	Fl/202	BaA/228	InP/276
Gasoline combustion	0.19	0.51	0.46	0.64
Diesel combustion	0.11	0.39	0.38	0.35
Coal combustion	0.08	0.72	0.44	0.57
Wood combustion	0.26	0.44	0.36	0.15

Table 2 Molecular ratios determined for all samples from the Yangtze Estuary and targeted sources

		An/178	Fl/202	BaA/228	InP/276
The Yangtze estuarine and nearby coastal areas	SPMs	0.21	0.57	0.45	0.52
	Surface sediments	0.09	0.56	0.35	0.49
	Urban central areas	0.09	0.58	0.34	0.42
PAH potential sources	Huangpu River	0.14	0.53	0.34	0.36
	Sewage discharge outlets	0.22	0.39	0.41	0.49
	Coastal rivers	0.13	0.59	0.49	0.37

Table 3 PAH compound-specific stable isotopes of SPMs and surface sediments from the Yangtze Estuary and targeted sources (‰)

		Phe	An	Fl	Py
Dry season	SPMs in the Yangtze Estuary	-23.94	-21.72	-26.39	-24.47
	Surface sediments in the Yangtze Estuary	-25.06	-24.92	-29.35	-24.04
	SPMs in sewage discharge outlets	-24.77	-26.14	-23.70	-25.19
	Sediments in Huangpu River	-26.88	-26.76	-27.88	-25.45
	Road dust in industrial areas	-25.28	-25.13	-25.65	-22.66
	Road dust in commercial districts	-25.34	-25.66	-25.23	-23.01
	Road dust in traffic lines	-25.43	-26.16	-25.29	-22.82
	Road dust in cultural and educational districts	-25.23	-25.29	-25.67	-22.62
	SPMs in the Yangtze Estuary	-25.56	-26.22	-26.12	-23.98
Flood season	Surface sediments in the Yangtze Estuary	-25.66	-26.53	-26.81	-24.51
	SPMs in sewage discharge outlets	-26.28	-27.63	-26.22	-25.32
	Sediments in Huangpu River	-25.84	-28.05	-26.58	-23.82
	Road dust in industrial areas	-24.55	-26.30	-24.91	-21.86
	Road dust in commercial districts	-24.56	-24.01	-26.15	-24.22
	Road dust in traffic lines	-24.72	-24.95	-25.35	-23.02
	Road dust in cultural and educational districts	-24.90	-24.36	-25.29	-22.46

Table 3). These $\delta^{13}\text{C}$ values suggest that the sources of PAHs in the surface sediments were similar to the sources of PAHs in the SPMs. In addition, these results suggest that wood combustion was also the predominant source of PAHs in the surface sediments.

When point sources such as the Wusong sewage discharge outlet and the Shidongkou sewage disposal plant were evaluated, the PAH $\delta^{13}\text{C}$ values for particles in the sewage ranged from -28.90‰ to -20.59‰ (Figure 5). Fl in the dry season had a heavier $\delta^{13}\text{C}$ (-23.70‰ , mean value) than Fl during the flood season (-26.22‰ , mean value). In addition, the $\delta^{13}\text{C}$ values for Phe, An and Py were light. When the Phe values were evaluated, the $\delta^{13}\text{C}$ mean value during the dry season was -24.77‰ , while it was -26.28‰ during the flood season. When An and Py were evaluated during the dry season, their $\delta^{13}\text{C}$ values were -26.14‰ and -27.63‰ , respectively, while they were -25.19‰ and -25.32‰ during the flood season (Table 3). These results indicate that PAHs in the point sources were primarily introduced by coal combustion, vehicle emissions, and petroleum.

3.3.2 Huangpu River

The compound-specific $\delta^{13}\text{C}$ values of samples collected from the Huangpu River ranged

from -29.36‰ to -22.06‰ . The $\delta^{13}\text{C}$ values for Py were the heaviest, with values in the dry season and flood season being -23.82‰ and -25.45‰ , respectively. These values were followed by the $\delta^{13}\text{C}$ values of Phe (-25.84‰ , dry season; -26.88‰ , flood season), Fl (-26.58‰ , dry season; -27.88‰ , flood season) and An (-28.05‰ , dry season; -26.76‰ , flood season). Incomplete combustion of wood and petroleum were the primary sources of PAHs in the river, while incomplete coal combustion and vehicle emission made lesser contributions (Figure 5 and Table 3).

3.3.3 Central Shanghai

The compound-specific $\delta^{13}\text{C}$ values in road dust samples collected from the central urban area ranged from -29.02‰ to -21.77‰ (Figure 5). The $\delta^{13}\text{C}$ values of Py that had accumulated in the road dust from the industrial area, traffic lines and cultural and educational districts were heavy, while the values of Phe, An and Fl did not differ among districts (Table 3). The distribution characteristics of $\delta^{13}\text{C}$ values in urban road dust demonstrated that, in addition to car emissions and incomplete combustion of coal, wood combustion also produced PAHs found in urban road dust. These findings differ from the results of samples collected from other districts. There were also coal combustion-derived PAHs in road dust samples collected from the industrial area. In addition, auto emission and coal combustion-derived PAHs were enriched in road dust from the commercial district, while coal combustion-derived PAHs were dominant in road dust from the cultural and educational districts.

It was preferable to infer the sources and input pathways of PAHs in SPMs and surface sediments from the Yangtze estuarine and nearby coastal areas by combining the PAH compound-specific $\delta^{13}\text{C}$ values of different environmental media in the study area with those of the targeted sources. In the dry season (winter), vehicle emissions (gasoline, diesel oil) and coal combustion were the primary sources of PAHs in the Yangtze estuarine and nearby coastal areas. Vehicle emissions were enriched in the road dust of the central urban area, and were then likely transferred into the estuary by the prevailing regional winds. Conversely, PAHs produced by coal combustion were likely input directly from coastal rivers (Huangpu River). Wood combustion-derived PAHs and petroleum-derived residues were also likely input directly from coastal rivers. During the flood season, vehicle emission and coal combustion were the primary sources of PAHs, which were abundant in the urban road dust. Moreover, petroleum-derived residues in the estuary also increased due to coastal runoff. The PAH sources mentioned above were also input directly following storm water runoff or entered from sewage discharge outlets.

4 Conclusions

(1) PAH compounds in the SPMs and surface sediments in the Yangtze estuarine and nearby coastal areas were primarily composed of 3-ring and 4-ring PAHs, including Phe, An, Fl, Py BaA and Chry. The incomplete combustion of gasoline, diesel oil, charcoal and wood and other petroleum-derived residues were the main sources of PAHs in the SPMs and surface sediments. The Wusong sewage discharge outlet, Shidongkou sewage disposal plant, Huangpu River, coastal rivers and central urban were also contributed PAHs to the Yangtze estuarine and nearby coastal areas.

(2) PAH compound-specific $\delta^{13}\text{C}$ values enabled identification of the sources of PAHs

and their transfer pathways in the complicated environment in the Yangtze estuarine and nearby coastal areas. PAHs formed by the incomplete combustion of wood and charcoal and PAHs associated with petroleum-derived residues were input directly into the system from coastal rivers and sewage discharge outlets during the dry season, while PAHs in urban road dust entered the system following rainstorms during the flood season. PAHs derived from auto emissions (gasoline, diesel) were abundant in road dust from urban traffic lines and commercial districts. These PAHs were then transferred to the estuary by regional prevailing winds during the dry season and storm water runoff during the flood season.

(3) The SPMs and sediments in the Yangtze estuarine and nearby coastal areas were strongly influenced by runoff and sand from the Yangtze River. Due to the high level of anthropogenic activities around the coastal areas and complicated hydrodynamic forces in the system, the PAHs in the SPMs and surface sediments have various sources. Although the PAH ring number, molecular weight ratios and organic compound-specific stable isotopes enabled qualitative identification of the source of PAHs, additional research is necessary to enable quantitative source identification.

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