Source apportionment of polycyclic aromatic hydrocarbons in soils of wetlands in the Liao River Delta, Northeast China

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ABSTRACT

The polycyclic aromatic hydrocarbons (PAHs) of 55 surface soil samples from the wetlands in the Liao River Delta, Northeast China were measured in order to apportion their sources. The total concentrations of 16 US EPA priority PAHs and alkyl-PAHs in this region ranged 106–3148 ng g^{-1} (dry weight) (average: 550 ± 565 ng g^{-1}) and 54–5564 ng g^{-1} (average: 517 ± 838 ng g^{-1}), respectively. Based on the positive matrix factorization analysis of alkylated and parent PAHs, six sources of PAHs were identified including petroleum (23%), biomass burning (23%), air–soil exchange (18%), coal combustion (17%), traffic emission (14%) and biogenic origin (6%). The positive correlation between low molecular weight (LMW) PAHs and TOC contents could demonstrate a potential positive influence of TOC on the accumulations of LMW PAHs in soils by the air–soil exchange. The petrogenic PAHs may pose a limited harmful effect on aquatic organisms although they were abundant in the area.

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1. Introduction

A group of chemical compounds known as polycyclic aromatic hydrocarbons (PAHs) that consist of two or more fused aromatic rings have been received a great concern due to their carcinogenic and mutagenic properties. Generally, PAHs are derived mainly from anthropogenic inputs, e.g., the fossil oil discharges and incomplete combustion of organic matter such as fossil fuels, biomass and municipal wastes (Yunker et al., 2002; Mai et al., 2003). Soils are usually regarded as one of the ultimate sinks of PAHs emitted from the point sources and non-point sources, either by atmospheric deposition or direct discharges from ambient environment.

The wetlands have been known as one of the most biologically important and productive ecosystems on the earth. With the fast industrialization and urbanization of China, the fossil fuel usage and spill may have caused a severe pollution problem in the coastal wetlands in China. The wetland in the Liao River Delta (LRD) is such a case. This wetland, (121°25′–122°31′E longitude, 40°40′–41°25′N latitude), one of the biggest and well preserved wetland ecological block in the world (about 223,000 ha), is a deposition plain situated in the lower reaches of Liao River (Fig. 1). It is a low-lying basin district with extensive freshwater marsh, salt marsh, and inter-tidal zone areas. The LRD has the largest reed stands in Asia, and it is the second largest one in the world. It has been shown that the Liao River Oilfield, once the third largest oilfield in China, has an ecological risk on the delta ecosystem due to oil leaks and spills from underground tanks, pipelines and illegal disposal. Thus, the unique environmental conditions of LRD have been of a great concern due to its environmental significance, ecological sensitivity and development potentials.

There were several studies on the ecological issues (Ji et al., 2009), sewage (mainly from Liao River Oilfield) treatment (Ji et al., 2007), and the PAH contamination level of limited samples in LRD (Wang et al., 2011b). However, the quantitative source apportionment of PAHs in soils in entire LRD based on the combining data sets of alkylated and parent PAHs has been untouched. This work aims to quantitatively apportion the sources of PAHs using principal component analysis (PCA) and positive matrix factorization (PMF), and assess the level of PMF-based PAH contamination and their ecological risks in the region.

2. Materials and methods

2.1. Sampling

Fifty-five surface soil samples (0–5 cm) mainly from reed wetlands and paddy fields were collected using a grab sampler in August, 2011 (Fig. 1). Subsequently, samples were wrapped in aluminum foil and stored at −20 °C until analysis. The locations

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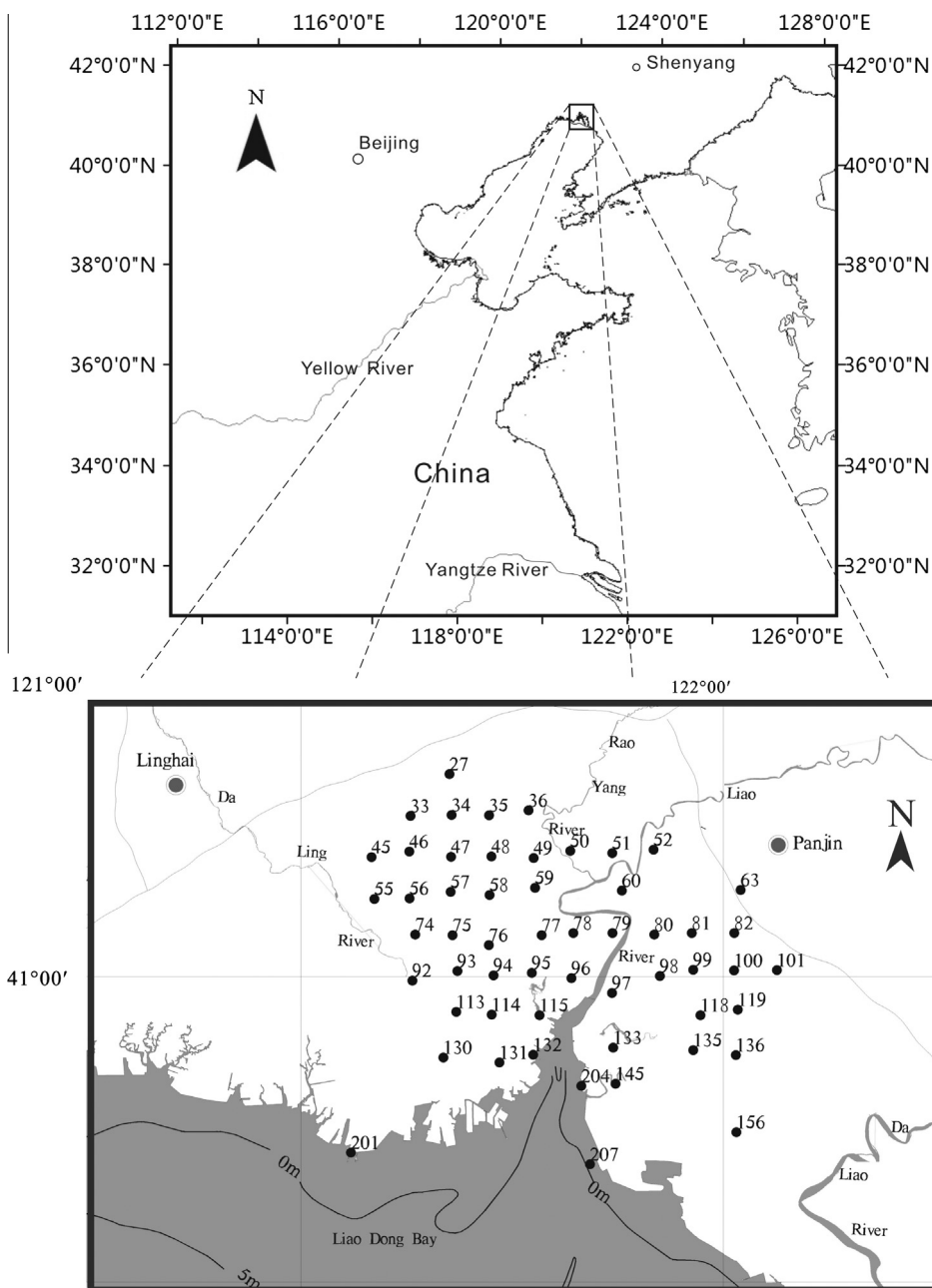
Fig. 1. Study area and the locations of the sampling sites.

of sampling sites were shown in Fig. 1. These sampling areas virtually covered the entire wetlands.

2.2. Analysis of total organic carbon (TOC)

Samples for TOC analysis were acidified with diluted HCl before analysis to remove carbonates. Contents of TOC were determined on a CHNS Vario E1 III elemental analyzer following the method described by Lin et al. (2011). Replicate analysis of one sample (n = 12) gave a precision of ±0.02 wt.% for TOC.

2.3. Extraction and PAH analysis

Analytical procedures and QA/QC essentially followed those methods reported by Guo et al. (2006). Briefly, homogenized samples were freeze-dried and ground. About 20 g of the sample was spiked with a mixture of recovery standards of three deuterated PAHs (phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}). The samples were extracted with dichloromethane in a Soxhlet extractor for 72 h, with activated copper added to remove the sulfur in the samples. The extract was concentrated and fractionated using a silica–alumina (1:1) column. PAHs were eluted using 35 ml of hexane/dichloromethane (1:1). The PAHs fraction was concentrated to 0.5 ml, and hexamethylbenzene was added as internal standard before the mixture was subjected to GC–MS analysis. An Agilent 5975C mass spectrometer interfaced to an Agilent 7890 gas chromatography was used to analyze the samples. The GC was equipped with a DB-5MS capillary column (30 m long × 0.25 mm inside diameter × 0.25 μm film thickness), with He as carrier gas. The chromatographic conditions were as follows: injector temperature, 290 °C; detector temperature, 300 °C; temperature program: 60 °C (3 min), 60–290 °C at 3 °C/min, held at

290 °C for 20 min. The 27 PAHs quantified were as follows: naphthalene (Nap), methylnaphthalene (C1-Nap), dimethylnaphthalene (C2-Nap), trimethylnaphthalene (C3-Nap), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl), methylfluorene (C1-Fl), phenanthrene (Phe), methylphenanthrene (C1-Phe), dimethylphenanthrene (C2-Phe), trimethylphenanthrene (C3-Phe), anthracene (Ant), fluoranthene (Flu), acephenanthrylene (ACP), pyrene (Pyr), methylpyrene (C1-Pyr), benz[a]anthracene (BaA), chrysene (Chr), methylchrysene (C1-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), perylene (Pery), and benzo[ghi]perylene (BghiP). Procedural blanks, standard-spiked matrix, and parallel samples were analyzed for quality assurance and control. Procedural blank samples contained no detectable amount of the target PAHs. The concentrations of 16 US EPA priority PAHs (16 PAHs) were determined by using authentic standards, while the concentrations of individual alkyl-PAH were quantified basing on its corresponding parent PAH. The average surrogate recoveries were $99 \pm 21\%$ for Phe-d$_{10}$, $63 \pm 16\%$ for Chr-d$_{12}$ and $66 \pm 22\%$ for Pery-d$_{12}$, respectively.

2.4. Statistic analysis by PMF modeling

Detailed concept and application of PMF source apportionment were described in EPA PMF 3.0 Fundamentals & User Guide (www.epa.gov/heasd/products/pmf). In brief, the PMF model is based on the following equation:

$$X_{ij} = \sum_{k=1}^{p} A_{ik}F_{kj} + R_{ij}$$

where X_{ij} is the concentration of the jth congener in the ith sample of the original data set; A_{ik} is the contribution of the kth factor to the ith sample; F_{kj} is the fraction of the kth factor arising from congener j; and R_{ij} is the residual between the measured X_{ij} and the estimated X_{ij} using p principal components.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} A_{ik}F_{kj}}{S_{ij}} \right)^2$$

where S_{ij} is the uncertainty of the jth congener in the ith sample of the original data set containing m congeners and n samples. Q is the weighted sum of squares of differences between the PMF output and the original data set. One of the objectives of PMF analysis is to minimize the Q value.

Before the analysis, undetectable value (null value) was replaced with concentration value of one half the method detection limit (Lin et al., 2011). Uncertainty file should be provided in the model as an estimate of the confidence level for each value. In this study, an uncertainty of 20% was adopted based on the results from regularly analyzing the standard reference material (Lin et al., 2011).

3. Results and discussion

3.1. Occurrence level of PAHs

The total concentrations of the 16 PAHs in LRD soil samples ranged between 106 and 3148 ng g^{-1} (dry weight) with a mean concentration of 550 ± 565 ng g^{-1} (Table S1). Compared with the other coastal wetlands in the world, the contamination level of PAHs in this area was close to those reported in the wetland sediments from Iraq marsh (590–2070 ng g^{-1} (Al-Saad and Al-Timari, 1989)), lower than those found in the wetlands of south Carolina marsh (69–37,000 ng g^{-1} (Sanger et al., 1999)), Elizabeth River wetland (1200–22,200 ng g^{-1} (Huggett et al., 1988)), but much

higher than those in the Chongming wetlands, Shanghai, East China (38.7–136.2 ng g^{-1} (Wang et al., 2012)), Yellow River Delta, North China (23.9–520.6 ng g^{-1} (Yang et al., 2009)). In this study, the concentrations of parent PAH could not be enough to reflect the real pollution status of the study area since there was a significant input from the crude oil due to the Liao River Oilfield production nearby. The total PAH (16 parent PAH species and 9 methylated PAH species) concentrations in the study area ranged between 168 and 7082 ng g^{-1} with a mean concentration of $1,060 \pm 210$ ng g^{-1}, and the alkyl-PAHs were in the range of 54–5564 ng g^{-1} with an average of 517 ± 838 ng g^{-1}, accounting for a half of the total measured PAHs. The average total concentration of alkyl-Phe was 164 ± 283 ng g^{-1}. It was reported that the alkylated homologue compounds could usually be as an indicative of crude oil contamination (Saha et al., 2009).

3.2. Source identification of PAHs using diagnostic ratios and PCA

For the 16 PAHs identified, the dominant compounds in the samples were Nap, Fl, Phe, Flu, Pyr and BbF which comprised 74% of the 16 PAH concentration. The abundance ratio of 2–3-ring to 4–6-ring PAHs could be used to distinguish the petrogenic and pyrogenic sources. Normally, petrogenic source PAHs (e.g., crude and fuel oil) contain lower molecular weight (LMW) 2–3-ring PAHs with a severe depletion of higher molecular weight (HMW) 4–6-ring PAHs and pyrogenic sources are abundant in HMW PAHs (Bouloubassi et al., 2012; Zakaria et al., 2002). Wang et al. (2011a) reported that the PAHs in the weathered petroleum residues consisted primarily of five families of PAH compounds (parent PAHs and alkylated PAHs) including Nap, Phe, dibenzothiophenes, Fl, and Chr in the sediments of Yellow River Delta, China. In this study, the range of LMW/HMW was 0.7–7.0 with a mean value of 2.1, and only one site was lower than 1 (Site 47), indicating a significant petrogenic source of PAHs in this delta. PAH isomer ratios, such as Flu/(Flu + Pyr) (m/z = 202), IP/(IP + BghiP) (m/z = 276), Phe/Ant (m/z = 178), were used as tracers to infer possible sources of PAHs (Yunker et al., 2002). These PAH isomer ratios indicated that the Phe and Ant were derived from mixture of petroleum and pyrogenic origin while HMW compounds were mainly from pyrogenic sources (Fig. 2). Overall, both PAH profiles and diagnostic ratios indicated a mixture of pyrogenic and petrogenic contributions. Furthermore, the combination of MP/Phe ratio and Phe/Ant indicated that MP was mixed sources as Phe (Fig. 2).

PCA was applied to identify the PAH sources based on the PAH data set (27 variables × 55 samples) without varimax rotation. Four factors (eigen value greater than 1) accounting for >95% of the variance in the data set were extracted by PCA, with factor loadings shown in Table S2. Fig. 3 shows that the factor score plot of the first and second principal components (PC1 and PC2) were responsible for 70% and 18% of the total variance, respectively. Factor 1 with high loading for Nap, Ac, Phe, Ant, Flu, ACP and Pry was identified as the mixed combustion emission sources (representative site 77), and factor 2 with high loading for alkyl-Nap and alkyl-Phe was suggested to be indicative of volatilization or spill of petroleum-related products (typical site 78). Factor 3 dominated by Inp, DBA and BghiP could be classified as the vehicular emission source (emblematic site 47). The factor 4 with a remarkable high loading of Pery could be believed to be from biogenic source (Guo et al., 2006). Based on the results of PCA of the four factors, the pattern of factor loading for each sample showed that the soil samples could be generally divided into three groups: Group A, the samples (sites 78 and 130) around the oil well point source characterized by the relatively high values of alkylated homologues to 16 PAHs; Group B, the samples with a comparative content of alkylated PAHs and 16 PAHs and the rest samples (Group C) with a relative high HMW PAH proportions. The largest variation in PCA
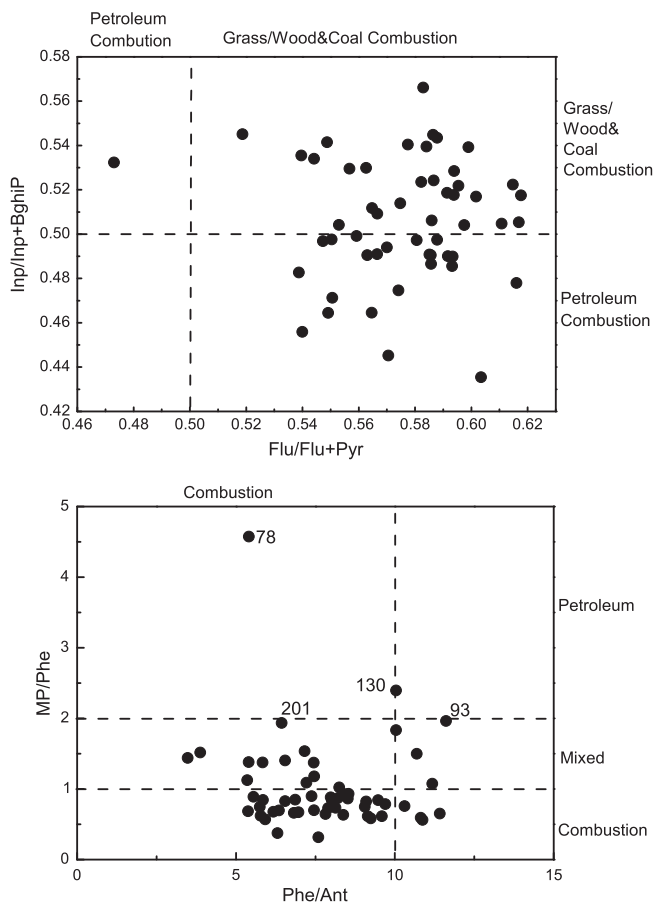
Fig. 2. PAH cross-plots for the ratios of IP/(IP + BghiP) and Flu/(Flu + Pyr); MP/Phe and Phe/Ant in the soil samples in LRD (no IP detected in site 63 and 78).

composition was observed for sites close to the point source (group A) to far away from the sites surrounding the oil well points (especially sites in group C). This composition change reflected a decrease in the proportion of the alkyl-PAHs with an increase in the percentage of the parent PAHs towards its exterior area. The clear trend between the samples from the central and periphery vortices region of wetlands suggested a diffusion process of crude oil contamination from the point sources.

3.3. Source apportionment using PMF modeling

Diagnostic ratios and PCA could not give the quantitative results of individual PAH source profiles for each factor. PMF modeling was developed in the early 1990s and it offered an advantage over PCA in that it could estimate the contribution from the specific source of individual sample without the need of providing source profiles of target compounds. Besides, PMF output nonnegative results and could provide more interpretable results well (Lin et al., 2011). In this study, 27 PAH species (alkylated homologues included) of 55 soil samples were used as the input data set. We defined DBA as a weak category since its S/N (signal/noise) ratio was less than 2. A critical process in PMF modeling is the determination of the correct number of factors. The factor number ranged three to eight was selected in order to choose a best solution which could interpret the sources of PAHs well in the soils of LRD. When the factor number for PMF was six, the value of R^2 was 0.785–0.997, indicating that the modeled concentrations fit the actual concentrations very well. Therefore, six-factor solution was adopted which gave the most stable results and easily interpretable factors

when taking the possible PAH sources into consideration. This solution produced a Q value close to the theoretical Q, indicating an appropriate 20% uncertainty in the modeling input. Factor profiles for the selected solution of PMF were shown in Fig. 4.

The first factor explained 18% of the total variance which were mainly consisting of LMW, relatively volatile PAHs, e.g., Ac, Ace, and Fl. They were considered as indicators of coking emissions in previous studies (Khalili et al., 1995; Simcik et al., 1999; Yang et al., 2002). Liaoning province is a heavy industry base in China and the coke oven used in the steel industry may explain the developed coking industry in this area. However, it should be noted that the LMW PAHs were normally far away from the sources to ultimate soil sinks, and they were usually present in the atmosphere as the gaseous phase. The gaseous PAHs could be partitioned directly from the atmosphere to soil organic matter during the air–soil exchange, and the fate and burden of those PAHs in soil was controlled by vapor pressure which was a key parameter for soil–air partitioning and depended on respective physicochemical properties (Agarwal, 2009). Thus, the original signal should be adjusted. The "source" of PAHs described by this process was the reservoir of PAHs in the soils, and similar factor or "source" was also observed in other references (Lee et al., 2004; Mai et al., 2003; Zhang et al., 2005). Thus, this factor could be mainly attributed to the air–soil exchange.

Factor 2 accounting for 23% of the total variance had a higher loading on the Nap, C1-Fl, and ACP with a moderate loading on C1-Nap, Phe, Flu, Pyr, and Chr. High content of Nap emission from straw burning were reported by Yang et al. (2006) and Lu et al. (2009). ACP was identified as tracer of wood burning, and high emissions of Phe, Flu, and Pyr were also observed in particulate matter of wood burning (Freeman and Cattell, 1990; Yunker et al., 2002). Besides, Bzdusek et al. (2004) pointed out that Flu, Pyr, and Chr were the predominant species in the fingerprint of wood burning. Therefore, this factor could be identified as a biomass burning contribution.

Factor 3 was responsible for 17% of the total variance having a high loading on Flu and Pyr with moderate loadings of C1-Fl, Phe, ACP, C1-Pyr, and BaA. Flu, Pyr as well as Phe, and BaA were usually used as markers for coal combustion (Larsen and Baker, 2003; Tian et al., 2009). This could be evidenced by nearby sources of coal burning power plants and heated residential areas.

Factor 4 was dominated by Inp, BghiP, and DBA and with moderate loading on BaP, BkF, BbF, Chr, and BaA. The BghiP was reported as an indicator of traffic-related emissions (Harrison et al., 1996; Nielsen, 1996; Simcik et al., 1999). The vehicle exhausts emissions also could highlight the content of Chr (Ye et al., 2006). Besides, BaA was classified as one of the most important species generated by gasoline and diesel combustion (Lee et al., 2004). Consequently, this factor could be attributed to the vehicle emission which explained 14% of the total variance.

Factor 5 accounting for 6% of the total variance was dominated by Pery, which was believed to be biogenic source in this study.

Factor 6 taking up 23% of the total variance was characterized by alkyl-homologues of Nap, Phe and Chr. The increase of temperature decreased the abundance of alkyl side chains in PAHs and alkyl-substituted PAHs were formed at low temperatures (~100–150 °C), while trace amounts were formed at higher temperatures (~2000 °C) (Garrigues et al., 1995). Parent PAHs were thermodynamically more stable than alkylated PAHs. Therefore, in combustion products formed at high temperatures, alkylated PAHs were depleted, whereas in petroleum, which was diagenetically generated at relatively low temperatures in the crust, they were abundant (Saha et al., 2009). Relatively high contents of more highly alkylated Phe homologues indicated a petroleum source (Steinhauer and Boehm, 1992). The maturity parameters in terms of alkyl-Nap and methyl-Phe in petroleum geochemistry were used as
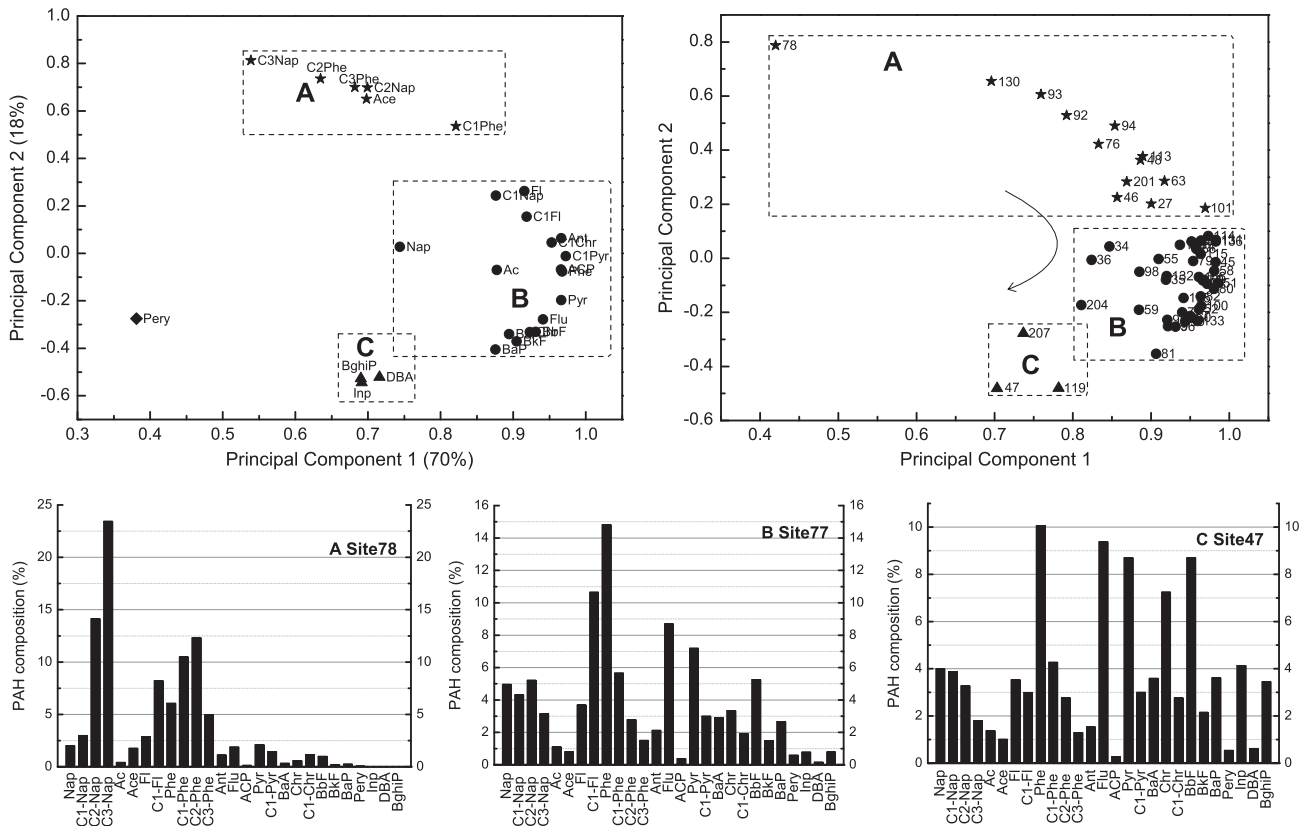
Fig. 3. Principal components analysis for PAHs of soil samples in LRD: (A) loadings, (B) sample scores and (C) PAH profiles of three representative samples including (A) site 78, (B) site 77 and (C) site 47.

diagnostic means for spilled source identification (Wang et al., 2011a). Lin et al. (2013a) found that there were strong correlations between the alkylated Chr and alkylated Nap or alkylated Phe series in this region. This indicated that those alkylated compounds had a main source. As a result, this factor could be identified as petroleum source.

The PMF results showed that the main sources of pyrogenic PAHs were biomass burning (23%), coal combustion (17%) and vehicle emissions (14%) (Fig. 5), suggesting that the release from energy consumption (53%) was an important contributor of the PAHs in LRD. Lin et al. (2013b) revealed that pyrogenic source contributed 84% of PAHs to the sediments from the Dahuofang Reservoir located in the Liao River's middle reaches. In comparison, pyrogenic PAHs accounted for relatively smaller proportion of total PAHs in the soils of the wetlands as the existence of crude oil contamination and significant soil–air exchange of volatile LMW PAHs due to high total organic carbon content residues in the soils. Liao River Oilfield now produces about 14–15 million tons, one-tenth of the national crude oil production annually. It was reported that approximately 8 million tons of petroleum could enter the soil every year during oil drilling, extraction, and accidents such as blowouts and leakage. More importantly, there was an oil production plant in the west part of the study region, thus, crude oil source contributing 23% was not surprising (Fig. 5). However, it should be noted that the large variations were occurred in contribution of petroleum with spatial distribution of sites as mentioned above. As PMF could estimate the contribution from the specific source of individual sample, sample groups identified by PCA which were further discussed here. The samples of Group A had a relatively high petroleum source contribution, especially at sites number 76, 78, 93, 94, 113, and 130 with each had a more than 30% contribution from petroleum source (40%, 71%, 54%, 32%, 38%, and

53% respectively); while Group B and Group C had only average 3.4% and 0.5% contribution from the petroleum source respectively. Besides, several paddy field samples around the oil well had a more than 10% petrogenic contribution (e.g. sites number 48, 56, 63 and 74). This could be attributed to the traffic or agricultural related leakage from the gasoline and diesel engines. Site 201 at the mouth of Daling River had 25% contribution from crude oil, which could be ascribed to the pouring out of heavy oil-polluted process water from the oil well work stations in the upper estuary.

Generally, pyrogenic PAHs were main contributors to atmospheric PAHs in China, for example, Xu et al. (2006) reported that the biomass burning, coal combustion (domestic coal and coking) and vehicular emission contributed over 90% of the total PAHs emission in the atmosphere. Consequently, the adsorption and accumulation of atmospheric PAHs by air–soil exchange and deposition from ambient environment could be important contributors to PAHs in soils. In this study, PMF results showed that the PAHs from the atmospheric reservoir pool consisting of air–soil exchange, biomass burning, coal combustion and traffic emissions accounted for 71% of total PAHs in the wetland soils. By conducting correlation analysis, a significant positive correlation between LMW PAHs and TOC content ($R^2 = 0.81$, $P < 0.01$, $n = 55$) was obtained while a relatively low R^2 (0.57, $P < 0.01$, $n = 55$) value was observed between HMW PAHs and TOC content. This could be due to the physicochemical differences among individual PAHs in that the LMW PAHs more readily tend to be accumulated in soils by air–soil exchange; while most of the HMW PAHs in soil are believed to result from atmospheric deposition. According to Lin et al. (2013a), the high TOC contents in the study area were likely caused by a combination of natural accumulation of high plant-derived organic matter because of the wet and anoxic soil conditions, and the contamination by petrochemicals from the oil industry. A positive
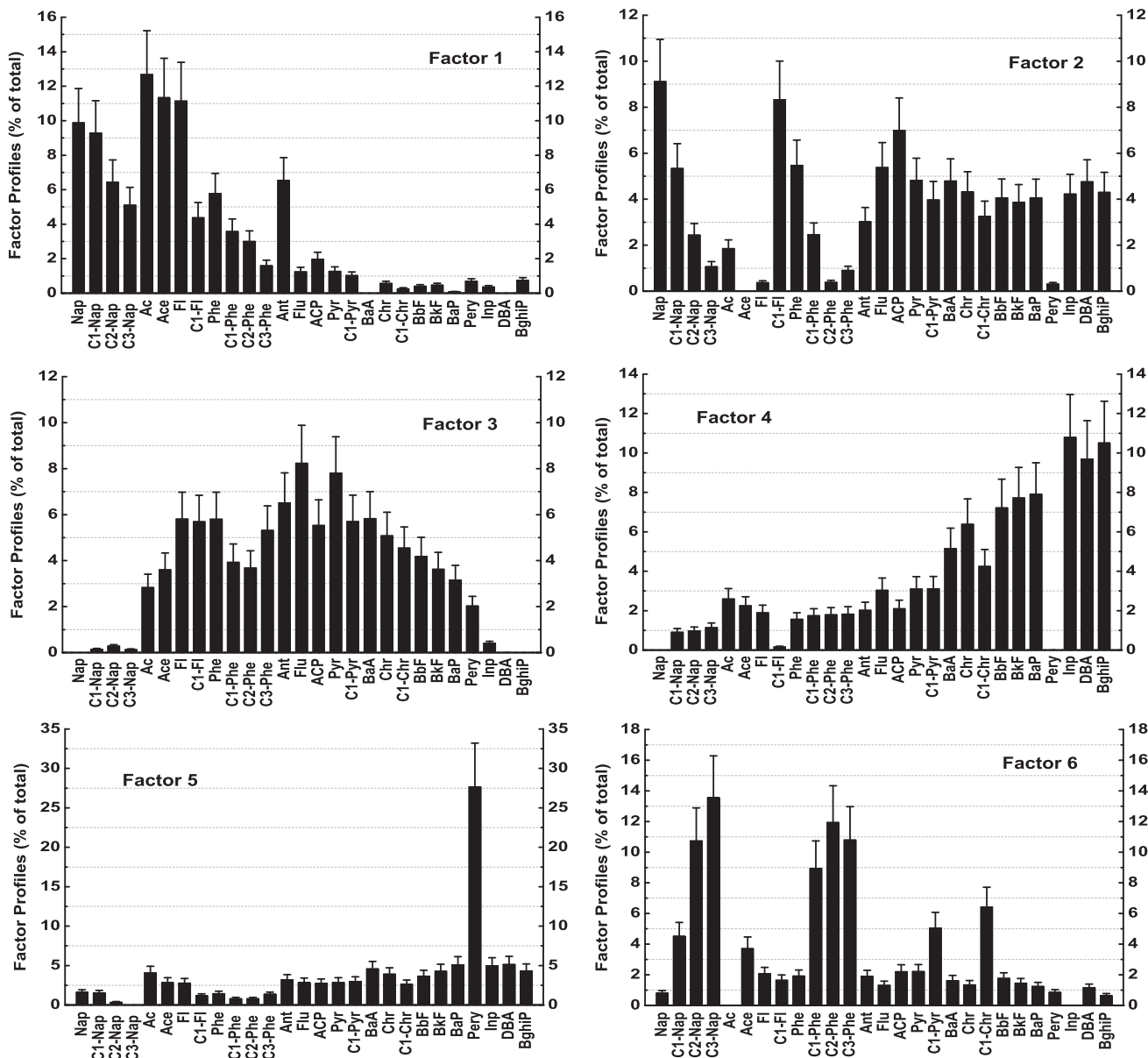
Fig. 4. Factor loadings obtained from PMF analysis for PAHs of soil samples in LRD.
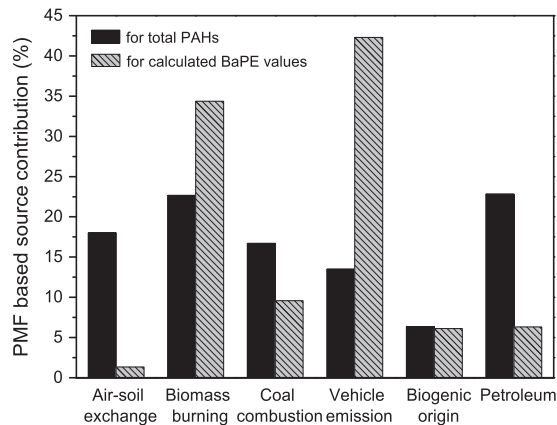

Fig. 5. PMF based average source mass contributions (%) of 6 factors for total PAHs and BaPE value for the measured PAHs in soils in LRD.

correlation between LMW PAHs and TOC contents could demonstrate a potential positive influence of TOC on the accumulations of LMW PAHs in the surface soils by the air–soil exchange process.

3.4. Risk assessment

In order to assess potential environmental impacts of PAHs on soils, PAH levels in surface soils of LRD were compared with soil quality guidelines (SQGs), which was an important tool to assess the contamination level in soils/sediments (Long et al., 1995; Long, 2006; Qiao et al., 2006). In this study, the effects range low (ERL) and effects range median (ERM) values were applied to assess the ecological toxicity of individual PAH (Table 1). According to Long et al. (1995), these values could be defined as three ranges in chemical concentrations that were anticipated to be rarely, occasionally, or frequently associated with the adverse biological effects. The comparison showed that the concentrations of all PAHs were below their respective ERM values in all samples. Fl concentrations were in the intermediate range (⩾ERL and <ERM) at most

Table 1
Sediment quality guidelines (SQG), final chronic value (FCV) of PAHs and ranges in the surface soils in LRD (SQGs are according to Long et al. (1995) and Quiroz et al. (2010); FCV are based on Ohio Environmental Protection Agency (2010)).

PAHs	SQGs		FCV	LRD		>ERL
	ERL	ERM		Ave	Max	
Nap	160	2100	385	51	426	2
Ac	44	640	452	12	57	1
Ace	16	500	491	13	124	9
Fl	19	540	538	42	202	47
Phe	240	1500	593	140	767	9
Ant	853	1100	594	18	110	0
Flu	600	5100	707	74	450	0
Pyr	665	2600	697	57	372	0
BaA	261	1600	841	18	150	0
Chr	384	2800	844	30	173	0
BbF	320	880	979	4	272	0
BkF	280	1620	981	10	78	0
BaP	430	1600	965	16	138	0
Inp	NA	NA	1115	13	75	NA
DBA	63.4	260	1123	3	15	0
BghiP	430	1600	1095	13	84	0

ERL: effects range low (ng g^{-1}); ERM: effects range median (ng g^{-1}); FCV: final chronic value (μg g^{-1}); Ave: average concentration (ng g^{-1}); Max: maximum concentration (ng g^{-1}); NA: not available.
>ERL: number of samples exceeding effects range low.

of the samples, indicating that occasionally adverse biological effects were likely to occur for Fl at most sites. The mean ERL quotients for PAHs were calculated by dividing the concentrations of the individual PAH compounds according to their respective ERL guidelines, summing these quotients and dividing them by the total number of PAH compounds. A mean ERL quotient greater than 1.0 implied that at least one species exceeded the ERL and adverse effects were predicted to occur occasionally (Long et al., 1998). Among the 55 soil samples, site 77 and site 78 had the mean ERL quotients of 1.4, implying a relatively higher potential of adverse ecological effects in this region. Forty-nine sites (89% of total) ranged between ERL quotient 0.1 and 1.0, which may pose a limited harmful effect on the aquatic organisms occasionally caused by low ring PAHs (Nap, Ace, Fl, and Phe).

It should be pointed out that the SQGs do not address the bioaccumulation issues via the fish consumption exposure pathway which should be taken into consideration. TOC plays an important role in the process of pollutants diffusion and bioaccumulation via the food chain. Site 77 and 78 had a relatively high TOC content, and the mean ERL quotients of them were both greater than 1.0; while adverse biological effect did not occur in site 36 and 59 in spite of their high TOC feature. Consequently, it is necessary to eliminate the influence of TOC on pollutant distribution and enrichment through food webs. For sediments/soils, the bioavailability of most contaminants is estimated using equilibrium partitioning sediment benchmarks (ESBs). To develop ESBs for PAHs in sediments/soils, TOC is usually used to normalize the amount of contaminant per gram of organic carbon, which is then compared against the final chronic value (FCV, Table 1) of the contaminant (Ohio Environmental Protection Agency, 2010). In this study, ∑ESB toxic unit (∑ESBTU) were found to be significantly lower than 1.0, thus adverse ecological effect could not happen (Ohio Environmental Protection Agency, 2010). In general, the two distinctive risk assessment results revealed that TOC was a positive accumulation factor for PAHs. Therefore, it should be reasonable to conduct risk assessment after correcting the concentration of PAHs by TOC.

Total concentration of potentially carcinogenic PAHs (∑CPAH) (BaA, BbF and BkF, BaP, InP and DBA) varied from 8 to 610 ng g^{-1} with a mean concentration of 90 ng g^{-1}. Similarly, the BaP equivalent (BaPE) carcinogenicity and mutagenicity was a useful index to quantitatively assess the potential health risk of PAHs, and this could be calculated according to the following equation (Liu et al., 2009).

$$BaPE = BaA \times 0.06 + BbF \times 0.07 + BkF \times 0.07 + BaP + DBA \times 0.60 + InP \times 0.08$$

The calculated BaPE values varied from 1.7 to 179.5 ng g^{-1} with an average of 23.3 ng g^{-1}. The high levels of BaPE were found at sites number 49, 59, 76, and 77, indicating that PAHs in these sites showed a relatively higher toxicity.

PMF modeling could offer or estimate the contribution from the each source of individual compounds. For example in this study, Phe was derived from air–soil exchange (24%), biomass burning (31%) and coal combustion (24%), respectively. Traffic emission was responsible for 58% and 57% of IP and BghiP, respectively. Petroleum source provided 50% of alkyl-Phe. Thus, PMF results could be used to quantitatively assess the contribution of the six sources identified above to ∑CPAH and BaPE value. The results showed that vehicular emission was the most significant contributor for both ∑CPAH and BaPE value (41% and 42%), followed by biomass burning (24% and 34%), and coal combustion (15% and 10%); while the last two contributors for BaPE value were petroleum and biogenic source, both only accounting for 6% (Fig. 5). This suggested that the biological risk in the wetlands were mainly from combustion-derived PAHs.

4. Conclusions

Higher concentrations of alkyl-PAHs were observed in the soils of LRD wetlands. The PCA results showed a clear trend between the samples from the heart and outskirts of wetlands, suggesting a diffusion process of crude oil contamination from the point sources. PMF results indicated the pyrogenic PAHs were mainly from coal combustion, biomass burning, and traffic emissions. The PAH risk assessment showed that the LMW PAHs may pose limited harmful effects on aquatic organisms occasionally due to its high TOC content; while a relatively high potential of adverse ecological effects were associated with the pyrogenic HMW PAHs. It was suggested that the correction of PAH concentration by TOC, especially in high TOC area, should be reasonable for the PAH risk assessment.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2014.01.019.

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