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Supporting Information

Molecular characterization of PAHs based on land use analysis and multivariate

source apportionment in multi-phases of Yangtze estuary, China

Xing Chen^{a, b}, Xinran Liu^{a, b, *}, Min Liu^{a, b, *}, Yi Yang^{a, b}, Shixue Wu^{a, b}, Chong Wang^a,

b

^a Key Laboratory of Geographic Information Science (Ministry of Education), East China Normal University, Shanghai, 200241, China

^b School of Geographic Sciences, East China Normal University, Shanghai, 200241, China

*Corresponding Authors:

Email addresses: xrliu@geo.ecnu.edu.cn (X. Liu), mliu@geo.ecnu.edu.cn (M. Liu) Telephone number: +862154341207

<u>S1. Supporting Methodology</u>

Sediment **pH** was measured using a Mettler-Toledo pH meter after soil was mixed with deionized water free of CO_2 at a sediment to water ratio of 1:2.5 (w/v).

Total organic carbon (TOC) in sediments was measured using the $K_2Cr_2O_7$ oxidationreduction titration method.

Sediment **black carbon (BC)** was measured by method chemical oxidation (dichromate oxidation, BC_{Cr}) and chemo-thermal oxidation (CTO-375, BC_{CTO}), respectively. The acidification of the sediment was processed with 1 M HCl to remove carbonate and oxidanted by the mixture solution of $K_2Cr_2O_7$ -H₂SO₄ to determine the BC_{Cr} ¹. Sediment was acidified with 1 M HCl and oxidation 375 C for the BC_{CTO} determination². The BC contents of the residues which survived after chemical oxidation and thermal were determined with a CHNS elemental analyzer (Vario MICRO cube, Elementar Inc., Germany).

Stable carbon isotope compositions (δ^{13} C) of TOC and BC (BC_{Cr}) were determined by a Flash Elemental Analyzer (EA1112) connected to an Isotope Ratio Mass Spectrometer (Model: DELTA plus/XP, Finnigan MAT Co.).

The contents of **total nitrogen (TN)** in the soil samples were determined using a CN thermal combustion furnace analyzer (Elementar analyzer vario Max CN, Germany) after soils were leached by 1 M HCl solution.

Total phosphorus (TP) in sediments was measured using spectrophotometer after fusing sediments with the mixture solution of concentrated H_2SO_4 -HClO₄, followed by dissolution with deionized water. TP in solution was measured using molybdenum blue

method^{3, 4}.

Grain size of each sediment sample was determined with a Microtrac S3500 Laser Particle Size Analyzer (Microtrac Inc., Montgomeryville, PA) after pretreatment. Firstly, approximately 0.1 g sediment sample was treated with 15 mL 10% H_2O_2 (v/v) to eliminate influence by organic matter. Then, the mixture of sediment and H_2O_2 was heated until no bubbles and it was heated again to remove extra HCl after adding 10 mL 1 M HCl to remove carbonate sequentially. Finally, 10 mL dispersant solution was added into treated samples and vibrated absolutely before analysis

PAHs analysis in water phase. Water sample was directly filtered by using calcined 0.45 μ m glass microfiber filter (GF/F, Whatman, USA, baked at 450 °C for 4 h). PAHs in filtrate were extracted through solid phase extraction (SPE). According to Wu et al.⁵, the SPE procedure using C-18 cartridges has been performed. Firstly, SPE column was activated into balance with 5 mL DCM, methanol and ultrapure water successively. Then, the controlling loading water velocity was 5 mL·min⁻¹. Next step, target PAHs was eluted with 15 mL of mixed solvent [DCM and n-hexane (3:7, v/v)] after extraction. Last, the PAHs eluent was reduced to 1 mL for gas chromatography/mass spectrometry (GC/MS) analysis.

PAHs analysis in suspended solid phase and sediment phase. The suspended solids that were separated by GF/F are filtered from 2.0 L water samples. Suspended solids and sediments were dried by freeze-drying. The PAHs in suspended solids and sediment samples were extracted according to Yu et al.⁶. An accelerated solvent extractor (ASE-350, Dionex, USA) was used for the extraction of PAHs. Suspended solids samples or

about 3 g of surface sediment samples were extracted under 1500 psi at 100 °C using a mixture of dichloromethane and acetone (1:1, v/v) in triplicates. The extract was then solvent-exchanged into hexane, and cleaned up over amorphous sodium sulfatealumina-silica gel columns⁷. The eluates were then concentrated and solvent exchanged and reduced to 1 mL. Sixteen EPA priority PAHs in concentrated extracts were identified by GC-MS equipped with a DB-5 polysiloxane polymer column (30 m×250 μ m×0.25 μ m) (Agilent 7890A/5975C). The oven temperature was held at 55 °C for 2 min, heated to 280 °C at a rate of 20 °C min⁻¹ and held for 4 min, and then heated to 310 °C at a rate of 10 °C min⁻¹ and held for 5 min. The injection volume was 1 μ L in a splitless mode. The experimental procedure was tested for recoveries by analyzing spiked blanks with 16 PAHs standards, and the recoveries of 16 PAHs ranged from 72% to 106%. Five deuterated PAH mixture standard solutions were added into the each extract solution prior to the measurement of PAHs to test accuracy. All samples were determined in triplicate. The relative standard deviations (RSDs) and relative average deviations for each compound were on average 13.4% and 9.8%, respectively. Two blanks and two standards (a mixture of 16 EPA PAHs and 5 deuterated PAHs) were carried out every 10 samples. Furthermore, method blanks were determined for any background contamination. The blanks were always negligible. All samples were corrected for both blanks and recoveries.

The experimental procedure was tested for recoveries by analyzing spiked blanks with 16 PAHs standards, and the recoveries of 16 PAHs ranged from 72% to 106%. Five deuterated PAH mixture standard solutions were added into the each extract solution prior to the measurement of PAHs to test accuracy. All samples were determined in triplicate. The relative standard deviations (RSDs) and relative average deviations for each compound were on average 13.4% and 9.8%, respectively. Two blanks and two standards (a mixture of 16 EPA PAHs and 5 deuterated PAHs) were carried out every 10 samples. Furthermore, method blanks were determined for any background contamination. The blanks were always negligible. All samples were corrected for both blanks and recoveries.

Ecological risk assessment in water and SPM phase by LC_{50} . The LC_{50} is the concentration of toxicant, which is lethal to 50% of the test organisms. The acute toxicity of PAHs to aquatic organisms data were based on US EPA AQUIRE ECOTOX database. Considering the trophic levels in different aquatic ecosystems, a variety of organisms including aquatic plants, fishes, amphibians, zooplanktons, and annelidas were selected. If one organism has multiple believable toxicity data, geometric mean value is used to represent the effective toxicity data⁸.

Collective damage of each independent single PAH can be considered as consummate damage of concerning various PAHs at definite location due to their alike biological toxicity behavior⁹. The superposition effect can be considered as the quantity of their equivalent concentrations¹⁰ or the sum of the equivalent coefficient of every PAH¹¹.

The relationship between measured concentration and lethal concentration can be presented as for a simple index reaction association¹²:

$$c = c \times LC_{50i}/LC_{50e}$$

Where, c is the measured concentration of given PAHs; c_{eq} represents the equivalent mass concentration (that is, the equivalent concentration of PAHs to BaP concentration); LC_{50i} and LC_{50e} represent concentration of BaP and specific PAHs that are lethal to 50% of testing organisms. Under this supposition, the ratio of c_{eq} and c determine the equivalent coefficient of all kinds of PAHs.

The risk characterization of PAHs was based on the risk quotient of total equivalent concentration of PAHs.

$$Q = \left(\sum c_{eq}\right) / LC_{50d}$$

When Q > 1, there was potential ecological risk, the greater potential risk was with larger values of Q. When Q < 1, there was little probability to break out ecological problems.

Mean sediment quality guideline. Long¹³ introduced the method of determining ecological risks of PAHs and some scholars¹⁴ applied the concentrations of effects range low (ERL) and effects range median (ERM) to evaluate the ecological toxicity of individual PAH. Furthermore, the quotient technique of average ERM was a complex manner of quantitative prediction for joint toxicity of pollutants in the estuary surface sediments.

$$ERMQ_{i} = C_{i} / ERM_{i}$$
$$MERMQ = \left(\sum_{i=1}^{n} ERMQ_{i}\right) / n$$

where C_i is the measured concentration of PAHs; ERM_i represents the effects rangemedian values. $ERMQ_i$ is the effects range-median quotient of PAH pollutant i. MERMQ stands for average risk quotients of ERM concentrations. Based on data from previously published results¹³, The *ERM* benchmark values for NaP, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA and BghiP in sediments are 2100, 640, 500, 540, 1500, 1100, 5100, 2600, 1600, 2800 , 1880, 1620, 1600, 260 and 1600 ng/g, respectively. Different *MERMQ* classifications are delineated in Table S1.

Toxicity assessment and health risk analysis. Among 16 PAHs, there are seven PAHs, including BaA, Chr, BaP, BbF, BkF, IcdP and DahA, with high toxic and carcinogenic effects. Toxic equivalent quantity (TEQ) method was suggested by the US EPA¹⁵ to estimate the relative toxicity of carcinogenic PAHs in the sediment, which can be calculated as following equation:

$$TEQ_i = TEF_i \times C_{PAH_i}$$
$$TEQ_{PAH} = \sum TEQ_i$$

where, TEQ_i is the toxic equivalent quantity of ith PAH in the sediment; TEF_i is the toxic equivalence factor of ith PAH. The *TEF* values of BaA, Chr, BaP, BbF, BkF, IcdP and DahA are 0.1, 0.001, 1, 0.1, 0.1, 0.1 and 1, respectively¹⁶; C_{PAHi} is the concentration of ith PAH in the sediment; Toxic equivalent quantity (TEQ_{PAH}) is the sum toxic concentration of total seven PAHs, which is equivalent to the toxic concentration of BaP.

The carcinogenic risk value is calculated according to the toxic concentration of total PAHs which is equivalent to the toxic concentration of BaP. This study focused on assessing the health risk of PAHs in the sediment through two main pathways: (1) direct ingestion of sediment particles and (2) dermal absorption of PAHs in sediment particles adhered to exposed skin. The following equations are proposed to calculate

exposure through these two pathways by US EPA¹⁷:

$$CR_{ing} = C_{sed} \times IngR \times EF \times ED \times CF \times SFO/BW \times AT$$
$$CR_{derm} = C_{sed} \times SA \times ABS \times EF \times ED \times CF \times SFO/BW \times AT$$

where, CR_{ing} , cancer risk via ingestion from the sediment; C_{sed} , the concentration equivalent to BaP toxicity in the sediment; IngR, ingestion rate, in this study, 100 mg day⁻¹; *CF*, conversion factor, 1×10⁻⁶ kg mg⁻¹; *EF*, exposure frequency, 350 d a⁻¹; *ED*, exposure duration, 70 a; *BW*, average body weight, 70 kg; *AT*, averaging time, 25,550 d; *SFO*, oral slope factor, 7.3 (mg/kg/d)⁻¹; *CR*_{derm}, cancer risk via dermal contact of the sediment; *SA*, exposed skin surface area, 5700 cm²; *AF*, adherence factor from the sediment to skin, 0.07 mg cm⁻²; *ABS*, dermal absorption from the sediment, 0.13. According to the different cancer risk ranges, the cancer risk classifications are delineated in Table S2¹⁸.

Positive matrix factorization (PMF). Positive matrix factorization (PMF) is an advanced method of multivariate factor analysis based on a weighted least-squared problem. PMF is used to determine factors for explaining sources or processes and latent information that dominate the characteristics of input variable data. PMF incorporates the variable uncertainties and forces all of values to be positive, which is reasonable to real environmental problem^{19, 20}. PMF factorizes the initial data matrix into factor score matrix and factor loading matrix, and expressed as the following equation²¹:

$$X = G \times F + E$$

where, matrix X is the measured concentration data matrix $(n \times m)$ with n samples and

m items of pollutants; matrix G is factor score matrix $(n \times p)$; matrix F is the factor loading matrix $(p \times m)$; matrix E is the residual $(n \times m)$. And p is the number of the sources. The model, in component form, is expressed as the following formula:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad i = 1 \text{K} \ n; j = 1 \text{K} \ p$$

where, X_{ij} are the elements of the input data matrix, each element represents the concentration of the *j*th species for sample *i*; the g_{ik} and f_{kj} are the elements of the factor scores and factor loading matrices; the e_{ij} are the elements of the residual matrix, and each element is the difference between input data value and the corresponding predicted value. To obtain the optimal solution for a special number of factors, PMF uses an iterative method to minimize the objective functions Q(E) function with the constraints that g_{ik} and f_{kj} are non-negative values, as follows:

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\left(X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \right) / S_{ij} \right]^2$$

where, S_{ij} are elements of the uncertainty matrix, each element is the uncertainty of the *j*th species for sample *i*. Before implementing PMF analysis, uncertainty file must be provided to give the model an estimation of each value²¹. In this study, the uncertainty estimates were defined as 5% of the concentration values for the measured values of raw dataset, and the uncertainty estimates were set at 5/6 of the detection limit values for the undetectable values of raw dataset^{22, 23}. For implementing PMF analysis, the SNR (Signal-to-noise ratio, S/N) of each variable must be greater than 0.2 for input data process, the value of Q(E) objective function should stabilize and is close to the value of freedom degree ($df = n \times m - p \times (n + m)$), and the standard residual value should be

between -3 and 3²¹. In this work, the USEPA PMF 5.0 software was used to finish PMF analysis.

Source apportionment of toxicity posed by PAHs in sediment. The toxicity posed by PAHs was assessed according to the source apportionment of PAHs estimated using PMF regression²⁴. The TEQ_{source} for the *j*th major source was calculated using the following formula:

$$(TEQ_{source - PAH_i})_j = TEF_{PAH_i} \times (s_j + f_{ij})$$

 $(TEQ_{source})_j = (\sum (TEQ_{source - PAH_i}))_j$

where TEF_{PAHi} is the toxic equivalence factor (*TEF*) of the *i*th PAH species; s_j is the contribution of the *j*th major source obtained using PMF; and f_{ij} is the fraction (%) of the *i*th PAH species in the *j*th major source profile, which was extracted using PMF.

S2. Supplementary Data Tables

MERMQ values	Ecological risk category
<i>MERMQ</i> values ≤ 0.1	No ecological risk
0.1 < <i>MERMQ</i> values < 0.5	Low ecological risk
$0.5 \leq MERMQ$ values ≤ 1.5	Moderate ecological risk
1.5 < MERMQ values	Very high ecological risk

Table S1 Potential ecological risk categories on the basis of MERMQ values.

Table S2 Potential ecological risk categories on the basis of health risk values.

CR values	Health risk category	
CR values $\leq 10^{-6}$	Very low risk	
$10^{-6} < CR$ values $< 10^{-4}$	Low risk	
$10^{-4} \le CR$ values $< 10^{-3}$	Moderate risk	
$10^{-3} \le CR$ values $< 10^{-1}$	High risk	
$10^{-1} \le CR$ values	Very high risk	

Samula			тос	BC _{Cr}	ВСсто	TN	ТР	Grainsize	Salinity
Sam	ple	рн	(mg g ⁻¹)	(µm)	(‰)				
	ХР	7.06	12.92	3.91	1.43	2.32	0.76	17.59	0.15
	QYK	7.00	19.38	4.47	1.03	2.59	0.76	12.06	0.43
	LHK	7.16	25.92	4.86	1.27	1.94	0.88	19.19	0.25
	SDK	6.90	32.96	7.58	1.53	2.36	1.00	17.08	0.21
Ostalian	WSK	6.81	19.16	4.94	1.18	2.33	0.86	15.14	0.23
October	BLG	7.38	6.15	2.35	1.14	0.98	0.61	7.58	0.21
2015	CY	7.13	13.04	4.00	1.50	1.89	0.64	4.61	0.74
	DH	7.93	18.98	5.19	1.56	1.77	0.66	19.49	6.77
	LCG	8.02	7.49	2.00	0.70	2.23	0.63	16.33	8.70
	FX	7.89	15.22	3.01	1.13	2.39	0.62	18.79	9.95
	JS	7.87	5.02	1.73	0.93	1.53	0.58	77.04	8.13
	XP	7.92	14.59	3.72	1.21	5.49	0.76	18.12	0.13
	QYK	7.89	18.07	3.84	1.13	4.91	0.77	12.42	0.15
	LHK	7.92	29.58	5.37	1.38	7.39	0.92	19.77	0.13
	SDK	7.47	36.69	9.52	1.40	6.11	1.08	17.59	0.30
T	WSK	7.42	19.75	5.22	1.04	4.77	0.93	16.20	0.40
January	BLG	8.23	3.68	1.32	0.63	4.98	0.57	8.11	0.36
2016	CY	8.03	11.99	2.55	1.05	5.14	0.66	4.94	3.00
	DH	7.98	16.57	4.51	1.50	7.84	0.69	20.85	6.20
	LCG	8.10	9.72	2.19	0.88	3.96	0.64	17.47	7.90
	FX	8.03	10.46	2.62	0.95	4.65	0.60	19.35	8.71
	JS	8.01	5.51	2.46	0.93	5.79	0.64	26.45	7.94
	XP	6.53	18.34	4.31	1.00	4.82	0.74	15.23	0.14
	QYK	6.61	21.21	4.74	1.39	5.58	0.75	13.37	0.16
	LHK	6.52	28.49	4.77	1.92	5.68	0.87	13.84	0.21
	SDK	6.42	27.05	6.82	1.59	7.22	0.85	11.66	0.21
	WSK	7.89	18.07	2.90	1.06	4.06	0.77	13.39	0.23
April	BLG	8.51	5.63	1.82	0.88	3.15	0.61	12.81	0.22
2016	CY	7.64	12.52	3.48	1.11	6.26	0.68	9.23	1.30
	DH	7.66	17.25	4.96	1.72	8.49	0.73	17.80	7.53
	LCG	7.68	11.51	2.81	1.13	4.32	0.58	22.91	7.15
	FX	7.73	9.54	1.68	1.37	4.45	0.60	19.26	8.42
	JS	7.69	6.03	3.00	1.16	6.09	0.55	19.73	7.63
	XP	7.73	20.58	3.72	1.41	2.37	0.67	11.72	0.18
	QYK	7.44	12.93	5.47	1.35	3.13	0.74	10.29	0.27
	LHK	7.52	16.74	5.00	1.38	2.81	0.70	10.64	0.26
	SDK	7.67	25.10	11.17	2.05	5.82	1.30	8.51	0.16

Table S3 Physicochemical variables of surface sediments in the Yangtze estuary.

July	WSK	7.76	18.40	3.71	1.40	3.24	0.92	9.77	0.28
2016	BLG	8.43	5.47	3.66	1.24	2.24	0.62	9.35	0.23
	CY	7.82	1.48	3.36	1.39	3.12	0.64	6.74	0.47
	DH	7.97	17.67	5.46	1.73	3.00	0.65	12.99	1.11
	LCG	7.84	9.37	1.19	0.71	1.57	0.52	16.72	6.74
	FX	8.36	7.15	2.20	1.57	2.94	0.53	13.76	8.62
	JS	8.39	1.47	1.84	1.16	3.31	0.47	14.09	7.26

Table S4 Pearson's correlations of individual PAH compound and total PAHs to TOC and BC.

	Correlatio	ons to TOC	Correlatio	ons to BC _{Cr}	Correlatio	Correlations to BC _{CTO}		
	r	Р	r	Р	r	Р		
Nap	0.66	< 0.001	0.65	< 0.001	0.25	0.10		
Acy	0.36	0.02	0.24	0.11	0.09	0.58		
Ace	0.76	< 0.001	0.71	< 0.001	0.34	0.03		
Fl	0.67	< 0.001	0.56	< 0.001	0.34	0.03		
Phe	0.80	< 0.001	0.79	< 0.001	0.48	< 0.001		
Ant	0.51	< 0.001	0.62	< 0.001	0.37	0.01		
Flu	0.79	< 0.001	0.66	< 0.001	0.39	0.01		
pyr	0.80	< 0.001	0.69	< 0.001	0.41	0.01		
BaA	0.73	< 0.001	0.65	< 0.001	0.24	0.12		
Chr	0.77	< 0.001	0.67	< 0.001	0.38	0.01		
BbF	0.65	< 0.001	0.57	< 0.001	0.48	0.001		
BkF	0.74	< 0.001	0.63	< 0.001	0.40	0.01		
BaP	0.68	< 0.001	0.55	< 0.001	0.33	0.03		
InP	0.69	< 0.001	0.56	< 0.001	0.28	0.06		
BghiP	0.71	< 0.001	0.62	< 0.001	0.40	0.01		
DBA	0.50	< 0.001	0.56	< 0.001	0.37	0.01		
2-ring	0.66	< 0.001	0.65	< 0.001	0.25	0.10		
3-ring	0.78	< 0.001	0.76	< 0.001	0.45	0.002		
4-ring	0.79	< 0.001	0.69	< 0.001	0.37	0.01		
5-ring	0.71	< 0.001	0.61	< 0.001	0.42	0.01		
6-ring	0.71	< 0.001	0.60	< 0.001	0.35	0.02		
LMW	0.80	< 0.001	0.78	< 0.001	0.38	0.01		
HMW	0.76	< 0.001	0.66	< 0.001	0.39	0.01		
TPAHs	0.79	< 0.001	0.70	< 0.001	0.40	0.01		

Table S5 Correlations coefficients (Pearson's r, top right half of the matrix) and p-values (lower left

	TOC	BC _{Cr}	BC _{CTO}	TN	ТР	pН	Grainsize	Salinity	PAHs
ТОС		0.80^{**}	0.53**	0.29	0.82**	-0.58**	-0.98	-0.46**	0.79**
BC _{Cr}	< 0.01		0.68**	0.29	0.87**	-0.46**	-0.18	-0.47**	0.70^{**}
BC _{CTO}	< 0.01	< 0.01		0.24	0.50**	-0.33*	-0.20	-0.25	0.40^{*}
TN	0.05	0.05	0.12		0.29	-0.07	0.21	0.01	0.32*
ТР	< 0.01	< 0.01	< 0.01	0.06		-0.46**	-0.09	-0.56**	0.77**
pН	< 0.01	< 0.01	0.03	0.65	< 0.01		0.14	0.45**	-0.42**
Grainsize	0.53	0.25	0.20	0.89	0.55	0.35		0.32*	-0.10
Salinity	< 0.01	0.01	0.10	0.97	< 0.01	< 0.01	0.03		-0.60**
PAHs	< 0.01	< 0.01	0.01	0.04	< 0.01	< 0.01	0.54	< 0.01	

half) between PAHs contents and physical parameters in surface sediments of the Yangtze Estuary.

 ** Correlation is significant at the 0.01 level.

* Correlation is significant at the 0.05 level

	Crude oil source ^a	Coal combustion ^b	Traffic-related source ^c	Biomass combustion ^d
Nap				
Acy	\checkmark	\checkmark		\checkmark
Ace	\checkmark	\checkmark		
Fl	\checkmark	\checkmark		\checkmark
Phe	\checkmark	\checkmark		\checkmark
Ant	\checkmark	\checkmark		\checkmark
Flu		\checkmark		\checkmark
Pyr		\checkmark		\checkmark
BaA		\checkmark		
Chry		\checkmark		
BbF			\checkmark	
BkF			\checkmark	
BaP			\checkmark	
InP			\checkmark	
DahA			\checkmark	
BghiP				

Table S6 PAHs fingerprints of various pollution sources summarized from literatures.

a: De Luca et al., 2004 Marr et al., 1999; Liu et al., 2015;

b: Harrison et al., 1996; Simcik et al., 1999; Kulkarni and Venkataraman, 2000; Bragato et al., 2012; Duval et al., 1981; Harrison, 1996;

c: Venkataraman et al., 1994; Larsen and Baker, 2003; Guarieiro et al., 2014; Marr et al., 1999;

d: Oanh et al., 2005; Zhang et al., 2008b.

PA	Hs	Measure	ed concentration	ns (Water + SPN	M phases)	Equivalent concentrations				
Equi	valent									
fac	tors	Oct., 2015	Jan., 2016	Apr., 2016	Jul., 2016	Oct., 2015	Jan., 2016	Apr., 2016	Jul., 2016	
Nap	0.061	0.133-1.209	0.212-3.528	0.179-3.203	0.061-1.845	0.008-0.073	0.013-0.214	0.011-0.195	0.004-0.112	
Ace	0.259	0.041-0.573	0.035-0.669	0.044-0.519	0.034-0.385	0.011-0.148	0.009-0.173	0.011-0.134	0.009-0.100	
Fl	0.167	0.011-0.355	0.027-0.699	0.010-0.986	0.010-0.410	0.002-0.059	0.005-0.117	0.002-0.165	0.002-0.069	
Phe	1.575	0.035-1.007	0.112-2.465	0.127-1.506	0.079-0.622	0.191-4.552	0.617-13.574	0.700-8.292	0.434-3.427	
Ant	5.506	0.030-1.007	0.096-1.872	0.110-0.743	0.053-1.547	0.047-1.586	0.151-2.948	0.173-1.170	0.083-2.437	
Flu	4.938	0.040-0.757	0.080-1.943	0.084-1.551	0.065-0.675	0.433-8.306	0.878-21.313	0.919-17.009	0.714-7.405	
Pyr	10.969	0.026-0.819	0.109-2.065	0.107-1.608	0.090-0.882	0.131-4.045	0.537-10.197	0.528-7.942	0.445-4.355	
Chr	0.165	0.004-0.104	0.017-0.463	0.009-0.151	0.005-0.136	0.001-0.017	0.003-0.077	0.002-0.025	0.001-0.022	
BaP	1	0.003-0.226	0.006-0.939	0.012-0.156	0.007-0.296	0.003-0.226	0.006-0.939	0.012-0.156	0.007-0.296	
$\sum c_{\rm eq}$	-	-	-	-	-	0.831-18.919	2.246-47.398	2.451-34.983	1.876-17.911	

Table S7 The measured concentrations, equivalent concentrations and equivalence factors of 9 PAHs $(\mu g/L)$ in water samples.

Table S8 Health risk caused by PAH contaminated sediment

Comm10	October, 2015		January, 2016			April, 2016			July, 2016			
Sample	Cr_{ing}	Cr _{derm}	TCR	Cr_{ing}	Cr _{derm}	TCR	Cr_{ing}	Cr _{derm}	TCR	Cr_{ing}	Cr _{derm}	TCR
XP	2.5E-06	1.3E-06	3.7E-06	3.5E-06	1.8E-06	5.3E-06	3.4E-06	1.8E-06	5.2E-06	3.8E-06	2.0E-06	5.8E-06
QYK	2.2E-06	1.1E-06	3.3E-06	2.4E-06	1.3E-06	3.7E-06	2.7E-06	1.4E-06	4.1E-06	4.4E-06	2.3E-06	6.7E-06
LHK	5.7E-06	2.9E-06	8.6E-06	1.2E-05	6.4E-06	1.9E-05	9.1E-06	4.7E-06	1.4E-05	1.3E-05	6.7E-06	2.0E-05
SDK	3.9E-06	2.0E-06	6.0E-06	1.2E-05	6.0E-06	1.7E-05	5.8E-06	3.0E-06	8.9E-06	7.6E-06	3.9E-06	1.2E-05
WSK	2.7E-06	1.4E-06	4.1E-06	6.1E-06	3.2E-06	9.3E-06	4.5E-06	2.3E-06	6.9E-06	5.4E-06	2.8E-06	8.2E-06
BL	1.5E-06	7.6E-07	2.2E-06	2.3E-06	1.2E-06	3.5E-06	1.9E-06	9.8E-07	2.9E-06	1.8E-06	9.5E-07	2.8E-06
CY	7.5E-07	3.9E-07	1.1E -0 6	2.0E-06	1.1E-06	3.1E-06	1.4E-06	7.3E-07	2.1E-06	1.5E-06	7.7E-07	2.3E-06
DH	8.2E-07	4.3E-07	1.2E-06	1.7E-06	8.9E-07	2.6E-06	1.1E-06	5.9E-07	1.7E-06	1.4E-06	7.2E-07	2.1E-06
LC	2.5E-07	1.3E-07	3.9E-07	1.1E-06	5.8E-07	1.7E-06	3.2E-07	1.6E-07	4.8E-07	1.0E-06	5.2E-07	1.5E-06
FX	3.5E-06	1.8E-06	5.3E-06	1.2E-06	6.0E-07	1.8E-06	3.4E-06	1.7E-06	5.1E-06	5.6E-07	2.9E-07	8.5E-07
JS	2.7E-07	1.4E-07	4.1E-07	2.5E-06	1.3E-06	3.8E-06	5.6E-07	2.9E-07	8.5E-07	4.9E-07	2.6E-07	7.5E-07

S3. Supplementary Figures



Fig. S1 Comparison of PAHs concentrations in (a) water (ng L⁻¹), (b) SPM (ng g⁻¹) and (c) surface sediments (ng g⁻¹) phases of the Yangtze Estuary and other representative areas. (a1: Yangtze Estuary, China (2006)²⁵; a2: Luan River estuary, China²⁶; a3: Hai River estuary, China²⁶; a4: Zhangweixin River estuary, China²⁶; a5: Yellow River estuary, China²⁷; a6: River Tiber, Italy²⁸; a7: Ary Parreiras Stream, Brazil²⁹; a8: Seine River, France³⁰; a9: Pearl River estuary, China³¹; a10: Daya Bay, China³²; a11: Gomti River, India³³; a12 Yangtze Estuary, China (this study); b1: Pearl River Estuary, China³⁴; b2: Daliao River Estuary, China³⁵; b3: Daliao River watershed, China³⁶; b4: Seine River and Estuary, France³⁰; b5: York River, VA Estuary, USA³⁷; b6: Yangtze Estuary, China (this study); c1: Yangtze Estuary, China (2006)²⁵; c2: Pearl River estuary, China³⁸; c3: Yellow River Estuary, China³⁹; c4: San Francisco Bay, USA⁴⁰; c5: Casco Bay, USA⁴¹; c6: Estuaries in Haihe river basin, China⁴²; c7: Patos

Lagoon Estuary, Brazil⁴³; c8: Lenga Estuary, Chile⁴⁴; c9: Hugli river, India⁴⁵; c10: Chitrapuzha River, India⁴⁶; c11: Cochin estuary, India⁴⁷; c12: Yangtze Estuary, China (this study)).



Fig. S2 Spatial–temporal variations of δ^{13} C in TOC and BC of the surface sediments of the Yangtze Estuary.



Fig. S3 Profiles of PMF factors for (a) sediment phase; (b) water phase; (c) SPM phase in four seasons; (d) source apportionment of PAHs in water; (e) source apportionment of PAHs in SPM



Fig. S4 Health risk of each site in sediments based on concentrations of PAHs in four seasons

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