

Multivariate assessment of polycyclic aromatic hydrocarbons in surface sediments of the Beijiang, a tributary of the Pearl River in Southern China

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Abstract To estimate the severity of polycyclic aromatic hydrocarbon (PAH) contamination in the upper sediment of the Beijiang River, 42 sediment samples were analyzed for the presence of 16 key PAHs using gas chromatography–mass spectrometry. The concentrations of PAH in the sediment ranged from 44 to 8,921 ng g⁻¹ dry weight. The four- to six-ring PAHs, contributing >50 % to PAHs in 34 of the 42 sites, were the dominant species. Based on a principal component analysis, combined with multivariate linear regression, it became clear that the most important contributors of PAH were fossil fuel combustion (48 %), diesel emissions plus oil spillage (33 %), and coke combustion (19 %). The surface sediments of Beijiang River were grossly contaminated by PAHs mainly derived from combustion.

Keywords PAHs · Sediments · Diagnostic ratio · PCA/MLR · Source apportionment · Beijiang River

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), a family of compounds which possess two or more fused benzene rings, are a common cause of environmental contamination (Pietzsch et al. 2010). Their specific hazard derives from their known carcinogenic, teratogenic, and mutagenic potential (Y. Liu et al. 2009; Ruiz et al. 2011). Owing to their high hydrophobicity and slow rate of degradation, PAHs are readily adsorbed onto particulate matter, which may end up being incorporated into river and lake sediments. The bulk of anthropogenic pollution by PAHs derives from incomplete combustion of biomass and fossil fuel, to which overlap occasional oil spills (Tobiszewski and Namieśnik 2012). As each of the various sources of pollution is associated with a characteristic profile of PAHs, it is often possible to infer the origin of the pollution (Mostafa et al. 2009; Yunker et al. 2012). Establishing the relative presence of low-molecular-weight PAHs carrying two or three fused benzene rings compared with higher-molecular-weight PAHs carrying four to six rings allows the differentiation between pyrogenic and petrogenic sources of PAH pollution (Brown and Peake 2006). Another widely used technique to identify sources is the diagnostic ratios (Bouloubassi and Salot 1993; Dickhut et al. 2000). A more sophisticated statistical approach used for source identification is represented by principal component analysis (PCA) in conjunction with multivariate linear regression (MLR); this allows both the identification and apportioning of the various PAHs present in sediments, suspended matter, and aerosols.

The Pearl River Delta (PRD) is an area with a high concentration of organic contaminants, including PAHs, affecting air and water quality and the whole food chain (Fu et al. 2003). The Beijiang River, the second largest tributary of the Pearl River, provides a major source of drinking water (Chen et al. 2009), as well as for irrigation and industry in the PRD and Guangdong province. The rapid industrial growth in the region has increased the discharge of waste materials into the Beijiang River (Song et al. 2011). Environmental protection requires knowledge of both the impact and the source of pollution. Here, we provide basic information regarding the level and origins of the PAHs accumulated in the Beijiang River sediment, using a variety of identification techniques, namely diagnostic ratios and PCA and MLR analysis.

Materials and methods

Study area and sampling strategy

The sampling sites were defined using Global Positioning System (Table 1), and a set of 12 sediment samples was collected over the period 10–15 January 2009 (Fig. 1). The top 5 cm of the sediment surface was collected and transferred into a 100 ml screw cap glass jar, then homogenized and stored at 4 °C in the dark (Shukla and

Upreti 2009). The material was then air-dried by exposing it to room temperature (25±1 °C) for 2 weeks and finally sieved through a 2 mm mesh. A further 30 samples were analyzed by Jing et al. (2009).

Chemical analysis and quality control

The sample extraction and PAH clean-up methods followed the relevant protocols given in US Environmental Protection Agency (EPA) Standard Methods 3540c and 3620b (USEPA 1996a, 1996b). Each 10-g sample was mixed with 10 g anhydrous sodium sulfate, then extracted by the addition of 80 ml of dichloromethane/acetone (v/v 1:1) for 16–24 h at 65 °C to which activated copper was added for desulfurization. The extract was concentrated to 2 ml by a rotary evaporator and the solvent exchanged to hexane. The hexane extract was fractionated and cleaned up by a silica gel/alumina (v/v 1:2) column. The column was eluted with 75 ml of *n*-hexane/dichloromethane (v/v 3:7) to obtain PAH. The PAH fraction was finally concentrated to 1.0 ml under a gentle stream of nitrogen (USEPA 1996c).

The 16 PAHs identified by US EPA as priority pollutants (naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA),

Table 1 Details of the sampling stations

Station	Name	Latitude	Longitude	Temp ^a (°C)	pH ^b	TOM ^{b,c} (%)
S1	Jiepai	N 23°28.982'	E 112°54.332'	13.90	6.21	0.51
S2	Qingyuan	N 23°41.332'	E 113°00.038'	13.80	7.68	2.70
S3	Bijia xincun	N 23°43.267'	E 112°59.628'	13.40	7.26	1.33
S4	Zhouxin	N 23°41.532'	E 113°05.609'	11.20	6.80	2.53
S5	Longtan	N 23°37.115'	E 113°03.808'	13.60	6.51	2.19
S6	Pajiangkou	N 23°43.967'	E 113°13.100'	10.90	6.63	2.29
S7	Lianjiangkou	N 24°02.947'	E 113°18.003'	12.80	7.20	0.97
S8	Yingcheng	N 24°09.881'	E 113°24.182'	13.40	7.15	2.55
S9	Shakou	N 24°25.214'	E 113°30.671'	13.70	6.69	2.78
S10	Xiniu	N 24°09.831'	E 113°06.960'	12.80	7.34	2.72
S11	Qinglian	N 24°27.446'	E 112°44.994'	11.60	7.34	2.74
S12	Lianzhou	N 24°46.226'	E 112°23.185'	10.40	7.25	2.97

^a Overlying water

^b Sediment

^c Total organic matter

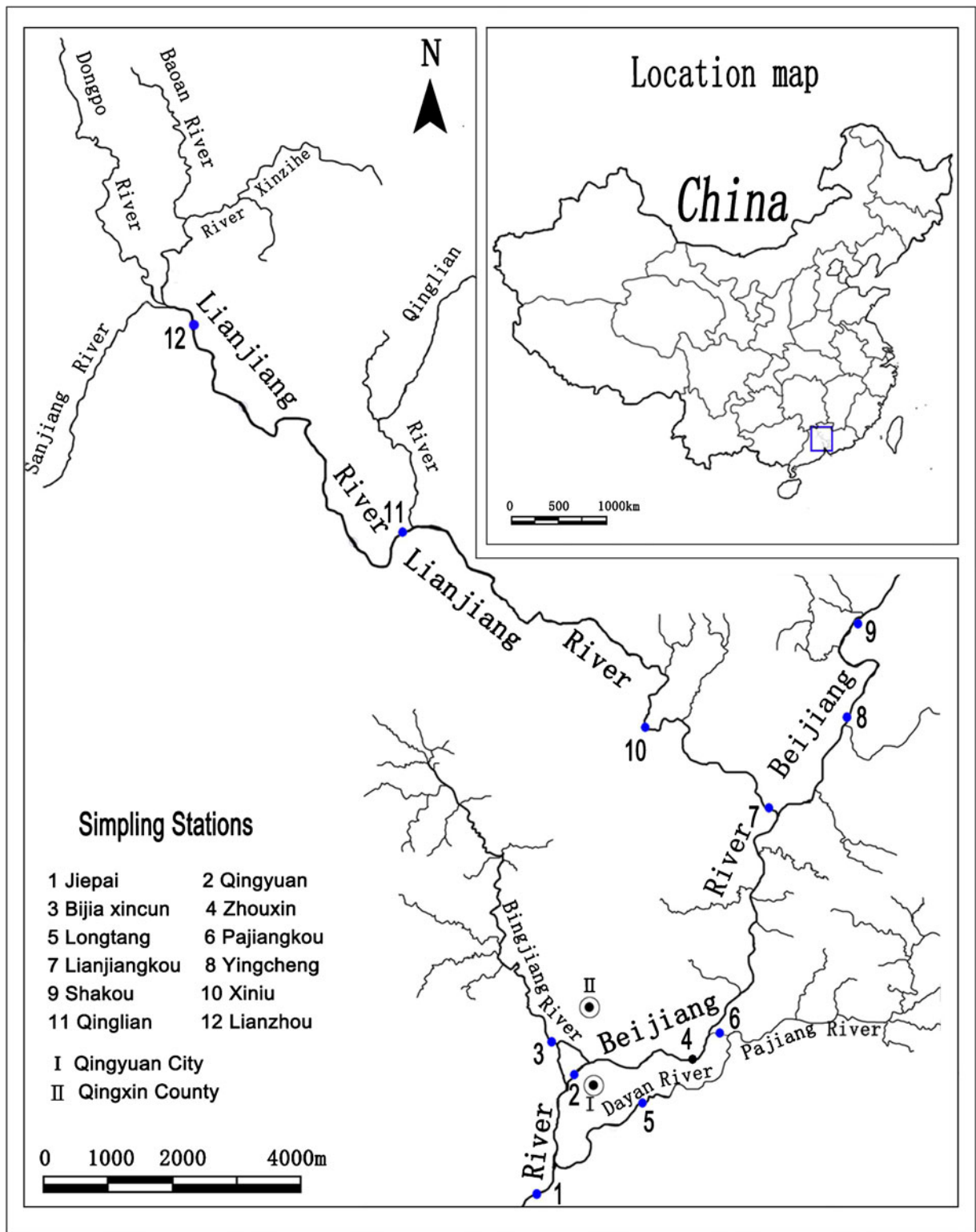


Fig. 1 Map of study area and sampling stations

chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IPY), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BPE)) were detected in sequence, using analytical methods based on US EPA Method 8270c (USEPA 1996d). Quantification of individual PAHs was achieved by gas chromatography (Hewlett Packard 5890) coupled to a GC/MS device (Hewlett Packard 5973). A silica fused capillary column (HP-5, 50 m×0.32 mm (i.d.)×0.17 μm (film thickness)) was used to separate the target analytes. The oven temperature was raised from 45 °C to 200 °C at a rate of 3 °C per min, then 200 °C to 285 °C at 5 °C per min, and held for 30 min. The injector temperature was maintained at 280 °C. Each 2-μl sample was delivered by manual splitless injection. Additional details of the chromatographic and spectrometric conditions are described elsewhere (Mai et al. 2002).

The identification of compounds was based on retention times recorded for calibration standards. The concentration of each analyte was determined in the form of nanograms per gram dry weight of sediment. Quality control was ensured by including blanks (solvent only), duplicate samples, and spiked blanks. The instruments were re-calibrated daily. The PAH recovery rates were quantified by using standard reference materials provided by NRCCRM (China National Research Center for Certified Reference Materials) and lay in the range 83–133 %. The total organic matter content (TOM) of each sample was determined by the method of loss in weight by ignition, as described by Byers et al. (1978).

Diagnostic ratio analysis

Since PAH concentration ratios can provide an important insight into the source of PAH contaminants, the ratios ANT/(ANT+PHE), FLT/(FLT+PYR), BaA/(BaA+CHR), and IPY/(IPY+BPE) were used to infer the likely origin of the sedimentary PAHs (Sierra et al. Sierra and d. R., Rosazza, N. G., and Préndez, M. 2005; Jiang et al. 2009; Yunker et al. 2012). An ANT/(ANT+PHE) greater than 0.1 implies a petrogenic (associated with petroleum) source, while a ratio below 0.1 is indicative of combustion. Similarly, an FLT/(FLT+PYR) of less than 0.4 implies a petrogenic origin, of 0.4–0.5 indicates petroleum combustion, and >0.5 grass, wood, or coal combustion. A BaA/(BaA+CHR) ratio below 0.2 indicates a petrogenic source, while one of 0.2–0.35 implies

petroleum combustion. An IPY/(IPY+BPE) ratio of less than 0.2 indicates a petrogenic source, of 0.2–0.5 implies petroleum combustion, and above 0.5 implies grass, wood, and coal combustion (Jiang et al. 2009).

Principal component analysis and multiple linear regression

PCA and MLR analysis were employed to quantify the relative contribution of each potential PAH source (Li et al. 2012; Yunker et al. 2011). The following seven steps are involved: (1) Bartlett's test of sphericity and the Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy to test the appropriateness of the data for PCA analysis (Bagozzi and Yi 1988); (2) the calculation of the correlation coefficients and the resulting covariance matrix; (3) the calculation of eigenvalues and their corresponding eigenvectors; (4) the discarding of components which only accounted for a small proportion of the variation; (5) the development of the PCA loading matrix and the performance of a Varimax rotation on the factor loading matrix to infer the principal components (PCs); (6) the calculation of the absolute PC scores (APCS) (Guo et al. 2004; Kowalkowski et al. 2006); and (7) the implementation of MLR using the de-normalized APCS values produced by the PCA as the independent variables and the measured concentrations of the particular pollutant (Simeonov et al. 2003). A more detailed explanation of the procedure can be found in Thurston and Spengler (1985) and Ouyang et al. (2006).

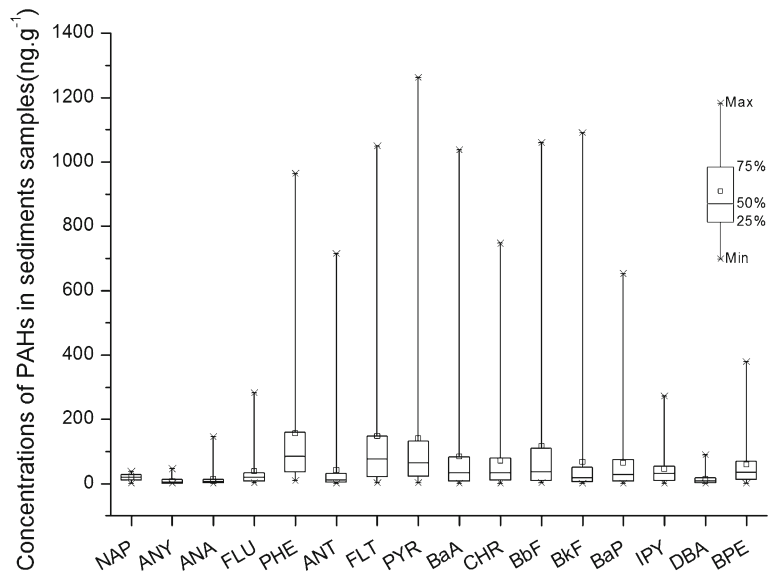
The PCA was performed using routines within SPSS v17.0 software (SPSS Inc, USA), selecting only Varimax rotation and PCs associated with an eigenvalue >1. Following Liu (2003), factor loadings of >0.75, 0.50–0.75, and 0.3–0.5 were interpreted as representing, respectively, “strong,” “moderate,” and “weak”. The factor scores were used to determine the relative contribution of each source by MLR. In all, 42 sediment samples were analyzed in this way.

Results and discussion

Pollution characteristics

Concentration values and basic statistics of the 16 key PAHs are synthetically presented in the box–whiskers plots of Fig. 2. Among the metals, PYR has the highest values (2.56–1,262 ng g⁻¹), followed by BkF (0.66–1,090 ng g⁻¹),

Fig. 2 Concentrations of PAHs in sediments samples



BbF (2–1,060 ng g⁻¹), BaA(1.1–1,038 ng g⁻¹), and FLT (2–1,049 ng g⁻¹). The aggregate PAH concentrations ranged from 44 to 8,921 ng g⁻¹ (mean 1,132.3). According to Baumard (2009), values <100 ng g⁻¹ can be considered to reflect a low level of pollution, those in the range 100–1,000 ng g⁻¹ a moderate level, those in the range 1,000–5,000 ng g⁻¹ a high level, and those >5,000 ng g⁻¹ a very high level. On this basis, only five of the samples were classified as being polluted at a low level and 23 as moderately polluted, and 12 samples are at high pollution level. The pollution levels of as highly polluted and two (S5 and BS3 are considered to be) as very high, and it clearly associated with point source pollution, because it was highly polluted. The S5 site is located in a major industrial zone of Qingyuan City and the BS3 site downstream of the outfall of the Shaoguan smelting plant. Overall, the PAH contamination level in the Beijiang River sediment was moderate to high. The Beijiang River sediments are more polluted than those from the Dongjiang (100–3,400 ng g⁻¹, mean 880 ng g⁻¹ (K. Zhang et al. 2011)), from the Yellow River (111–205 ng g⁻¹, mean 116 ng g⁻¹ (Ning-jing et al. 2010)), and from the Daliao River (62–840 ng g⁻¹, mean 287 ng g⁻¹, (Li et al. 2012)), but lower than those from the Fenhe River (539–6,282 ng g⁻¹, mean 2,215 ng g⁻¹). Since the predominance of low-molecular-weight PAHs indicated a petrogenic source and the higher-molecular-weight PAHs, a pyrogenic source, the relative amounts of these fractions were then determined (W. Zhang et al. 2008; Lichtfouse et al.

1997; Soclo et al. 2000). The composition of the PAHs is illustrated in Fig. 3. Higher-molecular-weight species predominated, contributing >50 % of the PAH content in 34 of the 42 sites. This suggests that the origin of the PAHs in the study area has derived mainly from the incomplete combustion of fossil fuel and wood (W. Zhang et al. 2008).

Diagnostic ratio analysis

The results have been presented in the form of a cross plot contrasting ANT/(ANT+PHE) with FLT/(FLT+PYR), and BaA/(BaA+CHR) with IPY/(IPY+BPE). The FLT/(FLT+PYR) ratio was >0.4 except at sites S1 and S7 (Fig. 4a), while the ANT/(ANT+PHE) ratio varied rather widely (although it was generally >0.1). Site S1 and S7 stood out as a result of their low level of PAH pollution. Neither of these sites lies in industrial zones. The ratios indicated a mixed origin of the PAHs, although the predominant one appears to be pyrogenic, with some contribution from petrogenic sources, probably accidental oil spills. Thus, the BaA/(BaA+CHR) ratio was >0.2 for most of the samples while the IPY/(IPY+BPE) ratio varied from 0.35 to 0.55, diagnostic of a pyrolytic origin (Fig. 4b). The predominance of pyrolysis as the major source of PAHs has been previously noted by Pies et al. (2008) and Men et al. (2009). Other diagnostic ratios, used to distinguish petrogenic from pyrolytic origin include FLT/(FLT+PYR), BaA/(BaA+PYR), IPY/(IPY+BPE), which are described

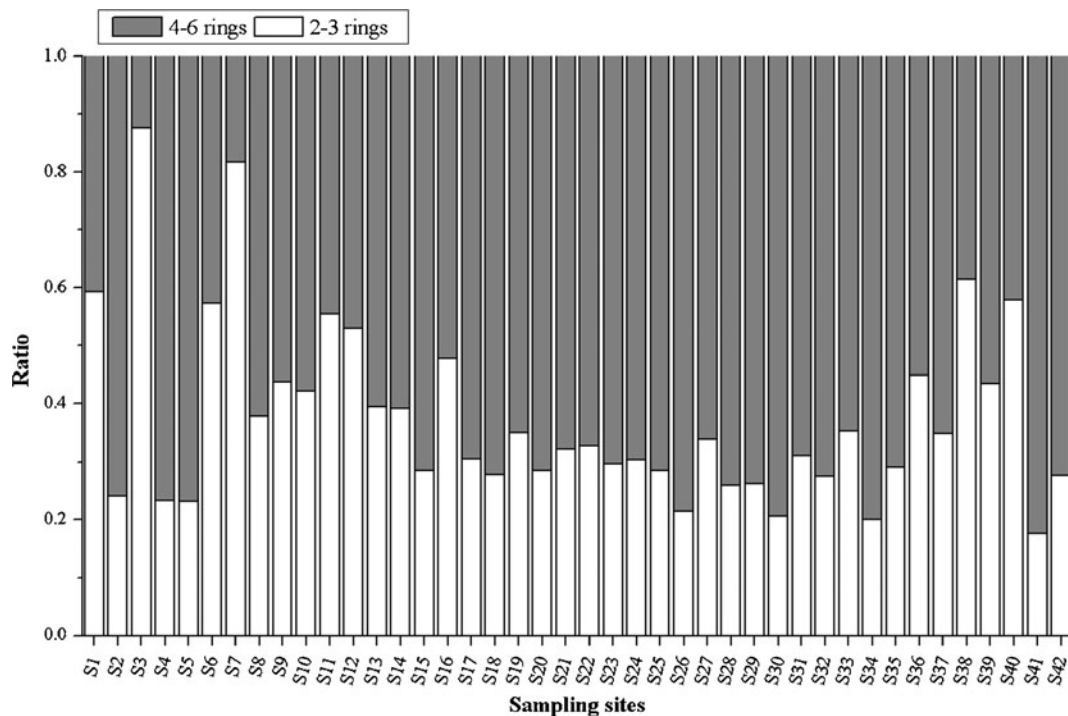


Fig. 3 Percentage level of two- to three-ring and four- to six-ring PAHs in sediment of Beijiing River

elsewhere (Ravindra et al. 2008; Tobiszewski and Namieśnik 2012).

PCA/MLR

The KMO value was 0.76, indicating that the PCA can be expected to be informative in reducing the dimensionality of the data. The component loadings of the three PCs retained are given in Fig. 5a, b, c and the correlations between the measured concentrations of the 16 PAHs in Table 2. The correlation efficient matrix demonstrated that nearly all of the variables were significantly and positively correlated with one another; the exception was ANA, a low-molecular-weight (two- to three-ring) group of compounds. Its poor correlation with the other PAHs may reflect a rather different origin for this pollutant, perhaps from quite remote locations via atmospheric transportation (Chung et al. 2007). As semi-volatile organic compounds, the property of PAHs vapor pressure determined the compounds vapor–particle partitioning, representing the available fraction for long-range atmospheric transport and phase transfer into sediment organic pollutions (Agarwal et al. 2009;

W. Wang et al. 2011b). The correlations between the various PAHs may aid in identifying the sources of the pollution.

Table 3 summarizes the PCA. Three PCs were identified, individually accounting for 77.8 %, 11.3 %, and 8.2 % of the total variance, and taken together for 97 %, and individually. Each of the PCs showing a loading value >0.75 is highlighted. PC1 had a high contribution from ANT, FLT, PYR, BaA, CHR, BaP, and IPY, all of which (except for ANT) are high-molecular-weight PAHs. FLT, PYR, and BaP are markers of coal combustion (Yang et al. 2013), IPY of automobile exhaust, BaA of diesel exhaust, and CHR of diesel and natural gas combustion. Thus, PC1 was largely reflective of fossil fuel combustion. PC2 was heavily influenced by NAP and BkF; the latter is associated with diesel exhaust and the former with oil spillage (C. Wang et al. 2011a; Y. Liu et al. 2009). As suggested by the correlation co-efficient matrix, NAP was significantly correlated with BkF; a possible explanation for this correlation is that both pollutants emanated from shipping along the river, in the form of exhaust emission and oil leakage. As a result, PC2 may well reflect diesel emissions plus oil spillage. PC3 was

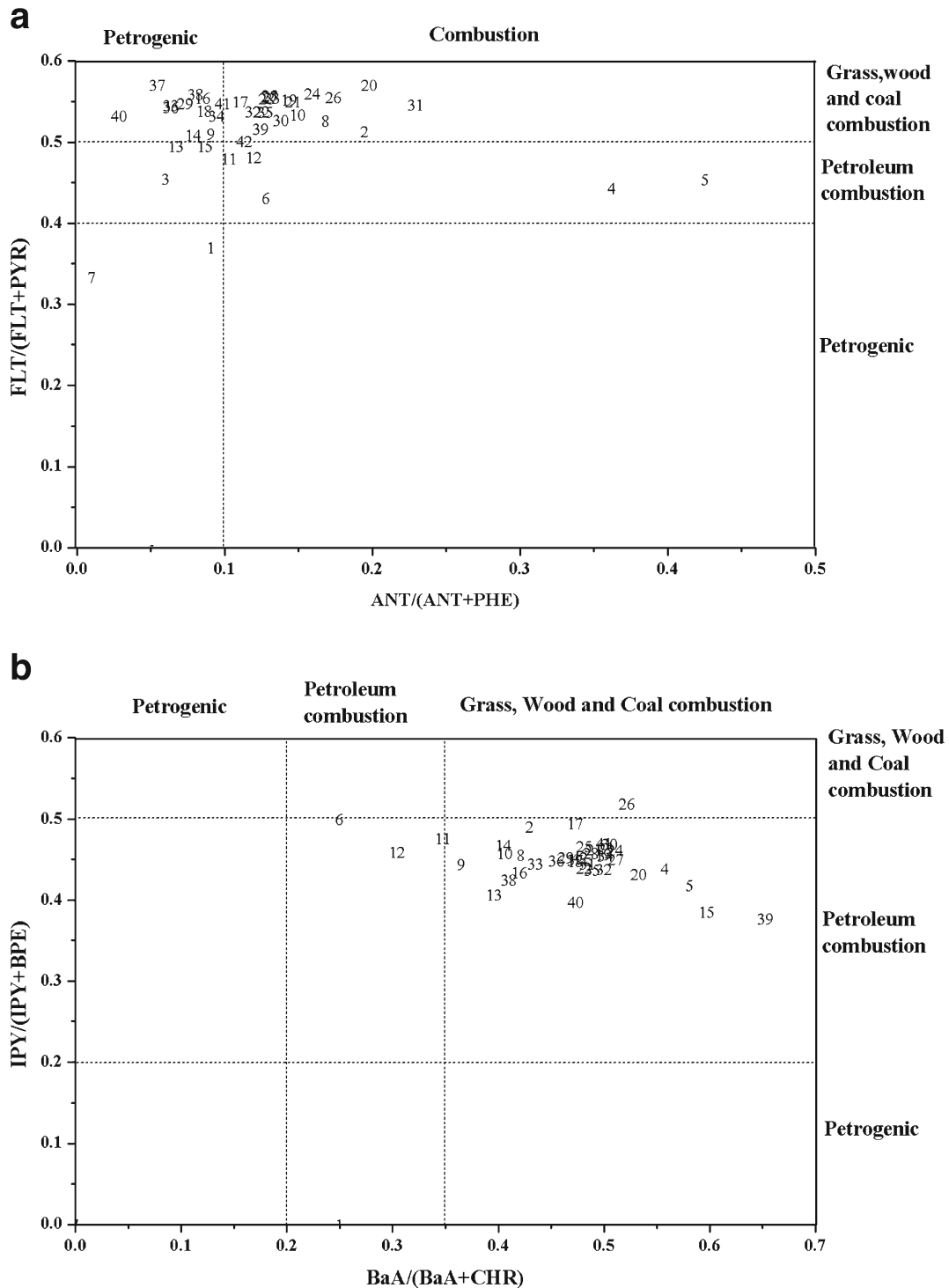


Fig. 4 Diagnostic ratio plot of ANT/(ANT+PHE) versus FLT/(FLT+PYR) (a) and BaA/(BaA+CHR) versus IPY/(IPY+BPE) (b)

dominated by ANY and ANA, both of which are low-molecular-weight PAHs, diagnostic of coke combustion

(Bixiong et al. 2006). The PCA indicated that the Beijing River sediment PAHs have arisen mostly from

Fig. 5 Component loadings for three components (PC1 (a), PC2 (b), PC3 (c))

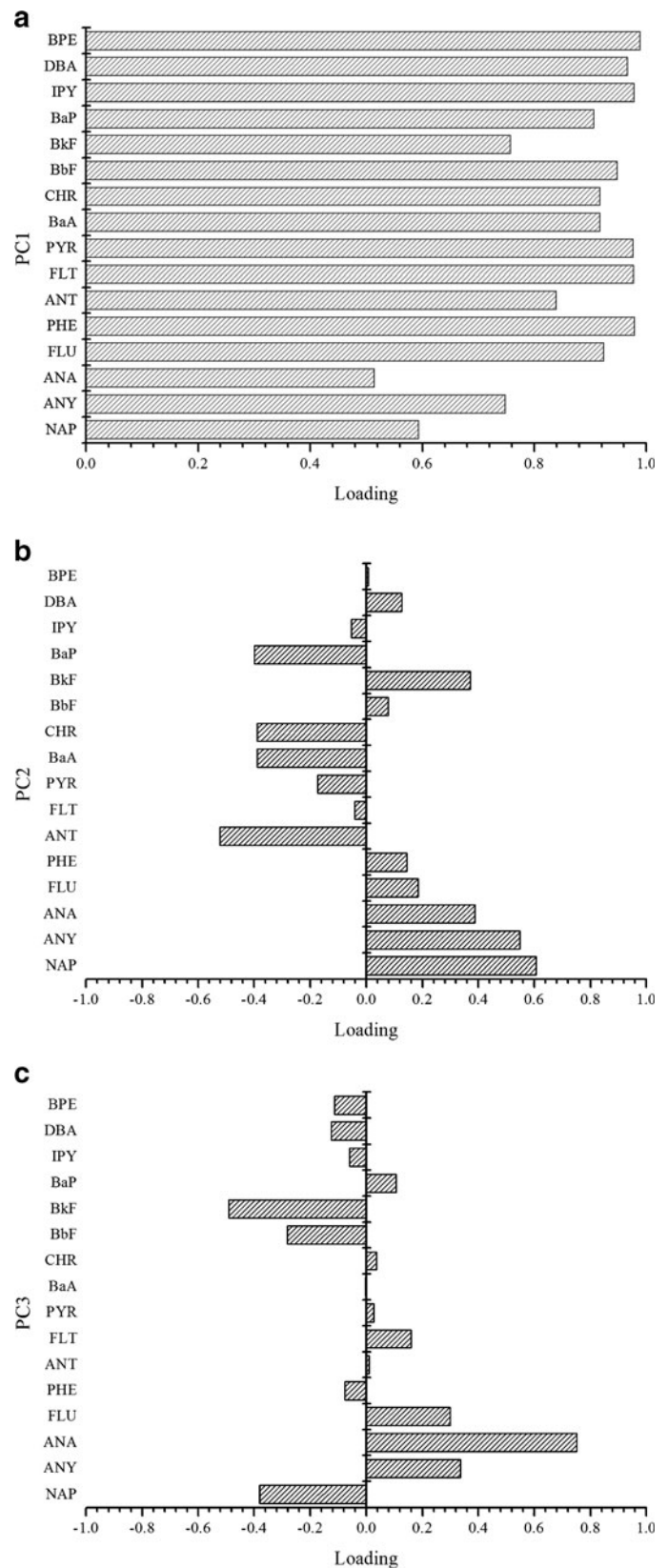


Table 2 Correlations matrix of the 16 priority PAHs

Parameter	NAP	ANY	ANA	FLU	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IPY	DBA	BPE
NAP	1															
ANY	0.632**	1														
ANA	0.271	0.836**	1													
FLU	0.530**	0.884**	0.770**	1												
PHE	0.709**	0.783**	0.498**	0.918**	1											
ANT	0.214	0.335*	0.248	0.684**	0.750**	1										
FLT	0.499**	0.767**	0.600**	0.942**	0.947**	0.834**	1									
PYR	0.493**	0.648**	0.450**	0.873**	0.939**	0.913**	0.977**	1								
BaA	0.336*	0.470**	0.326*	0.773**	0.843**	0.982**	0.909**	0.966**	1							
CHR	0.328*	0.486**	0.347*	0.789**	0.843**	0.968**	0.918**	0.963**	0.992**	1						
BbF	0.690**	0.658**	0.309	0.818**	0.958**	0.750**	0.878**	0.900**	0.842**	0.825**	1					
BkF	0.792**	0.610**	0.165	0.640**	0.829**	0.431**	0.649**	0.656**	0.550**	0.521**	0.910**	1				
BaP	0.282	0.498**	0.394*	0.792**	0.818**	0.965**	0.916**	0.953**	0.988**	0.995**	0.798**	0.478**	1			
IPY	0.560**	0.690**	0.430**	0.871**	0.944**	0.827**	0.944**	0.950**	0.908**	0.921**	0.934**	0.745**	0.906**	1		
DBA	0.658**	0.749**	0.449**	0.888**	0.971**	0.733**	0.914**	0.902**	0.828**	0.827**	0.966**	0.855**	0.805**	0.961**	1	
BPE	0.625**	0.708**	0.425**	0.883**	0.974**	0.818**	0.943**	0.954**	0.901**	0.901**	0.969**	0.808**	0.882**	0.989**	0.978**	1

**0.01 level showing significant correlation (two-tailed)

*0.05 level showing significant correlation (two-tailed)

Table 3 Rotated component matrix of 16 PAHs

Variable	Component 1	Component 2	Component 3
NAP	0.065	0.906	0.231
ANY	0.229	0.509	0.814
ANA	0.162	0.040	0.978
FLU	0.599	0.404	0.676
PHE	0.658	0.639	0.384
ANT	0.978	0.124	0.071
FLT	0.778	0.387	0.477
PYR	0.858	0.390	0.306
BaA	0.951	0.253	0.156
CHR	0.954	0.221	0.188
BbF	0.665	0.716	0.174
BkF	0.323	0.924	0.078
BaP	0.952	0.169	0.234
IPY	0.781	0.515	0.297
DBA	0.654	0.657	0.327
BPE	0.749	0.589	0.289
Eigenvalues	12.45	1.803	1.312
% of variance	77.780	11.266	8.198
Cumulative %	77.780	89.046	97.244

combustion, in good agreement with the analysis based on PAH ratios.

The relative contributions of the three major origins of PAH pollution were estimated using MLR, based on the model:

$$y = \sum a_i X_i + b \quad (1)$$

This model is valid only if there is no collinearity in X_i . Non-collinearity, by definition, is ensured by selecting the PCA factor scores as the independent variables, X_i . The dependent variable y is the overall PAH concentration. The influence of each dependent variable on the independent variable can be directly compared via the regression coefficients, provided that the independent and dependent variables are normally standardized, at which point, the regression coefficients can be represented as B_i (the intercept b is at $Y=0$). The standardized form of the model is represented by:

$$Y = \sum B_i X_i \quad (2)$$

where Y is the standardized normal deviate of the overall PAH concentration. The normal standardization equation is:

$$Y = \left(\sum PAH - \overline{\sum PAH} \right) / \sigma_{\sum PAH} \quad (3)$$

Where $\sum PAH$ is the total PAH concentration, $\overline{\sum PAH}$ is the $\sum PAH$ mean of $\sum PAH$, and $\sigma_{\sum PAH}$ is the standard deviation of $\sum PAH$.

The regression of the three leading PCs (X_1 – X_3), which represent fossil fuel combustion, diesel emission plus oil spillage, and coke combustion, were regressed against Y to give the relationship:

$$Y = 0.786X_1 + 0.536X_2 + 0.305X_3 \quad (4)$$

The associated R^2 value was 0.999, and the P values associated with the regression coefficients were all <0.05 , indicating that the MLR expression gave a good representation of the relative contributions. The percentage contributions to the mean for the three factors were calculated from $100 \cdot B_i / B_i$, producing estimates for the mean relative contributions of fossil fuel combustion, diesel emission plus oil spillage, and coke combustion of, respectively, 48 %, 33 %, and 19 %.

Conclusions

The present study has provided important data on the distribution characteristics of PAHs in the sediments of the Beijiang River. To minimize the selection uncertainties of source profiles and obtain the higher model performance, diagnostic ratio analysis and PCA/MLR were applied to estimate source contributions for sediment PAHs from the Beijiang River system. The derived individual PAH ratios suggested that most of this pollution has arisen from pyrogenic activity, while the PCA/MLR indicated that fossil fuel combustion, oil spillage, and coke burning have provided most of the locally produced PAH, with the former activity being the single most important contributor. Identifying the major emission sources is an essential step in seeking to control, manage, and ameliorate environmental pollution.

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Reference

- Agarwal, T., Khillare, P., Shridhar, V., & Ray, S. (2009). Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India. *Journal of Hazardous materials*, *163*(2), 1033–1039.
- Bagozzi, R. P., & Yi, Y. (1988). On the evaluation of structural equation models. *Journal of the Academy of Marketing Science*, *16*(1), 74–94.
- Baumard, P., Budzinski, H., & Garrigues, P. (2009). Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. *Environmental Toxicology and Chemistry*, *17*(5), 765–776.
- Bixiong, Y., Zhihuan, Z., & Ting, M. (2006). Pollution sources identification of polycyclic aromatic hydrocarbons of soils in Tianjin area, China. *Chemosphere*, *64*(4), 525–534.
- Bouloubassi, I., & Saliot, A. (1993). Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanologica Acta*, *16*(2), 145–161.
- Brown, J. N., & Peake, B. M. (2006). Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Science of the Total Environment*, *359*(1), 145–155.
- Byers, S., Mills, E., & Stewart, P. (1978). A comparison of methods of determining organic carbon in marine sediments, with suggestions for a standard method. *Hydrobiologia*, *58*(1), 43–47. doi:10.1007/bf00018894.
- Chen, L., Huang, Y., Peng, X., Xu, Z., Zhang, S., Ren, M., et al. (2009). PBDEs in sediments of the Beijiang River, China: levels, distribution, and influence of total organic carbon. *Chemosphere*, *76*(2), 226–231.
- Chung, M. K., Hu, R., Cheung, K. C., & Wong, M. H. (2007). Pollutants in Hong Kong soils: Polycyclic aromatic hydrocarbons. *Chemosphere*, *67*(3), 464–473. doi:10.1016/j.chemosphere.2006.09.062.
- Dickhut, R., Canuel, E., Gustafson, K., Liu, K., Arzayus, K., Walker, S., et al. (2000). Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. *Environmental Science & Technology*, *34*(21), 4635–4640.
- Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P., et al. (2003). Persistent organic pollutants in environment of the Pearl River Delta, China: An overview. *Chemosphere*, *52*(9), 1411–1422.
- Guo, H., Wang, T., & Louie, P. (2004). Source apportionment of ambient non-methane hydrocarbons in Hong Kong: application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. *Environmental Pollution*, *129*(3), 489–498.
- Jiang, Y. F., Wang, X. T., Wang, F., Jia, Y., Wu, M. H., Sheng, G. Y., et al. (2009). Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere*, *75*(8), 1112–1118.
- Jing, X., Ming-zhong, R., Gou-yong, D., Zhen-cheng, X., & Su-kun, Z. (2009). Content analysis and assessment of polycyclic aromatic hydrocarbons in surface sediments from Beijiang River, China. *Chinese Journal of Environmental Science*, *30*(11), 3269–3275.
- Kowalkowski, T., Zbytniewski, R., Szpejna, J., & Buszewski, B. (2006). Application of chemometrics in river water classification. *Water Research*, *40*(4), 744–752.
- Li, W. H., Tian, Y. Z., Shi, G. L., Guo, C. S., Li, X., & Feng, Y. C. (2012). Concentrations and sources of PAHs in surface sediments of the Fenhe reservoir and watershed, China. *Ecotoxicology and Environmental Safety*, *75*, 198–206.
- Lichtfouse, É., Budzinski, H., Garrigues, P., & Eglinton, T. I. (1997). Ancient polycyclic aromatic hydrocarbons in modern soils: ¹³C, ¹⁴C and biomarker evidence. *Organic Geochemistry*, *26*(5), 353–359.
- Liu, C. W., Lin, K. H., & Kuo, Y. M. (2003). Application of factor analysis in the assessment of groundwater quality in a black-foot disease area in Taiwan. *Science of the Total Environment*, *313*(1), 77–89.
- Liu, Y., Chen, L., Huang, Q., Li, W., Tang, Y., & Zhao, J. (2009). Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China. *Science of the Total Environment*, *407*(8), 2931–2938.
- Mai, B. X., Fu, J. M., Sheng, G. Y., Kang, Y. H., Lin, Z., Zhang, G., et al. (2002). Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. *Environmental Pollution*, *117*(3), 457–474.
- Men, B., He, M., Tan, L., Lin, C., & Quan, X. (2009). Distributions of polycyclic aromatic hydrocarbons in the Daliao River Estuary of Liaodong Bay, Bohai Sea (China). *Marine Pollution Bulletin*, *58*(6), 818–826.
- Mostafa, A. R., Wade, T. L., Sweet, S. T., Al-Alimi, A. K. A., & Barakat, A. O. (2009). Distribution and characteristics of polycyclic aromatic hydrocarbons (PAHs) in sediments of Hadhramout coastal area, Gulf of Aden, Yemen. *Journal of Marine Systems*, *78*(1), 1–8.
- Ning-jing, H., Xue-fa, S., Ji-hua, L., Peng, H., Ai-mei, Z., & Yan-guang, L. (2010). Distribution and origin of PAHs in the surface sediment of the Yellow River Estuary and its adjacent areas. *Bulletin of mineralogy, petrology and geochemistry*, *2*, 157–163.
- Ouyang, Y., Nkedi-Kizza, P., Wu, Q., Shinde, D., & Huang, C. (2006). Assessment of seasonal variations in surface water quality. *Water Research*, *40*(20), 3800–3810.
- Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T. A., & Hoffmann, T. (2008). Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere*, *72*(10), 1594–1601. doi:10.1016/j.chemosphere.2008.04.021.
- Pietzsch, R., Patchineelam, S. R., & Torres, J. P. M. (2010). Polycyclic aromatic hydrocarbons in recent sediments from a subtropical estuary in Brazil. *Marine Chemistry*, *118*(1–2), 56–66.
- Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment*, *42*(13), 2895–2921. doi:10.1016/j.atmosenv.2007.12.010.
- Ruiz, Y., Suarez, P., Alonso, A., Longo, E., Villaverde, A., & San Juan, F. (2011). Environmental quality of mussel farms in the Vigo estuary: Pollution by PAHs, origin and effects on reproduction. *Environmental Pollution*, *159*(1), 250–265.
- Shukla, V., & Upreti, D. K. (2009). Polycyclic aromatic hydrocarbon (PAH) accumulation in lichen, *Phaeophyscia hispidula* of DehraDun City, Garhwal Himalayas. *Environmental Monitoring and Assessment*, *149*(1–4), 1–7. doi:10.1007/s10661-008-0225-6.
- Sienra, M. D. R., Rosazza, N. G., & Préndez, M. (2005). Polycyclic aromatic hydrocarbons and their molecular

- diagnostic ratios in urban atmospheric respirable particulate matter. *Atmospheric Research*, 75(4), 267–281. doi:10.1016/j.atmosres.2005.01.003.
- Simeonov, V., Stratis, J., Samara, C., Zachariadis, G., Voutsas, D., Anthemidis, A., et al. (2003). Assessment of the surface water quality in Northern Greece. *Water Research*, 37(17), 4119–4124.
- Soclo, H., Garrigues, P., & Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: Case studies in Cotonou (Benin) and Aquitaine (France) areas. *Marine Pollution Bulletin*, 40(5), 387–396.
- Song, M. W., Huang, P., Li, F., Zhang, H., Xie, K. Z., Wang, X. H., et al. (2011). Water quality of a tributary of the Pearl River, the Beijiang, Southern China: Implications from multivariate statistical analyses. *Environmental monitoring and assessment*, 172(1–4), 589–603.
- Thurston, G. D., & Spengler, J. D. (1985). A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environment* (1967), 19(1), 9–25.
- Tobiszewski, M., & Namieśnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution*, 162, 110–119.
- USEPA. (1996a). *Method 3540c: Soxhlet extraction*. Washington, DC: United States Environmental Protection Agency.
- USEPA. (1996b). *Method 3620b: Florisil cleanup*. Washington, DC.: United States Environmental Protection Agency.
- USEPA. (1996c). *Method 3660b: Sulfur cleanup*. Washington, DC.: United States Environmental Protection Agency.
- USEPA. (1996d). *Method 8270c: Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)*. Washington, DC.: United States Environmental Protection Agency.
- Wang, C., Wang, W., He, S., Du, J., & Sun, Z. (2011a). Sources and distribution of aliphatic and polycyclic aromatic hydrocarbons in Yellow River Delta Nature Reserve, China. *Applied Geochemistry*, 26(8), 1330–1336.
- Wang, W., Huang, M.-j., Kang, Y., Wang, H.-s., Leung, A. O., Cheung, K. C., et al. (2011b). Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk assessment. *Science of the Total Environment*, 409(21), 4519–4527.
- Yang, B., Zhou, L., Xue, N., Li, F., Li, Y., Vogt, R. D., et al. (2013). Source apportionment of polycyclic aromatic hydrocarbons in soils of Huanghuai Plain, China: Comparison of three receptor models. *Science of the Total Environment*, 443, 31–39.
- Yunker, M. B., Macdonald, R. W., Snowdon, L. R., & Fowler, B. R. (2011). Alkane and PAH biomarkers as tracers of terrigenous organic carbon in Arctic Ocean sediments. *Organic Geochemistry*, 42(9), 1109–1146. doi:10.1016/j.orggeochem.2011.06.007.
- Yunker, M. B., Perreault, A., & Lowe, C. J. (2012). Source apportionment of elevated PAH concentrations in sediments near deep marine outfalls in Esquimalt and Victoria, BC, Canada: Is coal from an 1891 shipwreck the source? *Organic Geochemistry*, 46, 12–37. doi:10.1016/j.orggeochem.2012.01.006.
- Zhang, K., Wang, J. Z., Liang, B., & Zeng, E. Y. (2011). Occurrence of polycyclic aromatic hydrocarbons in surface sediments of a highly urbanized river system with special reference to energy consumption patterns. *Environmental Pollution*, 159(6), 1510–1515.
- Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., & Wang, X. (2008). Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environmental Pollution*, 153(3), 594–601.