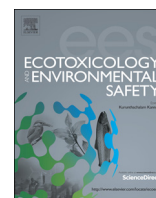




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Source identification of polycyclic aromatic hydrocarbons in different ecological wetland components of the Qinkenpao Wetland in Northeast China

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ABSTRACT

To determine the distribution and sources of polycyclic aromatic hydrocarbon (PAH), sixteen common PAHs were measured in various wetland components, including groundwater, surface water, sediments and soils collected from the Qinkenpao Wetland of Daqing City in Northeast China. High levels of PAHs were observed in the wetland due to the discharge of industrial wastewater including petrochemical products, such as petroleum and carboic acid, which can be traced back for nearly three decades. Diagnostic ratios of selected PAH compounds showed that PAHs were generated by a number of mixed sources dominated by petrogenic products. Factor analysis with nonnegative constraints (FA-NNC) was combined with Latin Hypercube Sampling (LHS) simulation, which is effective for using a relatively small sample size while preserving the desirable probabilistic features of simple random sampling, to quantitatively identify sources, source contribution, and uncertainty of PAH contamination. The profiles derived from FA-NNC coupled with LHS were compared with source fingerprints, which were modified based on the first order degradation reaction in different wetland components. Premium gasoline (high-octane) was found to be the largest contributor of PAHs in surface water, groundwater, and sediments (96.0 percent, 61.6 percent and 53.1 percent, correspondingly), while regular gasoline was the dominant source of PAHs in soils (49.0 percent). The results were in agreement with the area's environmental data and diagnostic ratio results. Diagnostic ratios and FA-NNC were shown to be an effective methodology for source identification of PAHs in different wetland components.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), which belong to persistent organic pollutants (POPs), are widespread environmental pollutants and are of great concern due to their carcinogenic, mutagenic, and toxic properties (Chen et al., 2013; Countway et al., 2003; Jones and de Voogt, 1999; Kalf et al., 1997). The United States Environmental Protection Agency (US EPA) has listed sixteen PAHs in their list of 129 priority pollutants (Simpson et al., 1996). PAHs producing activities include the following: combustion of fuels in vehicular engines, power generation from fossil fuels, coke production, wood burning, incineration of industrial and domestic wastes, oil refinery and chemical engineering processes (Baek et al., 1991). PAHs are also present in refined petrochemical products such as gasoline containing a higher predominance of low molecular weight and alkylated species (Christensen and Bzdusek, 2005).

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The identification of sources of PAHs found in the environment is essential to initiate an appropriate management and remediation plan. So far, there have been several methods applying to apportion the origins of PAHs presented in different environmental media. Diagnostic ratio is one of the widely used technique (Yuan et al., 2001; Yunker et al., 2002). Diagnostic ratios of different PAH compounds, which are useful for source identification, vary with the formation of specific PAHs under different combustion conditions. However, this method can only give qualitative analysis. Factor analysis (FA) is another tool for distinguishing the sources of pollutants quantitatively (Bzdusek et al., 2004; Ozeki et al., 1995; Rachdawong and Christensen, 1997). The utilization of FA for source characterization of pollution control can be potentially operated with limited knowledge about the source characteristics, transport and incorporation mechanisms of pollutants into particles, etc., which are not always available. Factor analysis with nonnegative constraints (FA-NNC) coupled with Monte Carlo sampling simulation was recently proposed as an alternative to enhance the interpretability of the results and to determine the uncertainties of FA-NNC model results (Chen et al., 2012; Rachdawong and Christensen, 1997; Wang et al., 2007).

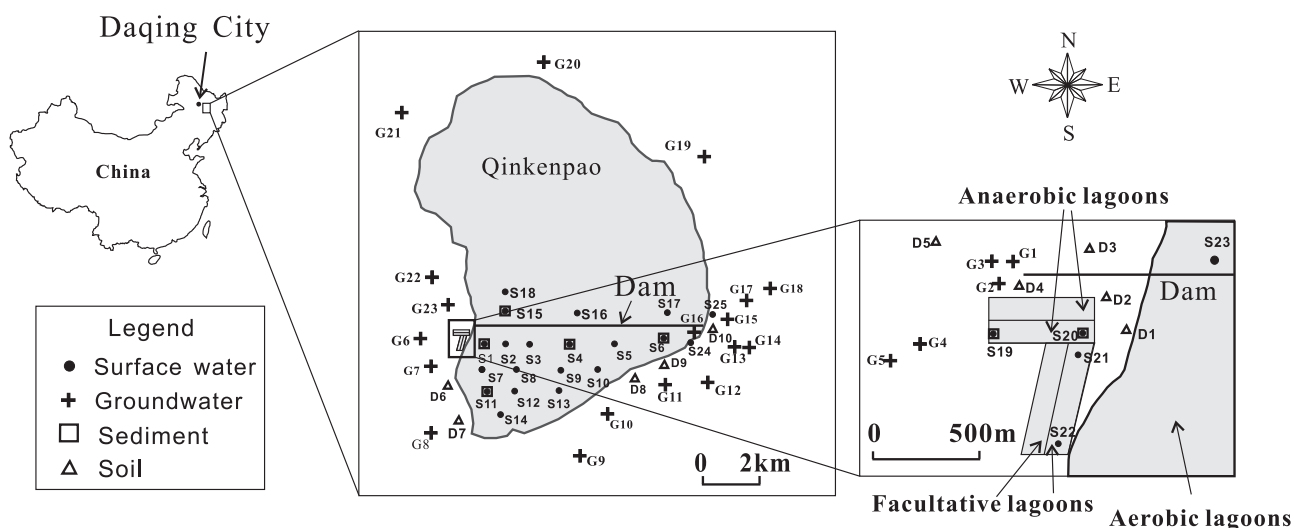


Fig. 1. Locations of the study area and sampling stations.

There are a number of sampling methods, such as Monte Carlo, Latin Hypercube Sampling (LHS), and bootstrap (Efron and Tibshirani, 1993; Hastings, 1970; Sallaberry et al., 2008). Monte Carlo is one of the most widely used sampling method. However, Monte Carlo simulation requires a large number of simulations to ascertain valuable estimations. This methodology is inefficient in sampling with potentially very large computational expenses. Bootstrap is a real data-based sampling method for statistical inference (Efron and Tibshirani, 1993). Instead of random and using real data-based sampling, Latin Hypercube Sampling (LHS) provides a dense stratification over ranges of uncertain variables with a relatively small sample size while preserving the desirable probabilistic features of simple random sampling (Sallaberry et al., 2008). Thus, FA-NNC coupled with Latin Hypercube Sampling was proposed and applied to estimate source contributions of PAHs. Furthermore, to evaluate possible degradation of PAHs transporting between source and receptor, source profiles were modified with a degradation factor based on two assumptions: PAH degradation is a first-order reaction for the degradation model in samples; and each source profile can be modified with degradation factors (Li et al., 2001). Therefore, source profiles of PAHs were modified for source identifications in surface water, groundwater, sediments, and soils, respectively.

Wetlands are considered to be the most biologically important and productive ecosystems on earth (Bedford et al., 1999). They provide habitat, food, and spawning grounds for a large number of plants and animals and therefore exhibit great biodiversity (Houlahan et al., 2006). Various natural processes also enable wetlands to remove or degrade pollutants discharged into the system. Daqing City in Northeast China is well-known not only as the largest petroleum production area in China (Ding et al., 2006; Tang et al., 2010), but also for its numerous wetlands (Yu et al., 2010) (Fig. 1). The Qinkenpao wetland is one of the largest wetlands near Daqing City and, due to the low cost and efficiency, has been used as an ecological treatment system for petrochemical sewage since 1980s. Similar to situations faced by other wetlands, the Qinkenpao Wetland is suffering from accumulative environmental stress due to the rapid industrialization and the resultant increase in waste loading. The objective of this study is to determine the major PAH sources in surface water, groundwater, sediments, and soils of the Qinkenpao Wetland using diagnostic ratios and FA-NNC combined with Latin Hypercube Sampling simulation.

2. Materials and methods

2.1. Study area

Our research was located in the Qinkenpao Wetland (125°29' E–125°42' E, 46°16' N–46°28' N), 28 km southeast to Daqing City, Northeast China. This wetland has an area of 148 km² with storage capacity of nearly 245 million m³. Lithology of the sediments is mainly clay, with an average thickness of more than 4 m. The wetland is divided into two parts by a dam. The northern wetland is reserved for tourism while the southern wetland is used as an aerobic lagoon. The aerobic lagoon, together with the western anaerobic lagoons and facultative lagoons (Fig. 1), is used as an ecological sewage treatment system. Industrial and domestic wastewater is continuously discharged into the two parallel-connected anaerobic lagoons, which connect to the facultative lagoons followed by the aerobic lagoon. The ecological sewage treatment system has a treating capacity of about 100,000 m³/d.

2.2. Sampling, extraction, and clean-up

Surface water, groundwater, sediment and soil samples were collected in April and October 2010 at the locations indicated in Fig. 1. Surface water samples were collected in lagoons at 25 sites at a depth of 0.50 m below the water surface; six sites were resampled in October 2010. Groundwater samples were collected around lagoons from 23 monitoring wells where stagnant water had been pumped out; sixteen sites were resampled in October 2010. Both surface water and groundwater were collected at least 1000 mL in pre-cleaned dark glass bottles without head-space. All samples were stored in an icebox, immediately transported to the laboratory, and stored in 4 °C refrigeration before analysis.

Surface sediments in lagoons at seven sites (Sites S1, S4, S6, S11, S15, S19 and S20) were sampled using a stainless-steel core sampler. The top 2 cm of sediments at Sites S1, S4, S6, S11, and S15 were scraped off using a stainless-steel spatula and the remaining parts (2–10 cm) were separated from top to bottom into 3 parts. Sediments at S19 and S20 were too liquid to separate, so each of these samples was collected as a whole. Therefore, the total number of surface sediment samples was seventeen. Deeper undisturbed soil samples of ten boreholes (the deepest sample is 9.74 m below ground level and the average depth of the ten boreholes is 7.68 m. The lithology can be found in Fig. S1) were collected using Geoprobe System direct-push auger transparent polycarbonate tubes. The soil cores were opened in the laboratory and split into several parts according to the lithology of stratum (with a total of 91 samples). The surface sediment and soil samples were kept in –20 °C freezers until analysis. The frozen samples were freeze-dried (FD-1A-50, Beijing Boyikang Instrument Co., Ltd., China), ground with a mortar, sieved to 38.0 μm, and stored in pre-cleaned dark glass bottles before extraction.

The water samples were filtered through 0.45 μm pore size, 12.5 mm diameter pre-cleaned glass fiber filters to separate suspended particulate materials from water. Next steps were followed according to the EPA Method 3510c (US EPA, 1996). Surrogate standards (2-Fluorobiphenyl, p-Terphenyl-d₁₄ (Chem Service, Inc.)) and internal standards of deuterated PAHs (Acenaphthene-d₁₀, Chrysene-d₁₂, 1,4-Dichlorobenzene-d₄, Naphthalene-d₈, Perylene-d₁₂, Phenanthrene-d₁₀ (Chem Service, Inc.)) were added by Fan et al. (2010), Guo et al. (2010), and Mai et al. (2001).

Freeze-dried, homogenized sediments and soils (10.0 g) were spiked with surrogate standards (2-Fluorobiphenyl, p-Terphenyl-d₁₄ (Chem Service, Inc.)) and extracted by sonication with a mixture of hexane and acetone (1:1, by volume) for 20 min. The extraction was repeated triplicated, then filtered, concentrated, and solvent-exchanged to hexane. The cleanup and fractionation was performed on a silica/alumina gel chromatography column. The extracts were successively eluted with 15 mL hexane and 70 mL hexane/dichloromethane (7:3 by volume). The second fraction was concentrated under nitrogen to 1 mL. Known quantities of internal standards mentioned above were added to the samples prior to instrumental analysis (Pointet and Milliet, 2000).

2.3. GC–MS analysis, quantification, and quality control/quality assurance

The PAHs were quantified by GC/MS (Agilent GC6890/5973MSD) operating in selected ion monitoring (SIM) mode with a DB-5 capillary column (Agilent, 60 m length × 0.25 mm inner diameter × 0.25 μm film thickness). Oven temperature was initially isothermal at 60 °C for 5 min, then increased from 60 to 255 °C at 15 °C/min, from 255 °C to 300 °C at 5 °C/min, and kept isothermal at 300 °C for 30 min. Helium is used as the carrier gas. Splitless injection of 1.0 μL sample was conducted with an auto-sampler.

The quantified compounds included the following sixteen PAHs (abbreviations in brackets): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DBA), and benzo[ghi]perylene (BghiP). Standards of these sixteen PAHs in a mixture solution of 2000 μg/ml were purchased from Supelco (USA).

All analytical data were subject to strict quality control. The method detection limits (MDLs) of PAHs were determined as the concentration of analyses in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The method detection limit (MDL) ranged from 1.6 to 3.9 ng L⁻¹ for surface water and ground-water samples and from 0.60 to 4.82 ng g⁻¹ for sediment and soil samples, respectively. Each sampling campaign was accompanied by blanks that were treated identically as the samples. Trace levels of targets detected in the controls were subtracted from the samples. In addition, surrogate standards were added to each of the samples to monitor procedural performance and matrix effects. The surrogate recoveries in all samples were 68.5 ± 9.68 percent for 2-Fluorobiphenyl and 95.4 ± 13.5 percent for p-Terphenyl-d₁₄. The mean recoveries for the blank spiked samples of the sixteen target PAHs ranged from 81.1 percent ± 7.4 percent (Ace) to 115.1 ± 12.8 percent (BbF) for surface water and groundwater and from 62.4 ± 17.3 percent (Acy) to 118.1 ± 16.7 percent (BaA) for sediments and soils.

2.4. FA–NNC

The details of FA with nonnegative constraints were previously described in literature (Ozeki et al., 1995; Rachdawong and Christensen, 1997). The fundamental equation is

$$D_{(m \times r)} = C_{(m \times n)} \times R_{(n \times r)} \quad (1)$$

where the data matrix D is factored into its components. C and R are the factor loading matrix (source composition) and the factor score matrix (source contribution), respectively. m , n and r are the number of PAHs, sources and samples, respectively.

The procedures of FA–NNC were described in detail in the literature (Christensen and Bzdusek, 2005; Imamoglu and Christensen, 2002; Ozeki et al., 1995; Rachdawong and Christensen, 1997). To reduce bias towards PAHs with high concentrations, average scaling was applied to the data matrix before factorization. Furthermore, a covariance matrix was factorized to derive the factor loading and factor score matrices. Both the factor loading matrix and the factor score matrix were rotated with nonnegative constraints until the sum of squares of negative values in the factor loading matrix fell below 0.0001 or the changing of the sum of squares of the factor loading matrix fell below 0.001 (Chen et al., 2012; Imamoglu and Christensen, 2002; Wang et al., 2007). Coefficient of determination (COD), cumulative percent variance, Exner function, and convergence of the non-negative rotations were all considered for the determination of significant factors.

As mentioned previously, the initial sediment data matrix consisted of sixteen PAHs and seventeen samples (the process for surface water, groundwater, and soils are similar thus not included for convenience of presentation). InP and DBA were removed from the data set due to excessive numbers of non-detects. Nap was removed because of solubility and volatility concerns. Three samples were identified as outliers due to high concentrations (the outlier samples were S19, S20, and the top part of S1. PAH concentrations of outliers range from 6098 to 68,799 ng/g; other PAH concentrations range from 32 to 3476 ng/g.). Accordingly, thirteen PAHs and fourteen samples were retained in the sediment data matrix.

2.5. Latin Hypercube Sampling simulation

Simulated sets of PAH sediment data were created by Latin Hypercube Sampling (LHS) simulation to determine the uncertainties of FA–NNC modeling results (Rachdawong and Christensen, 1997). Instead of random sampling using Monte Carlo simulations, LHS ensures that uniform random numbers are evenly spread over the range of uncertain variables, which increases the likelihood that the iterations will sweep out a wider set of scenarios. This method is effective for using a relatively small sample size while preserving the desirable probabilistic features of simple random sampling. Results have shown that LHS can give narrower confidence intervals than random samples. A detailed explanation of LHS is explained in published literature (Helton and Davis, 2003; Stein, 1987). The governing equation for LHS to determine the uncertainties of FA–NNC is the following:

$$D_{ij} = A_{ij} + C_{ij}A_{ij} \left[\sqrt{2} \operatorname{erf}^{-1}(2R_{ij} - 1) \right] \quad (2)$$

where D_{ij} is the generated PAHs concentration from PAH i and sample j ; A_{ij} is the starting concentration of PAH i from sample j ; C_{ij} is the coefficient of variation of PAH i from sample j ; erf^{-1} is the inverse Gaussian error function; and R_{ij} is the uniformly distributed random number between 0 and 1 generated using LHS.

The assumption in Eq. (2) is that all PAHs from a given source will co-vary. Ten artificial realizations using LHS of data matrix D were generated and modeled again by FA–NNC to yield ten factor loadings and factor score matrices. The standard deviation of the mean for each entry in the factor loadings and factor score matrices was calculated and was considered to be the uncertainty (Bzdusek et al., 2004; Chen et al., 2012; Rachdawong and Christensen, 1997; Tian et al., 2009).

2.6. Source identification

The profiles derived from FA–NNC were compared with values reported in the literature for coal fired power plant, coke oven, wood combustion, diesel engine exhaust, traffic tunnel, gasoline engine exhaust, regular grade gasoline, and premium grade gasoline (high-octane) (Bzdusek et al., 2004; Khalili et al., 1995; Li et al., 2003; Marr et al., 1999).

PAHs can react with other active species during specific transport mechanisms, such as hydroxyl radicals and ozone, which may result in shorter life-times of PAHs in the atmosphere, water, sediments, and soils (Li et al., 2001). Therefore, chemical, photochemical, and biological degradation of these compounds should be considered before occurring in surface water, groundwater, sediments, and soils. To consider the degradation of PAHs from source to receptor, source profiles were modified with a degradation factor. The assumption was made that PAH degradation was a first-order reaction for the degradation model in the samples (Chen et al., 2012; Li et al., 2001). Each source profile could be modified by degradation factors for atmospheric and wetland components, which were related with the first order rate constant of degradation of PAHs and defined as follows:

$$C_{ja} = 1/(1 + k_{ja} \times t_a) \quad (3)$$

$$C_{jw} = \exp(-k_{jw} \times t_w) \quad (4)$$

$$C_{jg} = \exp(-k_{jg} \times t_g) \quad (5)$$

$$C_{js} = \exp(-k_{js} \times t_s) \quad (6)$$

$$C_{jo} = \exp(-k_{jo} \times t_o) \quad (7)$$

where C_{ja} , C_{jw} , C_{jg} , C_{js} , and C_{jo} are estimated degradation factors for PAHs j in the atmosphere, surface water, groundwater, sediments, and soils, respectively. k_{ja} , k_{jw} , k_{jg} , k_{js} , and k_{jo} are apparent first order rate constants of degradation for compounds j in the atmosphere (h^{-1}), surface water (d^{-1}), groundwater (d^{-1}), sediments (d^{-1}), soils (d^{-1}), respectively. t_a is the reaction time for photo oxidation in the atmosphere (h), and t_w , t_g , t_s , and t_o are the reaction time for aerobic biodegradation or photolysis in surface water (d), groundwater (d), sediments (d), and soils (d), respectively.

In this study, the rate constants of degradation of selected PAHs of different types of sources were diverse. The values of k_{ja} , k_{jw} , k_{jg} , k_{js} , and k_{jo} were taken from literature by Mackay et al., (1992) and Mackay and Hickie (2000). In order to find the optimum reaction time of PAHs, we selected 240 h, 10 days, 20 days, 365 days, and 365 days as the optimum reaction time of PAHs in the atmosphere, surface water, groundwater, sediments, and soils, respectively, because the results of source apportionment were satisfactory when calculated with them (Chen et al., 2012; Mackay and Hickie, 2000; Mackay et al., 1992; Xue et al., 2010).

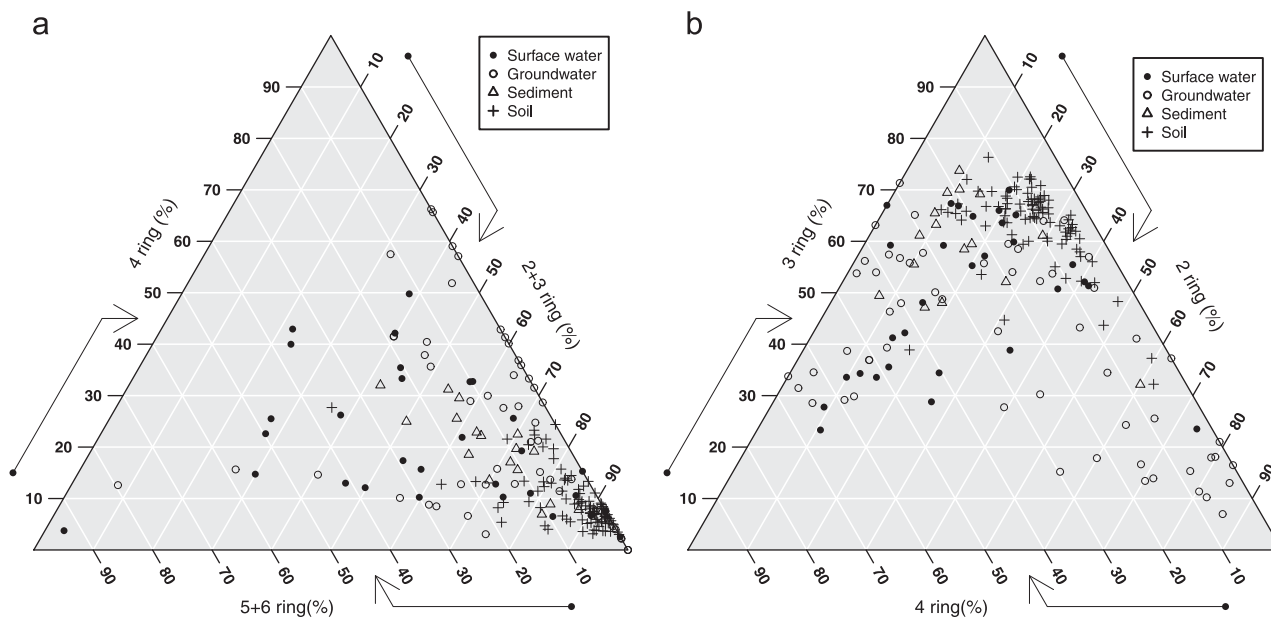
Applying the first order reaction rate constants and optimum reaction time of selected PAHs, the modified PAHs source profiles in sediment are shown in Fig. S2 with error bars representing a constant relative error of 40 percent. The results of surface water, groundwater, and soil are shown in Figs. S3 S4, and S5, respectively.

The sum of squares (SS) between the predicted and actual fractional composition over all PAHs (from 1 to m) for the profile of interest was used as an indicator of

Table 1

Basic statistics for the PAHs concentration levels in surface water, groundwater, sediments and soils of the Qinkepa Wetland, China.

PAHs	Surface water (ng/L) n=31			Groundwater (ng/L) n=39			Sediments(ng/g dw) n=17			Soil (ng/g dw) n=91		
	DF ^a (%)	Range	Mean ± SD	DF (%)	Range	Mean ± SD	DF (%)	Range	Mean ± SD	DF (%)	Range	Mean ± SD
Nap	96.8	BLD ^b –9730.0	338.0 ± 1743.3	94.8	BLD–5067.0	334.3 ± 1134.9	100.0	3.5–4875.1	535.5 ± 1301.4	100.0	6.6–95.0	21.2 ± 13.7
Acy	48.4	BLD–268.0	16.6 ± 53.5	12.8	BLD–384.0	147.6 ± 163.0	100.0	0.7–2160.6	215.5 ± 577.2	98.9	BLD–3.4	1.0 ± 0.7
Ace	29.0	BLD–144.0	8.1 ± 26.7	28.2	BLD–705.0	123.4 ± 258.5	100.0	0.6–867.5	96.8 ± 230.6	100.0	0.8–29.4	2.6 ± 3.7
Fl	48.4	BLD–2440.0	94.6 ± 438.7	84.6	BLD–1830.0	130.7 ± 416.1	100.0	1.7–3357.1	353.3 ± 894.4	100.0	2–22.0	8.0 ± 3.9
Phe	100.0	5.5–4140.0	161.9 ± 740.0	100.0	6.7–1840.0	125.9 ± 402.5	100.0	8.7–12553.1	1257.2 ± 3353.3	100.0	3.5–67.8	19.7 ± 14.0
Ant	96.8	BLD–5100.0	205.9 ± 912.0	82.1	BLD–2470.0	185.6 ± 544.6	100.0	11.6–16377.6	1624.0 ± 4377.8	100.0	5–69.5	22.6 ± 14.9
Flu	93.5	BLD–633.0	31.4 ± 113.8	66.7	BLD–418.0	49.3 ± 97.0	100.0	1.9–3677.1	370.6 ± 981.1	100.0	0.6–11.5	2.7 ± 2.0
Pyr	96.8	BLD–603.0	43.5 ± 126.8	89.7	BLD–223.0	29.4 ± 45.0	100.0	1.7–7220.4	728.6 ± 1928.1	100.0	0.6–29.5	3.5 ± 4.5
BaA	64.5	BLD–129.0	13.8 ± 31.0	69.2	BLD–69.2	11.4 ± 14.7	100.0	0.9–3246.4	323.3 ± 867.0	84.6	BLD–9.8	1.6 ± 2.1
Chr	64.5	BLD–243.0	19.3 ± 49.3	79.5	BLD–99.3	11.3 ± 18.4	100.0	0.6–3433.2	335.3 ± 918.7	94.5	BLD–17.3	1.4 ± 2.2
BbF	41.9	BLD–92.7	10.7 ± 20.7	33.3	BLD–508.0	49.9 ± 144.3	82.4	BLD–2737.6	212.7 ± 570.8	76.9	BLD–19.9	1.7 ± 2.9
BkF	35.5	BLD–90.8	7.5 ± 18.1	28.2	BLD–378.0	47.0 ± 116.5	82.4	BLD–1953.8	192.7 ± 522.3	74.7	BLD–9.5	1.0 ± 1.3
BaP	35.5	BLD–106.0	12.9 ± 28.0	23.1	BLD–60.1	12.9 ± 19.5	100.0	0.6–6159.5	587.9 ± 1652.1	57.1	BLD–16.7	1.1 ± 2.2
InP	16.1	BLD–63.8	5.2 ± 14.0	10.3	BLD–185.0	57.2 ± 86.3	23.5	BLD–174.3	20.0 ± 46.1	5.5	BLD–12.1	0.2 ± 1.3
DBA	25.8	BLD–122.0	6.8 ± 22.4	5.1	BLD–147.0	82.5 ± 91.2	64.7	BLD–77.3	18.9 ± 30.0	17.6	BLD–8.2	0.3 ± 1.0
BghiP	71.0	BLD–214.0	17.1 ± 38.4	15.4	BLD–418.0	67.5 ± 154.6	100.0	1.2–780.3	85.1 ± 207.2	29.7	BLD–11.5	0.2 ± 1.2
ΣPAHs16 ^c		36.4–23984.6	991.3 ± 4289.2		25.7–12700.0	892.6 ± 2726.1		36.4–68799.1	5428.7 ± 16486.4		23.1–250.4	88.8 ± 51.2

^a Detection frequency: number of detected samples divided by number of tested samples.^b Below Limit of Detection.^c Total of sixteen PAHs.**Fig. 2.** Distribution of PAHs with (a) two+three, four, five+six rings, and (b) two, three, four rings in surface water, groundwater, sediments, and soils from the Qinkepa Wetland in a piper diagram.

similarity

$$SS = \sum_{j=1}^l \sum_{i=1}^m (\bar{C}_{ik} - C_{ij})^2 \quad (8)$$

where \bar{C}_{ik} and C_{ij} are the fraction of modeled and candidate source profiles and k and l are the number of significant factors and candidate sources, respectively.

3. Results and discussion

3.1. Relationship between PAHs in surface water, groundwater, sediments and soils

Table 1 demonstrated that the mean concentration of total PAHs in groundwater was slightly lower than that in the surface water. In contrast to water, the proportions of sixteen PAHs in sediment samples varied significantly. The significant differences

in the proportions of the sixteen PAHs may result from the hydrophobic nature of these organic compounds and its accumulation over time, which can reflect the historical deposition of PAHs (Fan et al., 2010; Usenko et al., 2007, 2010). Compared to the distribution of individual PAHs in sediments, few individual PAHs were detected in soils. The mean concentration of total PAHs in soils was two orders of magnitude lower than that in sediments. The average total PAHs in surface water and groundwater of this area are comparable to the Tonghui River, Beijing, China (762.3 ng/L) (Zhang et al., 2004), but higher than those in Seine River, France (20 ng/L) (Fernandes et al., 1997), surface water in Northern Greece (465 ng/L) (Manoli et al., 2000), and water in the Yellow River Delta, a newly born wetland in China (121.3 ng/L) (Wang et al., 2009), and lower than those in Jiulong River Estuary, China (17,050 ng/L) (Maskaoui et al., 2002). The average total PAHs in the sediments are higher compared to sediments (1001.9 ng/g)

from Liaohe estuarine wetland, China (Lang et al., 2012), sediments (634 ng/g) from Sundarban Mangrove Wetland, India (Domínguez et al., 2010), sediments (150.9 ng/g) from the Yellow River Delta, China (Yang et al., 2009), and sediments (1019 ng/g) from sub-lake Xihulu of Lake Lianhuan in Northeast China (Sun and Zang, 2013). The average total PAHs in soils are less than those shown in soils from rural sites (233 ng/g) in Dalian, China (Wang et al., 2007), soils from remote sites (450 ng/g) in the Seine River basin, France (Motelay-Massei et al., 2004), soils (128 ng/g) of Huanghuai Plain, China (Yang et al., 2013), and soils (209 ng/g) of the Songhua River Basin, China (Ma et al., 2013). By comparing the total PAH concentrations in this study with those of the above reported similar areas, the PAH values in surface water and groundwater of this area were found to be at medium or high levels. Furthermore, PAH values in sediments were at high levels, while PAH values in soils were at low levels. From the sum of PAH concentrations with uncertainties, it can be found that PAHs varied widely in surface water and sediments, but more uniform in soils and groundwater.

Fig. 2(a) shows a higher concentration of five-, six-rings PAHs in surface water compared to groundwater. If the five-, six-rings PAHs compounds are excluded (Fig. 2(b)), two-rings PAHs are the predominant compounds in groundwater samples, whereas three-, four-rings PAHs are the abundant compounds in surface water. This may result from the higher likelihood that low molecular weight PAHs are more likely to transport, whereas high molecular weight PAHs may tend to stay in surface water (Selck et al., 2005; Van Noort et al., 2004).

Two-, three-ring PAHs are the predominant compounds in sediment and soil samples compared to the four-, five-, six-ring PAHs. If the five-, six-rings PAHs compounds are excluded, three-, four-ring PAHs are more abundant in sediments, whereas three-ring PAHs are prevalent in soils, followed by the two-ring PAHs (Fig. 2(b)).

3.2. Source identification by diagnostic ratios

Source identification is of great significance for the determination of control strategies for environmental pollution. In order to identify sources for the levels of PAHs in this study, a source analysis was undertaken. Ratios of PAHs, such as Ant/(Ant+Phe), BaA/(BaA+Chr), Fl/(Fl+Pyr), and InP/(InP+BghiP), have been developed to identify the possible sources of PAHs (Yang, 2000; Yuan et al., 2001; Yunker et al., 2002).

In the present work, the ratios of Ant/(Ant+Phe) and Fl/(Fl+Pyr) in surface water ranged from 0.09 to 0.63 and 0.29 to 1.00, respectively (all non-detected values were not included in statistics and were not plotted in Fig. 3). This result suggested that PAHs inputs are mainly from petroleum, petroleum combustion, and grass, wood, coal combustions. The values of BaA/(BaA+Chr) and InP/(InP+BghiP) ranged from 0.32 to 1.00 and 0.20 to 0.46, respectively, which indicated PAHs mainly came from petroleum, petroleum combustion, and mixed sources.

In groundwater, the ratios of Ant/(Ant+Phe) and Fl/(Fl+Pyr) ranged from 0.10 to 0.62 and 0.09 to 1.00, respectively. This suggested that petroleum, petroleum combustion, and grass, wood, coal combustions origin were the possible PAH sources. The ratios of BaA/(BaA+Chr) and InP/(InP+BghiP) varied from 0.18 to 0.5 and 0.30 to 1.00, respectively, which indicated the same origin as suggested by the ratios of Ant/(Ant+Phe) and Fl/(Fl+Pyr).

In the case of sediments, ratios of Ant/(Ant+Phe) and Fl/(Fl+Pyr) ranged from 0.51 to 0.57 and 0.26 to 0.82, respectively, which suggested origins of petroleum, petroleum combustion, and grass, wood, coal combustions were the important PAH sources. The ratios of BaA/(BaA+Chr) and InP/(InP+BghiP) ranged from 0.31 to 0.66 and 0.24 to 0.74, respectively, which indicated origins

of petroleum combustion, mixed sources, and grass, wood, coal combustions.

When it came to soils, the values of Ant/(Ant+Phe) and Fl/(Fl+Pyr) ranged from 0.13 to 0.61 and 0.28 to 0.95, respectively, showing origins of petroleum, petroleum combustion, and grass, wood, coal combustions were possible PAH sources. The ratios of BaA/(BaA+Chr) and InP/(InP+BghiP) ranged from 0.18 to 0.65 and 0.51 to 0.79, respectively, which showed the same origin as the ratios indicated by Ant/(Ant+Phe) and Fl/(Fl+Pyr).

It seemed that different isomer ratios presented different source identification information in surface water and sediment. This may be due to the different sampling locations with different hydrologic conditions and geographical variations (Chen et al., 2012). Generally, the isomer ratios of Ant/(Ant+Phe), BaA/(BaA+Chr), Fl/(Fl+Pyr), and InP/(InP+BghiP) showed that the sources of PAHs identified in surface water, groundwater, sediments, and soils seemed to be mixed sources, while petrogenic sources were the main origins of PAHs.

3.3. Factor loadings derived from FA-NNC

FA-NNC coupled with LHS was used to quantitatively model the data of PAHs associated with surface water, groundwater, sediments and soils. The criteria for selecting significant number of factors associated with sediments are listed in Table S1. Three diagnostic tools, the cumulative percent variance, the Exner function and coefficient of determination (COD), were calculated using FA-NNC. Based on the diagnostic tools, the number of significant factors was selected. The COD gives PAH specific goodness of fit information for each additional factor, where 1.0 represents a perfect fit. The Exner function approaches the best fit at zero (Imamoglu and Christensen, 2002; Molinowski, 2002). From Table S1, the first three factors explain 95.62 percent of the variance of the data matrix. COD is nearly 1.0 for all the PAHs modeled. The coefficient of determination for BaP improved greatly after the inclusion of the third factor. Addition of the fourth factor marginally improved the coefficient of determination and cumulative variance. Thus, three factors were selected. The source profile plot is shown in Fig. S2 with error bars representing a constant relative error of 40 percent. The source profile was modified by the degradation factor for PAHs in sediment. The factor loading plot is shown in Fig. S6 with error bars representing the standard deviation of the mean for ten FA-NNC models created by LHS simulation. Table S5 presents the values of sum of squares (SS) for eight literature PAH sources. The criteria for selecting significant number of factors, factor loading plot, and SS value table for surface water, groundwater, and soils can be found in Tables S2–S4, S6–S8, and Figs. S7–S9.

Loading one of three factors, which was responsible for 53 percent for the total variance, was predominantly loaded on Ant, Phe, and Fl. By comparing PAH patterns from the SS result (Table S5), the factor appeared to be related to regular grade gasoline and premium grade gasoline, but more related to premium grade gasoline. Similarity between loading one of three and premium grade gasoline was remarkable. The use of Ant and Phe as a marker for gasoline has been reported in literature (Marr et al., 1999). It was reasonable to assign this factor to premium grade gasoline.

Loading two of three factors, which accounted for 37 percent for the total variance, was predominantly loaded on Pyr, moderately weighted by Phe, Ant, and Flu. The SS calculation demonstrated this factor seemed to be related to premium grade gasoline and traffic tunnel source. Pyr is predominant in traffic tunnel sources, so it was rational to assign this factor to traffic tunnel emissions (Li et al., 2003).

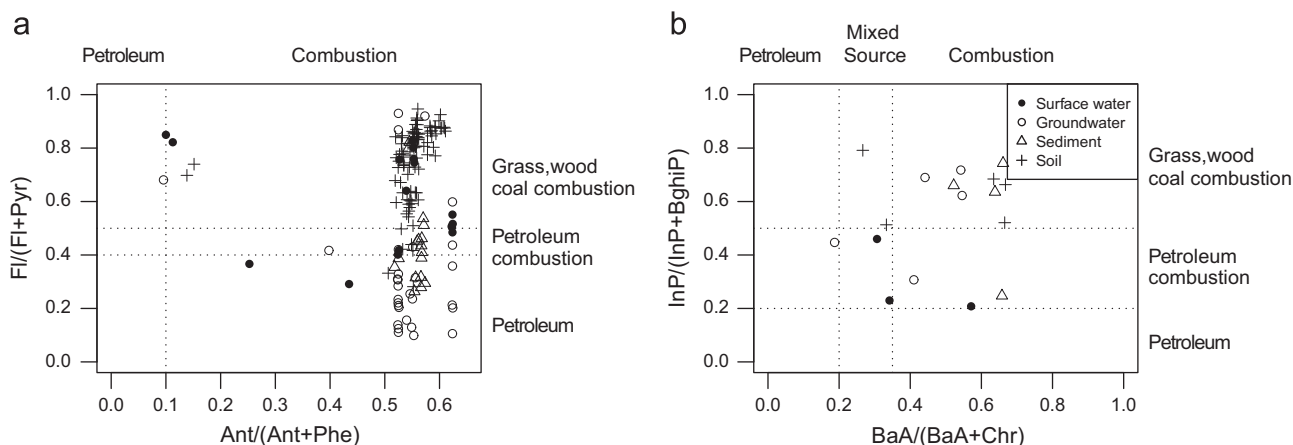


Fig. 3. Diagnostic ratio plots of (a) Ant/(Ant+Phe) vs. FI/(FI+Pyr) and (b) BaA/(BaA+Chr) vs. InP/(InP+BghiP).

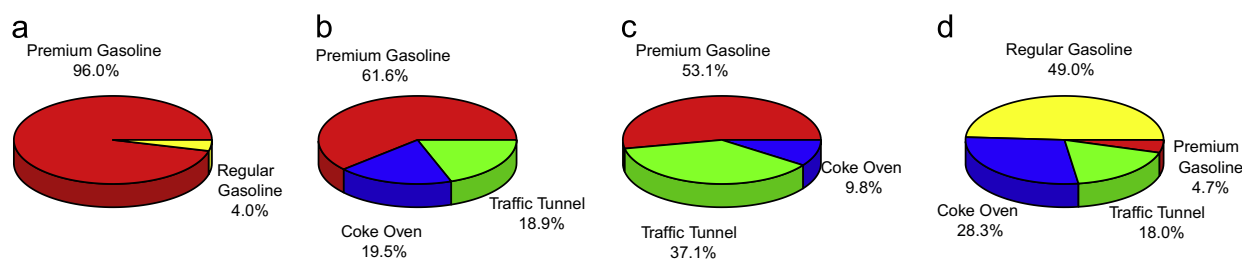


Fig. 4. Source contributions derived from FA-NNC for sediments, soils, surface water, and groundwater.

Loading three of three factors, which was responsible for 10 percent of the total variance, was mainly weighted by BaP and BaA, and moderately weighted by other high molecular PAHs. This factor seems linked to a coke oven source. Although the molecular weight PAHs vary from the candidate source profiles, it captures the general trend that high molecular PAHs are abundant, and low molecular PAHs have lower loadings (Li et al., 2003).

3.4. Source contribution

Fig. 4 shows the overall contributions estimated by FA-NNC with PAH sources modified with degradation factors associated with surface water, groundwater, sediments, and soils.

Premium grade gasoline made the largest contribution (96.0 percent) for PAHs in surface water, followed by regular grade gasoline (4.0 percent). Premium grade gasoline also occupied the largest contribution (61.6 percent) for PAHs in groundwater, followed by coke oven (19.5 percent), and traffic tunnel (18.9 percent). Furthermore, premium grade gasoline accounted for the largest contribution (53.1 percent), followed by traffic tunnel (37.1 percent) and coke oven source (9.8 percent) in sediments. In soils, regular grade gasoline were the major contributor (49.0 percent) of the PAH sources, followed by coke oven (28.3 percent), traffic tunnel (18.0 percent), and premium grade gasoline (4.7 percent).

It is interesting to note that gasoline (including premium grade gasoline and regular grade gasoline) accounted for the largest contribution of PAH sources in all of the listed environmental components. It has been found that industrial and domestic wastewater including petrochemical products, such as petroleum and carbolic acid, contaminates the lagoons by mixing with surface water. Due to the long-term operation, the wastewater may transport underground and become a part of the groundwater, while some wastewater is likely to deposit into sediments and soils. This may be critical to explain why gasoline accounted for

the largest contribution of PAH sources in surface water, groundwater, sediments, and soils.

Coke oven and traffic tunnel sources occupy contributions in groundwater, sediment, and soil samples. These groundwater, sediment, and soil samples can reflect the historical deposition of PAHs accumulation over time, while coke oven and traffic tunnel sources might come from historical input. This area had a coke oven plant that was not active during sampling, but the coke oven source may have been generated from this facility. Fig. 1 shows that a dam had been built to separate the wetland. The increased volume of road transportation and tourism may result in increased traffic tunnel sources. It is worth noting that sediment samples have higher contributions from traffic tunnel than groundwater and soil samples do. Sediments were sampled in the lagoons, while groundwater and soils were sampled around the lagoons. Sediment samples were closer to the dam and more traffic tunnel sources may deposit into the sediments. This may be the reason why sediment samples have higher traffic tunnel contribution.

These apportionment results are compatible with the area's environmental data that Daqing city is the largest petroleum production area in China and the Qinkenpao wetland has been used as an ecological treatment system for petrochemical sewage since the 1980s. It is also in agreement with PAH concentration analysis and source identification by diagnostic ratios that sources of PAHs identified in surface water, groundwater, sediments, and soils seem to be mixed sources, while petrogenic sources are the predominant origins of PAHs. Although some research shows that in cities of northern China, raw coal represents the primary energy consumption mixed by the residential coal consumption and coal burning power plants, thus leading to large amounts of PAH emissions. Unfortunately, surface sediments is the primary research focus (Chen et al., 2012). In short, source identification by diagnostic ratios and FA-NNC with PAH sources modified with degradation factors provides reasonable PAH

contributions in the previously listed environmental components in the Qinkenpao Wetland of Daqing City.

4. Conclusions

We investigated the distribution and source identification of PAHs in surface water, groundwater, sediments, and soils of the Qinkenpao Wetland, Northeast China. The distribution and composition of PAHs varied between surface water, groundwater, sediments, and soils, possibly as a result of temporal variation in the historical inputs from various contamination sources. Concentrations of PAHs varied widely in surface water and sediment, but were more uniform in groundwater and soils.

It was successful to employ diagnostic ratios of selected PAH compounds and FA-NNC combined with LHS simulation for source identification of PAHs in surface water, groundwater, sediments, and soils, and source profiles were modified with a degradation factor. The diagnostic ratios, including $Ant/(Ant+Phe)$, $BaA/(BaA+Chr)$, $Fl/(Fl+Pyr)$, and $InP/(InP+BghiP)$, showed that the sources of PAHs seemed to be mixed, while petrogenic sources were the main origins of PAHs. Visually comparing PAH patterns and analyzing sum of squares of differences between modeled and literature PAHs profiles modified with degradation factors, FA-NNC coupled with LHS simulation was used to quantitatively identify sources, source contribution, and uncertainty of PAH contamination in the wetland components. It was suggested that premium grade gasoline accounted for the largest contribution for PAHs in surface water, groundwater, and sediment (96.0 percent, 61.6 percent, and 53.1 percent, correspondingly), while regular grade gasoline occupied the largest contribution for soil PAHs (49.0 percent). The results were in agreement with the area's environmental data and diagnostic ratios results. Thus attention should be paid to the petroleum contamination for control of PAH sources.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ecoenv.2014.01.030>.

References

- Baek, S.O., et al., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water Air Soil Pollut.* 60, 279–300.
- Bedford, B.L., et al., 1999. Patterns in nutrient availability and plant diversity of temperate North American wetlands. *Ecology* 80, 2151–2169.
- Bzdusek, P.A., et al., 2004. Source apportionment of sediment PAHs in Lake Calumet, Chicago: application of factor analysis with nonnegative constraints. *Environ. Sci. Technol.* 38, 97–103.
- Chen, H.-Y., et al., 2012. Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Rizhao coastal area (China) using diagnostic ratios and factor analysis with nonnegative constraints. *Sci. Total Environ.* 414, 293–300.
- Chen, H.-Y., et al., 2013. Source apportionment for sediment PAHs from the Daliao River (China) using an extended fit measurement mode of chemical mass balance model. *Ecotoxicol. Environ. Saf.* 88, 148–154.
- Christensen, E.R., Bzdusek, P.A., 2005. PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis. *Water Res.*, 39, pp. 511–524.
- Countway, R.E., et al., 2003. Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. *Org. Geochem.* 34, 209–224.
- Ding, J.L., et al., 2006. Flow behavior of Daqing waxy crude oil under simulated pipelining conditions. *Energy Fuels* 20, 2531–2536.
- Dominguez, C., et al., 2010. Quantification and source identification of polycyclic aromatic hydrocarbons in core sediments from Sundarban Mangrove Wetland, India. *Arch. Environ. Contam. Toxicol.* 59, 49–61.
- Efron, B., Tibshirani, R., 1993. *An Introduction to the Bootstrap*. CRC press, New York.
- Fan, C.W., et al., 2010. Characteristics of sedimentary polycyclic aromatic hydrocarbons (PAHs) in the subtropical Feitsui Reservoir, Taiwan. *J. Hydrol.* 391, 217–222.
- Fernandes, M., et al., 1997. Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. *Mar. Pollut. Bull.* 34, 857–867.
- Guo, J.Y., et al., 2010. Anthropogenic input of polycyclic aromatic hydrocarbons into five lakes in Western China. *Environ. Pollut.* 158, 2175–2180.
- Hastings, W.K., 1970. Monte Carlo sampling methods using Markov chains and their applications. *Biometrika* 57, 97–109.
- Helton, J.C., Davis, F.J., 2003. Latin hypercube sampling and the propagation of uncertainty in analyses of complex systems. *Reliab. Eng. Syst. Saf.* 81, 23–69.
- Houlahan, J.E., et al., 2006. The effects of adjacent land use on wetland species richness and community composition. *Wetlands* 26, 79–96.
- Imamoglu, I., Christensen, E.R., 2002. PCB sources, transformations, and contributions in recent Fox River, Wisconsin sediments determined from receptor modeling. *Water Res.* 36, 3449–3462.
- Jones, K.C., de Voogt, P., 1999. Persistent organic pollutants (POPs): the state of the science. *Environ. Pollut.* 100, 209–221.
- Kalf, D.F., et al., 1997. Environmental quality objectives for 10 polycyclic aromatic hydrocarbons (PAHs). *Ecotoxicol. Environ. Saf.* 36, 89–97.
- Khalili, N.R., et al., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emission. *Atmos. Environ.* 29, 533–542.
- Lang, Y., et al., 2012. Distribution and risk assessment of polycyclic aromatic hydrocarbons (PAHs) from Liaohu estuarine wetland soils. *Environ. Monit. Assess.* 184, 5545–5552.
- Li, A., et al., 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ. Sci. Technol.* 37, 2958–2965.
- Li, K., et al., 2001. PAHs in dated sediments of Ashtabula River, Ohio, USA. *Environ. Sci. Technol.* 35, 2896–2902.
- Ma, W.L., et al., 2013. Polycyclic aromatic hydrocarbons in water, sediment and soil of the Songhua River Basin, China. *Environ. Monit. Assess.* 185, 8399–8409.
- Mackay, D., Hickie, B., 2000. Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. *Chemosphere* 41, 681–692.
- Mackay, D., et al., 1992. *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals. Volume II: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*. Lewis Publishers, Boca Raton, FL p. 597.
- Mai, B.X., et al., 2001. Polycyclic aromatic hydrocarbons in sediments from the Pearl river and estuary, China: spatial and temporal distribution and sources. *Appl. Geochem.*, 16, pp. 1429–1445.
- Manoli, E., et al., 2000. Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere* 41, 1845–1855.
- Marr, L.C., et al., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environ. Sci. Technol.* 33, 3091–3099.
- Maskaoui, K., et al., 2002. Contamination by polycyclic aromatic hydrocarbons in the Jiulong River estuary and Western Xiamen Sea, China. *Environ. Pollut.* 118, 109–122.
- Molinoski, E., 2002. *Factor Analysis in Chemistry*. Wiley, New York.
- Motelay-Massei, A., et al., 2004. Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere* 55, 555–565.
- Ozeki, T., et al., 1995. Evaluation of sources of acidity in rainwater using a constrained oblique rotational factor analysis. *Environ. Sci. Technol.* 29, 1638–1645.
- Pointet, K., Milliet, A., 2000. PAHs analysis of fish whole gall bladders and livers from the Natural Reserve of Camargue by GC/MS. *Chemosphere* 40, 293–299.
- Rachdawong, P., Christensen, E.R., 1997. Determination of PCB sources by a principal component method with nonnegative constraints. *Environ. Sci. Technol.* 31, 2686–2691.
- Sallaberry, C.J., et al., 2008. Extension of latin hypercube samples with correlated variables. *Reliab. Eng. Syst. Saf.* 93, 1047–1059.
- Selck, H., et al., 2005. Impact of sediment organic matter quality on the fate and effects of fluoranthene in the infaunal brittle star *Amphiuira filiformis*. *Mar. Environ. Res.* 59, 19–45.

- Simpson, C.D., et al., 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. *Sci. Total Environ.* 181, 265–278.
- Stein, M., 1987. Large sample properties of simulations using latin hypercube sampling. *Technometrics* 29, 143–151.
- Sun, L., Zang, S., 2013. Relationship between polycyclic aromatic hydrocarbons (PAHs) and particle size in dated core sediments in Lake Lianhuan, Northeast China. *Sci. Total Environ.* 461, 180–187.
- Tang, X., et al., 2010. Forecast of oil reserves and production in Daqing oilfield of China. *Energy* 35, 3097–3102.
- Tian, F., et al., 2009. Sources and seasonal variation of atmospheric polycyclic aromatic hydrocarbons in Dalian, China: factor analysis with non-negative constraints combined with local source fingerprints. *Atmos. Environ.*, 43; , pp. 2747–2753.
- Usenko, S., et al., 2007. Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to rocky mountain national park. *Environ. Sci. Technol.* 41, 7235–7241.
- Usenko, S., et al., 2010. Sources and deposition of polycyclic aromatic hydrocarbons to Western US National Parks. *Environ. Sci. Technol.* 44, 4512–4518.
- Van Noort, P.C.M., et al., 2004. Modeling maximum adsorption capacities of soot and soot-like materials for PAHs and PCBs. *Environ. Sci. Technol.* 38, 3305–3309.
- Wang, L., et al., 2009. Characterization, ecological risk assessment and source diagnostics of polycyclic aromatic hydrocarbons in water column of the Yellow River Delta, one of the most plenty biodiversity zones in the world. *J. Hazard. Mater.* 169, 460–465.
- Wang, Z., et al., 2007. Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: a case study in Dalian, China. *Chemosphere* 68, 965–971.
- Xue, L., et al., 2010. Application of CMB model for source apportionment of polycyclic aromatic hydrocarbons (PAHs) in coastal surface sediments from Rizhao offshore area, China. *Environ. Monit. Assess.* 163, 57–65.
- Yang, B., et al., 2013. Source apportionment of polycyclic aromatic hydrocarbons in soils of Huanghuai Plain, China: comparison of three receptor models. *Sci. Total Environ.* 443, 31–39.
- Yang, G.P., 2000. Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. *Environ. Pollut.* 108, 163–171.
- Yang, Z., et al., 2009. Pollution assessment and source identifications of polycyclic aromatic hydrocarbons in sediments of the Yellow River Delta, a newly born wetland in China. *Environ. Monit. Assess.* 158, 561–571.
- Yu, X.F., et al., 2010. Effects of pipeline construction on Wetland Ecosystems: Russia–China oil pipeline project (Mohe–Daqing Section). *AMBIO* 39, 447–450.
- Yuan, D.X., et al., 2001. Status of persistent organic pollutants in the sediment from several estuaries in China. *Environ. Pollut.* 114, 101–111.
- Yunker, M.B., et al., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.
- Zhang, Z.L., et al., 2004. Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. *Environ. Pollut.* 130, 249–261.