Characterization of PAHs in surface sediments of aquaculture farms around the Pearl River Delta

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The distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of freshwater fishponds and mariculture rafts around the Pearl River Delta (PRD) were investigated. Twenty-one sample sites were chosen, consisting of fifteen freshwater fishponds and six mariculture rafts. The total PAH ($\Sigma$PAH) concentrations measured in all the sediment samples ranged from 52.7 to 717 ng g\(^{-1}\), with mean of 184 ng g\(^{-1}\). The marine sediment samples contained higher levels of $\Sigma$PAH, high molecular weight (HMW) PAHs and carcinogenic PAHs than freshwater sediments ($p < 0.05$). Principal component analysis/multiple linear regression analysis (PCA/MLRA) indicated that the source of PAHs in freshwater sediment was mainly derived from mixed combustion of coal, wood, and vehicle emissions (66.2%). Vehicle emissions and coal combustion were the main sources (52.5 and 47.5% of $\Sigma$PAH, respectively) of PAHs contaminated in the marine sediments. The present study indicated that surface sediments of freshwater fishponds and mariculture rafts around the PRD were grossly contaminated by PAHs derived from combustion sources.

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1. Introduction

The Pearl River Delta (PRD), located in the southern part of Guangdong Province, has been the most economically dynamic region in China during the last three decades. The population increased from 50.6 million in 1979 to 81.7 million in 2007, while the regional gross domestic product (GDP) grew from US$8 billion in 1980 to more than US$390 billion in 2007 (Bureau, 2008). The region occupied about 0.4% of the total land area, but contributed over 30% of imports and exports as well as 9.8% of China’s GDP in 2004 (Bureau, 2005). The main cities (i.e. Guangzhou, Shenzhen) in the PRD, together with Hong Kong and Macao constitute one of the largest metropolitan regions in the world. The explosive increases in industrial and agricultural activities, rapid population growth, and abuse of chemicals have resulted in serious impacts on the environment. Recent studies showed that the concentrations of organic contaminants, including polycyclic aromatic hydrocarbons (PAHs), were high in the air, water, fish, vegetable, soil, river, and estuarine sediments collected from the PRD including Hong Kong and Macao (Fu et al., 2003).

PAHs are by-products of incomplete combustion of organic materials and have raised severe environmental concerns, owing to their carcinogenic properties. PAHs can enter the environment primarily through human activities such as combustion of fossil fuels, various industrial processes, biomass burning, waste incineration, and oil spills (Dickhut et al., 2000; Chang et al., 2006). In general, these sources can be classified into petrogenic, pyrogenic, and diagenetic sources (Doong and Lin, 2004; Jiang et al., 2009). Previous studies showed that PAH levels were very high in different ecological compartments of the PRD. These included soils (33.7–350 ng g\(^{-1}\), mean 144.3 ng g\(^{-1}\), Li et al., 2008), vegetables (7.0–5353 ng g\(^{-1}\), Mo et al., 2009), sediments from the Pearl River Estuary (PRE) (323–14,812 ng g\(^{-1}\), Mai et al., 2002), and coastal sediments of Macao (80–8415 ng g\(^{-1}\), Mai et al., 2003). In fact, the PRD estuary has been considered the second most polluted coastal region in China after the Gulf of Bo Hai (Nie et al., 2003).

PAHs could contaminate pond sediments through irrigation and atmospheric deposition over a long period, subsequently entering into food chains, accumulating in fish, and finally reaching humans. Earlier studies indicated that PAH concentrations of fish collected from the PRD were rather high: 1050–4260 ng g\(^{-1}\) in wild fish (Fang et al., 2009), 62–196 ng g\(^{-1}\) in freshwater fish (Kong et al., 2005), and 46.5–354 ng g\(^{-1}\) in market fish (Cheung et al., 2007), respectively. However, information concerning PAH levels in sediments of fishponds and mariculture zones of the PRD is scarce. There is only one study reported in the literature involve in the measurement of PAH
2. Materials and methods

2.1. Study area and sample collection

The sampling stations are illustrated in Fig. 1. Seventy fishpond surface sediment samples (0–10 cm) were collected from July 2008–May 2009, using a stainless steel grab sampler from twenty-one fish farms around the PRD. Among the total twenty-one locations, fifty sites were freshwater fishponds at major fish culture cities in the PRD which included Guangzhou, Shunde, Nanhai, Jiangmen, Huadu, Dongguan, and Zhongshan, and six were marine sediments beneath major mariculture rafts of Hong Kong. For each site, at least three samples were collected. All sediment samples were packed into Reynolds’66 foil immediately after collection, stored in a refrigerator (0 °C) and transported to the laboratory where they were stored at −20 °C until analysis. Detailed information of sample collection sites is shown in Table 1.

2.2. Chemical analyses

Sediment samples were freeze-dried, ground, and homogenized by passing through a stainless steel 75-mesh (0.5-mm) sieve and stored in glass containers at −20 °C until extraction. Samples (5–10 g) were extracted for 16–18 h with a mixture of acetone, dichloromethane (DCM), n-hexane (v:v:v 1:1:1, 120 ml) in a Soxhlet extractor, according to Standard Method 3540C (USEPA, 1996a). Florisil column cleanup was used for purification of the concentrated extract according to Standard Method 3620B (USEPA, 1996b). Deuterated PAHs internal standard (acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) was added into all extracts at a concentration of 320 ng g−1 prior to instrumental analysis for quantification. Concentrations of PAHs were determined with a Hewlett-Packard (HP) 6890 N gas chromatograph (GC) coupled with a HP-5973 mass selective detector (MSD) and a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column (J & W Scientific Co. Ltd., USA), using Standard Method 8270C (USEPA, 1996c). The PAH standards (AccuStandard, New Haven, CT) consisted of 16 priority pollutant PAHs: naphtalene (Nap), acenaphthylene (Ace), acenaphthene (Ace), phenanthrene (Ph), anthracene (An), fluoranthene (FIA), pyrene (Py), benz(a)anthracene (BaA), chrysene (Chry), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), dibenz(a,h)anthracene (DahA) and benzo(g,h,i)perylene (BghiP). The peaks of benzo(b)fluoranthene contamination in freshwater fishpond sediments (Kong et al., 2005). To fill this information gap, therefore the objectives of the present study were (1) to measure the concentrations and distribution characteristics of PAHs in sediments of freshwater fishponds and mariculture rafts around the PRD and (2) to identify possible sources of PAHs using isomer ratio and principal component analysis/multiple linear regression analysis (PCA/MLRA). It is hoped that the characteristics of PAHs revealed in this study could serve as a reference for the sustainable management of freshwater fishpond culture and mariculture in Hong Kong and the PRD region. Seventy surface sediment samples from twenty-one fish farms including fifteen freshwater fishponds and six mariculture rafts of Hong Kong and major cities of the PRD were collected for the measurement of the concentrations of the sixteen prioritized PAHs, as identified by the US Environmental Protection Agency (USEPA).

Table 1

Detailed information about sampling sites.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sampling site</th>
<th>No. of samples</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Huadu, Guangzhou</td>
<td>3</td>
<td>23 25.038'N</td>
<td>113 02.708'E</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>23 23.463'N</td>
<td>113 03.576'E</td>
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<tr>
<td>3</td>
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<td>6</td>
<td>22 53.843'N</td>
<td>113 01.516'E</td>
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<tr>
<td>4</td>
<td>Nanhai, Foshan</td>
<td>3</td>
<td>22 53.764'N</td>
<td>113 01.278'E</td>
</tr>
<tr>
<td>5</td>
<td>Shunde</td>
<td>3</td>
<td>23 51.318'N</td>
<td>113 09.218'E</td>
</tr>
<tr>
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<td>3</td>
<td>22 50.179'N</td>
<td>113 07.605'E</td>
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<tr>
<td>7</td>
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<td>22 51.344'N</td>
<td>113 09.241'E</td>
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<tr>
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<td>113 04.421'E</td>
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<tr>
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<td>113 04.634'E</td>
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<tr>
<td>10</td>
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<td>3</td>
<td>23 32.709'N</td>
<td>113 13.046'E</td>
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<tr>
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<td>3</td>
<td>22 42.067'N</td>
<td>113 24.342'E</td>
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<tr>
<td>12</td>
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<td>4</td>
<td>22 39.493'N</td>
<td>113 37.193'E</td>
</tr>
<tr>
<td>13</td>
<td>Dongguan</td>
<td>3</td>
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<tr>
<td>14</td>
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<tr>
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<td>22 12.700'N</td>
<td>114 04.313'E</td>
</tr>
<tr>
<td>16</td>
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<td>3</td>
<td>22 33.243'N</td>
<td>113 51.738'E</td>
</tr>
<tr>
<td>17</td>
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<td>3</td>
<td>22 21.047'N</td>
<td>114 03.366'E</td>
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<td>3</td>
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<td>114 13.481'E</td>
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<tr>
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<td>22 33.870'N</td>
<td>114 31.260'E</td>
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<tr>
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<td>22 20.483'N</td>
<td>114 19.043'E</td>
</tr>
<tr>
<td>21</td>
<td>Tung Lung Chau, Hong Kong</td>
<td>3</td>
<td>22 15.400'N</td>
<td>114 17.228'E</td>
</tr>
</tbody>
</table>

Fig. 1. Map of sampling sites. 1–15 represent sites of freshwater fishponds in the PRD, 16–21 represent sites of marine sediments beneath mariculture rafts around Hong Kong.
(Bbf) and benzok(3)fluoranthen (Bkf) were extremely close and difficult to be distinguished, therefore these two compounds were combined as one, namely B(b+k)F. The standard curve was obtained by using 0, 2, 5, 10, 20, 50, 100, 200 ng g\(^{-1}\) PAH standards. Concentrations based on individually resolved peaks (excluding Nap) were summed to obtain the total PAH concentrations (ΣPAH).

Three grams of each sediment sample was combusted in a furnace at 550 °C for 4 h to determine weight loss-on-ignition (LOI). Total organic matter (TOM) content was calculated by the empirical formula: STOM = 0.9 × LOI (van der Oost et al., 1996).

2.3. QA/QC

Using the National Institute of Standards and Technology (NIST, USA) standard reference material (SRM) 1941b as a reference, the recoveries of individual PAHs ranged from 66.2% for Nap to 105.7% for DahA. For each batch of 20 field samples, a method blank (solvent), a spiked blank (standards spiked into solvent), a sample duplicate, and a standard reference material (NIST SRM 1941b) sample were processed. The variation coefficient of PAH concentrations between duplicate samples was less than 10%. The limit of detection (LOD) using the present method was determined as the concentrations of analytes in a sample that gave rise to a peak with a signal-to-noise ratio (S/N) of 3, which ranged from 0.03 to 0.10 ng g\(^{-1}\).

Three grams of each sediment sample was combusted in a furnace at 550 °C for 4 h to determine weight loss-on-ignition (LOI). Total organic matter (TOM) content was calculated by the empirical formula: STOM = 0.9 × LOI (van der Oost et al., 1996).

2.4. Data analyses

The means of ΣPAH, LMW PAHs (low molecular weight PAHs, 2–3-ring PAHs) and HMW PAHs (high molecular weight PAHs, more than 3 rings PAHs) were compared between freshwater and marine sediments using the Wilcoxon rank sum test of two independent sets of samples. Isomer ratio of Fl/Fl+Py vs An/An+Pba (An/178) and BaA/BaA+Chry (BaA/228) vs IP/IP+BghiP were used to identify the possible sources of PAHs. The PCA/MLRA was conducted to identify the possible sources of PAHs. The significance level and KMO and Bartlett’s test of sphericity were performed to test the adaptability of PCA. Individual PAH concentrations in each sample were divided by ΣPAH to remove concentration between samples as a variable. The number of significant factors was determined during the stepwise multiple linear regression, which identified the factors that significantly improved the regression between the factors and the measured total PAH concentrations (Luo et al., 2008). The eigenvalues of components less than 1 were not investigated and assumed to be mostly a result of noise (Fang et al., 2007). PCA with varimax rotation was performed using SPSS 13.0 for Windows. MLR was conducted using PCA factor scores and total PAH concentrations as independent and dependent variables, respectively (Hartmann et al., 2004). The standardized regression coefficients were used to represent the relative contributions from various sources. To reduce the uncertainty in the source apportionment caused by spatial variation, PCA and MLR were also run for three separate zones.

3. Results

3.1. The concentrations of sediment PAHs

As shown in Tables 2 and 3, a wide range of ΣPAH concentrations was detected in the surface sediments of freshwater fishponds and mariculture rafts around the PRD, ranging from 52.7 ng g\(^{-1}\) at Huizhou to 717 ng g\(^{-1}\) at Xixiang, with a mean of 184 ng g\(^{-1}\). In all the surface sediments, the most abundant PAH compounds were HMW PAHs, contributing 53–89% of ΣPAH. The sum concentrations of seven carcinogenic PAHs (BaA, BaP, Bbf, Bkf, Chry, DahA, and IP) ranged from 10.8 to 306 ng g\(^{-1}\), with a mean of 74.2 ng g\(^{-1}\). BaP, which is considered to be the most hazardous of all (Cai et al., 2007), was detected in all of the analyzed samples (ranging from 0.87 to 62.9 ng g\(^{-1}\)) with a mean of 14.5 ng g\(^{-1}\). The maximum and minimum BaP concentrations were found in sediments collected from Tsing Yi and Huizhou, respectively.

3.2. The isomer ratios and PCA/MLRA

PAHs are produced mainly from incomplete combustion of organic materials (pyrogenic), the discharge of petroleum and its products (petrogenic), or the post-depositional transformation of biogenic precursors (diagenetic) (Atal et al., 1997). The parental PAH diagnostic ratios of An/An+Pba (An/178), FIA/FIA+Py, BaA/BaA+Chry (BaA/228), and IP/IP+BghiP may be integrated from a large number of environmental samples or single source and have been proven to be useful in PAH source identification. They have been commonly used to evaluate the relative contribution of specific types of combustion, such as vehicle exhaust, coal, coke, and wood combustion (Yunker et al., 2000; Fang et al., 2007; Sprovieri et al., 2007; Jiang et al., 2009). In the present study, the isomer ratios of An/178 vs FIA/FIA+Py and BaA/228 vs IP/IP+BghiP were calculated to identify the possible sources of PAHs. For An/178, a ratio below 0.1 indicates petrogenic origin, while a ratio at 0.1 and above indicates pyrogenic origin (Yunker et al., 2002; Liu et al., 2008). For FIA/FIA+Py and IP/IP+BghiP, the ratios below 0.4 and 0.2, respectively, suggest petrogenic origin, while the ratios at 0.5 and above indicate coal, grass and wood combustion origins (Yunker et al., 2002). In the case of BaA/228, a ratio below 0.2 is probably attributed by petrogenic origin while a ratio at and above 0.35 suggests pyrogenic origin (Yunker et al., 2002). As shown in Fig. 2A and B, the ratio of FIA/FIA+Py ranged from 0.46 to 0.54 and the ratio of An/178 ranged from 0.06 to 0.17 for all samples, while ratio of BaA/228 ranged from 0.37 to 0.58 and the ratio of IP/IP+BghiP ranged from 0.14 to 0.53.

Diagnostic ratios provide only qualitative information about the contribution of various sources with regards to PAH contaminations. Quantitative assessments were therefore conducted using PCA/MLRA to represent the total variability of the original PAH data using the minimum number of factors and PAHs which have similar sources and modes of input (Luo et al., 2008; Pies et al., 2008). For the freshwater sediments, PCA of the PAHs resulted in the first three factors (68%, 17%, and 9%) accounting for 94% of the total variability (Table 4). For each factor, the PAHs with relatively high loadings were highlighted (printed in bold). Factor 1 was heavily weighted by An, FIA, Py, BaA, Chry, Bbf, BaP, IP, DahA, BghiP, and Ace. Factor 2 contributed to 17.3% of the total variability and was heavily weighted by Fl and PhA; while factor 3 loading of Acel accounted for 9% of the total variation. For marine sediments, the loading of the first 2 factors accounted for 96.2% of the total variability (Table 4). Factor 1 had a high loading of PAHs mainly consisting of 4–6 rings, including DahA, BghiP, IP, B(b+k)F, FIA, Py, BaA, and BaP. Factor 2 had a high loading of PAH compounds including 3 ring PAH compounds, including Fl, PhA, An, and Chry.

4. Discussion

4.1. The levels and distribution of sediment PAHs

The PAH concentrations of all sediment samples were below the Dutch target value of 1,000 ng g\(^{-1}\) dry wt set by Nederland Ministry of Housing (1994). The HMW PAHs were the most abundant PAHs that indicated the major source of these HMW PAHs may be derived from anthropogenic activities (Dickhut et al., 2000). The concentrations of BaP were below the US control standard (110 ng g\(^{-1}\)) however the levels of B(b+k)F (23.3 ng g\(^{-1}\)) and Chry (11.1 ng g\(^{-1}\)) measured in the present study exceeded the US control standard levels (4 ng g\(^{-1}\) for Chry, 22 ng g\(^{-1}\) for B(b+k)F, New York State Department Conservation, 2003). This raises a serious health concern with regards to the human consumption of fish produced from these areas, because PAHs could enter food webs from the aquaculture sediments, and eventually impose human health hazard.

Among the freshwater and marine sediment samples, the highest ΣPAH level was detected in Xixiang marine sediments (717 ng g\(^{-1}\)). This sampling site is located at the Pearl River Estuary where has been heavily polluted, with ΣPAH...
concentrations ranging from 323 to 14,812 ng g⁻¹ in estuarine sediment samples [Mai et al., 2002]. In addition, it is also adjacent to the city of Shenzhen, a densely populated metropolis with rapid industrialization and socio-economic development in past 20 years. Among the freshwater fishpond sediments, site number 6 located at Shunde, a highly industrialized city near Guangzhou, contained the highest $\Sigma$PAH level (242 ng g⁻¹).

To identify whether there was any difference in PAH contamination between the marine and freshwater sediments, the Wilcoxon rank sum test of two independent sets of samples was conducted. The results revealed that the marine sediments are more enriched than those at the reference stations (Gao et al., 2005). In the present study, the average TOM in the freshwater fishpond sediments (9.64%) (Table 2). Enrichment of marine sediments are commonly enriched with high content of organic matters, derived from unconsu...
The total levels of the 15 USEPA prioritized PAHs (defined as \( \Sigma \)PAH, excluding Nap) measured in the present study were compared with other reports. In general, the levels of \( \Sigma \)PAH obtained were similar with some river sediments of the PRD (e.g. Dongjiang River: 36–539 ng g\(^{-1}\) dry wt, Liang et al., 2008) and the coastal wetland sediments in Hong Kong (180–830 ng g\(^{-1}\) dry wt, Zheng et al., 2002), but were lower than the harbor sediments (e.g. Victoria Harbor: 700–26,100 ng g\(^{-1}\) dry wt, Hong et al., 1995) and the estuarine sediments (e.g. Pearl River Estuary: 323–14,812 ng g\(^{-1}\) dry wt, Mai et al., 2002). For freshwater fishpond sediments, the \( \Sigma \)PAH concentrations obtained in the present study (52.7–242 ng g\(^{-1}\) dry wt) were similar with our previous study, regarding the freshwater fishponds of the PRD (62–196 ng g\(^{-1}\) dry wt, Kong et al., 2005). In prawn ponds near the Kolleru lake wetland of India, the maximum concentrations of PAHs (An (0.90 ng g\(^{-1}\)), FlA (0.60 ng g\(^{-1}\)), Py (0.79 ng g\(^{-1}\)), Chry (0.19 ng g\(^{-1}\)), BaP (0.18 ng g\(^{-1}\)), and BghiP (227 ng g\(^{-1}\))) were detected in the sediments (Amaraneni, 2006). Except for BghiP, the concentrations of all other individual PAHs in the PRD fish farms were much higher than that measured in the freshwater prawn ponds sediments in India. For marine aquaculture sediments, the \( \Sigma \)PAH concentrations detected in the present study (163–717 ng g\(^{-1}\) dry wt) were also higher than that detected in Daya Bay (42.5–158.2 ng g\(^{-1}\), mean of 126.2 ng g\(^{-1}\), dry wt), a key marine aquaculture area in Guangdong Province (Yan et al., 2009).

4.2. Sources apportionment by isomer ratios

PAH isomeric ratio of sediments beneath mariculture rafts was different from the freshwater one. Nearly all marine sediments were located in the area of petroleum combustion (Fig. 2A), indicating that the major source of PAHs in the surface sediments beneath mariculture rafts was derived from petroleum combustion. This claim was further supported by the data of BaA/228 > 0.2 and IP/IP+BghiP < 0.5 (Fig. 2B), which also indicated a combustion source. The present results are in line with the isomer ratio plots (A) An/178 vs FlA/FlA+Py and (B) BaA/228 vs IP/IP+BghiP.

### Table 4

| Factor Loadings of PCA based on the measured PAHs of fishpond sediments. |
|---------------------------------|------------------|------------------|
|                                | Freshwater sediments | Marine sediments |
|                                | PC1   | PC2   | PC3   | PC1   | PC2   |
| Acel                            | -0.21 | 0.28  | -0.32 | 0.93  | 0.22  |
| Ace                             | 0.89  | 0.31  | 0.00  | 0.86  | 0.22  |
| Fl                              | 0.02  | 0.94  | 0.28  | 0.15  | 0.98  |
| PhA                             | 0.35  | 0.91  | 0.01  | 0.38  | 0.92  |
| An                              | 0.82  | 0.53  | 0.01  | 0.47  | 0.88  |
| FlA                             | 0.93  | 0.33  | -0.02 | 0.72  | 0.68  |
| Py                              | 0.89  | 0.25  | 0.04  | 0.73  | 0.66  |
| BaA                             | 0.97  | 0.08  | 0.20  | 0.82  | 0.55  |
| Chry                            | 0.95  | 0.19  | -0.18 | 0.55  | 0.82  |
| BbkF                            | 0.96  | 0.09  | -0.23 | 0.84  | 0.53  |
| BaP                             | 0.95  | 0.10  | -0.13 | 0.91  | 0.37  |
| IP                              | 0.96  | 0.03  | -0.25 | 0.87  | 0.48  |
| DahA                            | 0.97  | 0.04  | -0.17 | 0.74  | 0.66  |
| BghiP                           | 0.80  | 0.25  | 0.31  | 0.71  | 0.69  |

Variance (%): 67.7 17.3 9.0 52.6 43.6

Rotation method: Varimax with Kaiser normalization.
with the former studies concerning PAHs sources apportionment of soil and aerosol in Hong Kong (Zheng et al., 1997; Zhang et al., 2006), which confirmed that PAHs in Hong Kong are mainly derived from vehicular emissions and coal combustion. For the freshwater fishpond sediments, the integrated analysis of the data, FIA/(FIA+Py) > 0.4 and An/178 < 0.1 as well as BaA/228 vs IP/IP+BgH1P, suggested mixed combustion sources. This is in line with the results of former studies in the PRD that suggested combustion sources being the major source of PAHs detected in the riverine and estuarine sediments (Luo et al., 2008) and in the soils (Li et al., 2008). However the sources of PAHs identified in freshwater fishpond sediments seemed to be more complicated than the marine ones, with mixed sources dominated by combustion. It may be due to the different sampling locations with different socio-economic and geographical variations.

4.3. Sources identification by PCA/MLRA

The PCA/MLRA was performed to determine the percentage contributions of different PAH sources for a given sediment sample (Larsen and Baker, 2003; Luo et al., 2008). For freshwater sediments, the PAH profile of factor 1 was consistent with the emission characteristic of PAH composition from coal combustion (Chen et al., 2005) and motor vehicle exhaust (Luo et al., 2008) in the PRD. It was also similar to that of biomass burning (Simonett, 2002). Therefore, this profile was possibly representative of the mixed combustion of fuel, coal, and wood. The constituents of factor 1 were further analyzed by PCA and were divided into two sub-factors. Sub-factor 1, accounting for 56.3% of factor 1 including BaA, Chry, B(b+k)F, BaP, IP, and DahA, indicated vehicle emission as the major source, whereas sub-factor 2 with Ace, An, FlA, and BghiP accounted for 33% to factor 1. The PAH profile of sub-factor 2 was consistent with the emission characteristics of PAH composition related to coal combustion (Chen et al. 2006) and biomass burning in China (Luo et al. 2008). Therefore, this sub-factor could represent the coal and biomass combustion sources. For factor 2, Fl and PhA were used as indicators for coke oven sources (Khalili et al., 1995; Simcik et al., 2003). According to the Guangdong Year Book (2007), the total coal consumption in Guangdong Province for coke oven was over 1 million tones. Therefore, factor 2 appeared to represent emission from coke oven. Factor 3 was generally a unique-component factor in which loading of AceL generated a single important factor and accounted for nearly 10% of the total variation (Zuo et al., 2007). However, there was little information about the sources of this PAH profile. Jenkins et al. (1996) indicated that AceL may be produced from biomass burning, which could explain the present results observed in the fish pond sediments. Due to the fact that fishponds are commonly located near farm lands whereby biomass burning is a common practice. As a consequence, large amounts of PAHs were generated and accumulated in fishpond sediments through water flow and atmospheric deposition.

For marine sediments beneath mariculture rafts, the profile of factor 1 is identified as typical tracers of vehicular source of PAHs (Simcik et al., 1999; Larsen and Baker, 2003). This PAH profile was in line with the PAH composition of vehicle exhaust in city tunnels around the PRD (Li et al., 2006), and USA (Dickhut et al., 2000; Hartmann et al., 2004). For Hong Kong, the profiles of FIA, PhA, Py, BaP, and BghiP were considered as markers of vehicular emissions and BaA, BaP, BbF, BghiP, and IP of gasoline-powered vehicular emissions (Guo et al., 2003). Therefore, this factor which accounted for 52.6% of the total variability appeared to be related to vehicular emissions. As to factor 2, the PAHs profile was consistent with the emission characteristics of PAH composition in coal combustion (Chen et al., 2005), and accounted for 43.8% of the total variability in marine sediment samples. Marine sediments can be regarded as good historical records for human activities (Ruiz-Fernandez and Hillaire-Marcel, 2009). The results of the PAHs source apportionment reflected that vehicle emission and coal combustion were the major sources for total PAHs. This was in line with former studies of PAH source apportionment in air, soil, and wetland sediment in Hong Kong (Zheng et al., 2002; Guo et al., 2003; Chung et al., 2007). The difference in PCA results between marine and freshwater sediments suggested different sources of PAHs, which was ascribed to different geographical locations and fish culture activities as mentioned above.

MLRA was performed to determine the percentage contributions of PAH sources. For the freshwater sediments, the regression coefficients for factors 1–2 were 0.94, 0.37, and 0.11, respectively. Thus a mean percentage contribution of 66.2% was due to the combustion of coal, wood and vehicle emission, 26.1% from coke oven, and 7.7% ascribed to Acel for biomass burning. For the marine sediments, the regression coefficients for factors 1–2 were 0.74 and 0.67. A mean percentage contribution of 52.5% was attributed to vehicle emission and exhaust, and 47.5% from coal combustion. The results of simple liner regression showed that the linear relationship between the calculated results and observed results was significant (p < 0.05). The values of $R^2$ were 0.997 (p < 0.05) and 0.997 (p < 0.05), respectively, for freshwater and marine sediments. It indicated that the PCA/MLRA method was effective for the investigation of PAH concentrations. The results of PCA/MLRA supported the conclusion derived from the analysis of isomer ratios. Both analyses indicated that fuel combustion was the main source of PAHs in the marine sediments, and that mixed combustion was the main component source for PAHs in the fishpond sediments.

5. Conclusion

The PAH levels in fishpond sediments were relative high in the PRD and were dominated by HMW PAHs indicating pyrogenic sources. Therefore, more attention needs to be paid on the safety of food produced in these aquatic systems, in particular the high levels of carcinogenic PAHs are the concern. The concentrations of $\sum_{i}^{PAH}$, HMW PAHs and carcinogenic PAHs in the marine sediments were significantly higher than in the freshwater sediments (p < 0.05) due to the different geographical positions and aquaculture activities. Isomer ratios indicated that the main source of PAHs was from combustion. The PCA/MLRA results showed that PAHs in freshwater sediments were mainly derived from mixed combustion (66.2%), while vehicle emission and coal combustion (52.5% and 47.5%, respectively) were the main sources in the marine sediments. The significant linear relationship between calculated results and observed concentrations confirmed that PCA/MLRA was effective for the identification of PAH sources in sediments around the PRD.

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