Occurrence and distribution of polycyclic aromatic hydrocarbons in reclaimed water and surface water of Tianjin, China

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Abstract

Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) are of great concern due to their persistence, bioaccumulation and toxic effects. In this work, 16 PAHs included in the US Environmental Protection Agency's (EPA) priority pollutant list were analyzed using solid-phase extraction–gas chromatography–mass spectrometry (SPE–GC–MS) with a selected ion monitoring (SIM) mode. Reclaimed water and surface water sampling was undertaken in Tianjin, northern China. Total PAH concentrations varied from 1800 to 35,000 ng/L in surface waters (main rivers, tributaries, ditches, etc.) with mean value of 14,000 ng/L and from 227 to 600 ng/L in reclaimed water with mean value of 352 ng/L, respectively. The PAH profiles were dominated by low molecular weight PAHs (two- and three-ring components) in reclaimed water samples and surface water samples. These indicated that PAHs in reclaimed water and surface water might origin from oil or sewage contamination (petrogenic input). To elucidate sources, molecular indices based on indices among phenanthrene versus anthracene and fluoranthene versus pyrene were used to evaluate the possible source (pyrogenic and petrogenic sources, respectively) of PAH contamination in reclaimed water and surface water. The collected data showed that petrogenic input was predominant at almost all the stations investigated. To discriminate pattern differences and similarities among samples, principal component analysis (PCA) was performed using a correlation matrix. PCA revealed the latent relationships among all the surface water stations investigated and confirmed our analytical results. The analysis results of the ratios and PCA in this study showed that the ratios and PCA could be applied to the surface water investigation to some extent.
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1. Introduction

Water pollution by organic compounds, many of which are known to be toxic or carcinogenic, has caused considerable and worldwide concern. Polycyclic aromatic hydrocarbons (PAHs), hydrocarbons containing two or more fused benzene rings, are a group of ubiquitous organic pollutants of great environmental concern because of the documented carcinogenicity in experimental animals and the widespread occurrence of several of its members [1]. Due to their ubiquitous occurrence, recalcitrance and suspected carcinogenicity and mutagenicity, PAHs are included in the U.S. Environmental Protection Agency (EPA) and in the European Union priority lists of pollutants. The US EPA fixed 16 parent PAHs as priority pollutants, the latest being effective from 1997 [2–6], some of which are considered to be possible or probable to human carcinogens, and the endocrine disrupting activities of PAHs have been recently reported [7,8]. Therefore, their distributions in the environment and potential human health risks have become the focus of much attention.

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Most surveys of PAH contamination in water bodies have been in conducted North America and Europe, such as in USA [9–11], Canada [12], Germany [13–16], England [17], France [18], Greece [1] and other countries [19]. Information concerning water pollution with PAHs in Asia has been reported for Korea [20], Malaysia [21] and China [22–24]. The majority of these surveys worldwide were mainly focused on seawater (coastal of offshore) and estuarine water. However, few data are available for PAH contamination of the inland waters of China, which usually act as receptors for sewage, industrial effluents and urban or rural run off [22]. As streams and rivers, lakes and ponds are frequently used for potable water supply, where water reuse is practiced, contamination of water sources is particularly undesirable [25].

PAHs are introduced into the environment mainly as a consequence of incomplete combustion originating from both, natural and anthropogenic processes. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Volcanic eruptions and forest and prairie fires are among the major natural sources of PAHs to the atmosphere. Anthropogenic sources include automobile exhaust and tire degradation, industrial emissions from catalytic cracking, air-blowing of asphalt, coking coal, domestic heating emissions from coal, oil, gas and wood, refuse incineration and biomass burning.

Over 100 PAHs have been identified and occur as complex mixtures, never as individual components. The two most common methods to measure PAHs are by HPLC with fluorescence detection [26,27] and gas chromatography with mass spectrometry detection (GC–MS) [28–30]. Although variable excitation and emission wavelengths may be chosen for detection of different PAHs by fluorescence, the method still lacks specificity and false positive results may occur. GC–MS combined with the use of stable, isotopically labeled internal standards (IS) ensures high resolution chromatography with unambiguous identification of PAHs and quantification by mass detection [28].

In China, very limited study on surface water and reclaimed water monitoring of PAHs is performed [31–35]. In order to evaluate the contamination status of PAHs in surface water and reclaimed water from Tianjin, northern China, an investigation has been performed with a quantitative SPE–GC–MS–SIM method.

2. Materials and methods

2.1. Chemicals

Standard PAHs (16 compounds specified on EPA Method 610, each at 100, 200, 1000 or 2000 µg/mL) in a mixture were obtained from Supelco (Bellefonte, PA, USA). These compounds are as follows: naphthalene (Np), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (Ph), anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Chry), benzo[a]anthracene (BaAn), benzo[b]fluoranthene (BbFl), benzo[k]fluoranthene (BkFl), benzo[a]pyrene (BaPy), indeno[1,2,3-c,d]pyrene (I[1,2,3-cd]Py), benzo[g,h,i]perylene (B[ghi]Pe) and dibenzo[a,h]anthracene (dB[ah]An). Deuterated internal standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12}) were obtained from Sigma–Aldrich. Working standards of PAHs were prepared by combining the standard mixture with the corresponding IS stock solution, respectively. These solutions were further diluted with dichloromethane to prepare calibration solutions in the range 0.01–10 ng/µL. All solvents used for sample processing and analyses (dichloromethane, ethyl acetate, acetone, hexane and methanol) were analytical grade and further distilled twice to remove impurities.

2.2. Area description and sampling

During the last quarter of the 20th century, the benefits of promoting wastewater reuse as a means of supplementing water resources have been recognized by most state legislatures in the United States as well as by the European Union. In the 1990s, increased interest in wastewater reuse in many parts of the world is occurring in response to growing pressures for high quality, dependable water supplies by agriculture, industry and the public, a situation that is exacerbated in drought years [36]. The introduction of wastewater effluent into drinking water aquifers and surface waters as a deliberately planned activity is becoming more common throughout the world. Growing populations and increasingly scarce new water sources have spurred a variety of water management measures over the last few decades, including the processing and reuse of water for many purpose. In a small but growing number of communities, these measures include the use of highly treated municipal wastewater to augment the raw water supply. This trend is motivated by need, but made possible by advances in treatment technology [37].

Due to water resource shortage and socio-economic development, China also faces serious problems of water supply and water pollution. In the future, reclaimed municipal wastewater can be an important water resource but its use must be carefully planned and regulated to prevent adverse health effects and ensure a safe water reuse. Concerns about the presence of effluent-derived microcontaminants in recycled water are raising questions about existing practices and impeding new water recycling projects.

Tianjin city is situated on the north of China. With a population of almost 4 million and the surface area of the city about 315 km^2, it is a huge commercial and industrial center. Tianjin has a warm and dry climate with distinct four seasons, sufficient sunshine and moderate rainfall. The annual mean temperature is 13.1 °C and the annual average rainfall is 500–700 mm. The Tianjin urban/industrial complex is highly polluted with the development of industry and rapid urbanization. Industry and automobiles are two major sources of pollution. On an average, the industrial corporation burned 15 million tonnes of coal per year and discharged
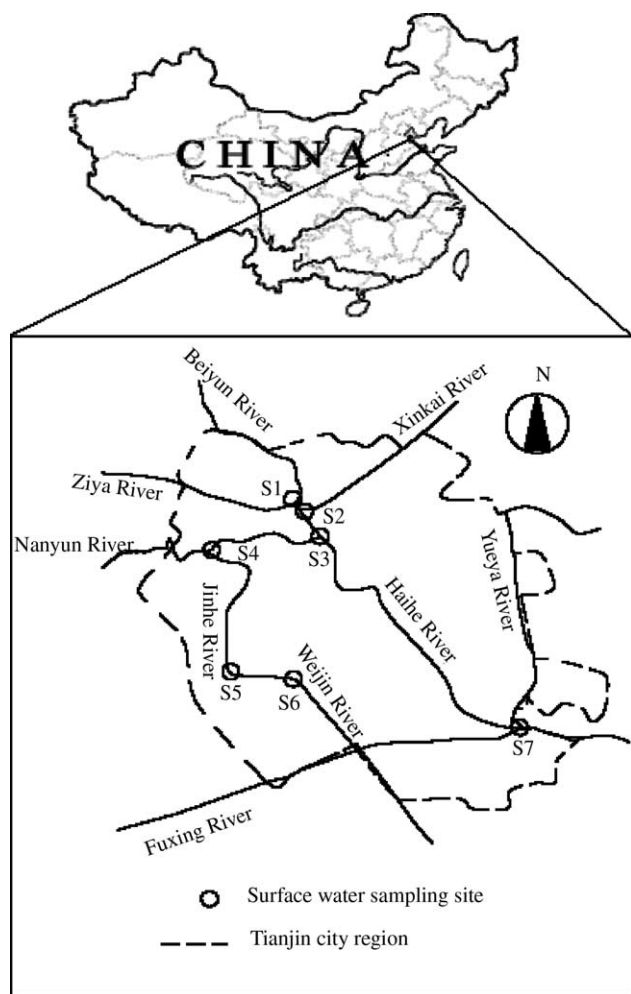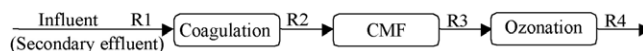
Fig. 2. Schematic of the reclaimed water plant treatment process and the points in the treatment process at which samples (R1, R2, R3 and R4) were collected for analysis.

tinuous micromembrane filtration (CMF) treatment (0.2 μm pore size), ozonation treatment (dosage of O_3: 5–6 mg/L). The treatment processes of Jizhuangzi STP includes screening, grid removal, primary sedimentation without use of chemical coagulants, conventional activated sludge treatment and secondary sedimentation.

Reclaimed water samples were taken on April 18, 2004. The treatment processes of the reclaimed water plant and the four points of collecting water samples are shown in Fig. 2. The average flow rate of the reclaimed water plant during the sampling period was 20,000 m^3/day.

2.3. Sample treatment and sample extraction

After returning to the laboratory, aliquots of the sample (1.0 L) were filtered through 0.45 μm microporous filter membrane under vacuum in order to remove algae, zooplankton and suspended particles and a measured aliquot of an internal standard mixture containing naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} was added to each sample. Then, the water samples were extracted using a solid-phase extraction (SPE) system (Zymark), following published procedures [38,39]. The SPE cartridges were first conditioned with 2×5 mL of methanol followed by 2×5 mL of deionized water. Water samples were passed through the cartridges at a flow rate of 6 mL/min under vacuum. Following extraction, the cartridges were eluted with 6 mL of ethyl acetate, which was combined with an ethyl acetate rinse (5 mL) from the extraction glassware. After water was removed from the extracts by ashed Na_2SO_4, the volume of the extracts was reduced by N_2 blow-down in a water bath (35 °C) to a final volume of 1 mL.

2.4. Sample analyses

A gas chromatography coupled to mass spectrometry (trace 2000 GC–MS, Thermo Finnigan, USA) was used for determining PAHs with selected ion monitoring (SIM). A fused-silica DB-5MS capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used. Helium with a purity of 99.999% was used as the carrier gas at a constant flow of 1.0 mL/min. A 2 μL volume was injected by applying a hot splitless injection technique. The temperature program of the oven was started at 70 °C (for 1 min) and increased at a rate 10 °C/min to 300 °C and was held for 10 min. The mass spectrometer was operated in the electronic impact (EI) mode with an ion source at 200 °C and the electron impact energy was set at 70 eV. Identification of the PAH compounds was performed by comparing GC retention time with those of authentic standards. Quantification of individual compounds

Fig. 1. Sampling sites of surface water in Tianjin, China.

180 million tonnes of wastewater. Rivers in the Tianjin area are severely polluted with high loads of persistent organic pollutants. According to the Reports of Tianjin Environmental Quality in 2002, the sewage discharge was 497 million tonnes including 220 million tonnes industrial effluents and 277 million tonnes domestic wastewater. Industrial effluent was treated completely by sewage treatment plants (STP); the total treatment ratio of sewage was up to 50%. There are mainly nine rivers in Tianjin: Haihe River, Beiyun River, Ziya River, Nanyun River, Xinkai River, Jinhe River, Weijin River, Yueya River and Fuxing River. The surface water samples were collected (0–10 cm) by using cylinder samplers aboard a chartered vessel during axial surveys on April 19, 2004, and the seven locations of sampling site of surface water are shown in Fig. 1.

Reclaimed water samples were collected at each stage of treatment processes of a reclaimed water plant in Tianjin, China. The reclaimed water plant receives secondary (activated sludge) treated wastewater (mainly domestic) derived from Jizhuangzi Sewage Treatment Plant, and puts it through a tertiary treatment train: coagulation–flocculation treatment (polyaluminum chloride (PAC) as coagulant: 15 mg/L), con-

was based on comparison of peak areas with those of the recovery standards.

Before sample analysis, relevant standards were analyzed to check column performance, peak height and resolution, and the limits of detection (LOD). With each set of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Compounds were identified mainly by their retention times.

2.5. Analytical quality controls

All data were subject to strict quality control procedures. For PAHs, deuterated IS were used to compensate for losses involved in the sample extraction and work-up. The four IS in water were determined with good precision, and their recoveries ranged from 70 ± 5 to $93 \pm 10\%$ for water samples. Detection limits derived from replicate procedural blanks were approximately 1 ng/L. GC/MS data were acquired and processed by using Xcalibur software.

3. Results and discussion

3.1. PAH concentrations and compositional patterns

This report presents results from analyses of parent PAHs in Tianjin, China. The concentration ranges of individual and total PAHs in reclaimed water and surface water are shown in Table 1.

The total PAH concentrations ranged from 227 to 601 ng/L in reclaimed waters with mean value of 352 ng/L and from 1765 to 35,210 ng/L in surface waters (main rivers, tributaries, ditches, etc.) with mean value of 14,066 ng/L, re-
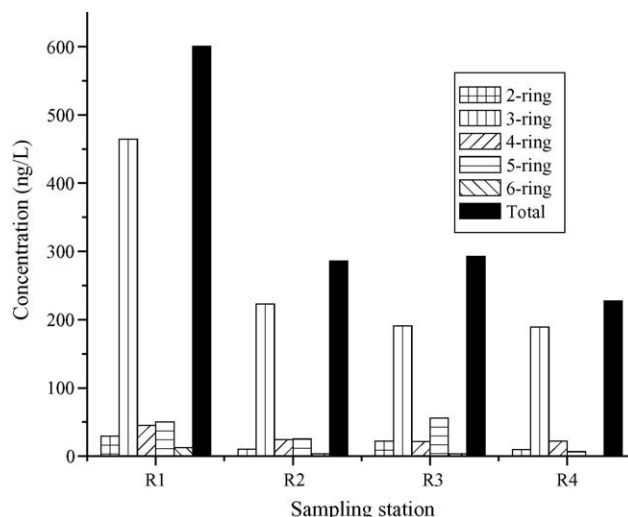

Fig. 3. Concentrations of two-, three-, four-, five-, six-ring and total PAHs in the reclaimed water column of Tianjin. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.

spectively (Figs. 3 and 4). The highest concentration of surface water was observed at station S3, which is situated in the mouth where Nanyun River merges into the main river—Haihe River. With increasingly intense urban and industrial development in Tianjin, the amount of PAHs detected there is obviously related to urban runoffs, sewage discharges, vehicular exhaust emission and intense shipping activities that were observed during the sampling. Similarly, high concentration (>30,000 ng/L) was also found at station S7, which

Table 1
Range of concentrations (ng/L) of parent PAHs in reclaimed water and surface water from Tianjin, China

Water sample	Reclaimed water			Surface water		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
Naphthalene	10	29	18	294	32432	11719
Acenaphthylene	31	100	54	169	915	498
Acenaphthene	9	36	18	<1	<1	–
Fluorene	66	171	94	303	821	496
Phenanthrene	78	157	100	531	1420	887
Anthracene	<1	<1	–	<1	<1	<1
Fluoranthene	5	20	10	34	120	64
Pyrene	11	19	14	66	306	134
Benzo[a]anthracene	<1	<1	–	<1	<1	–
Chrysene	1	6	4	6	70	19
Benzo[b + k]fluoranthene	1	16	–	16	591	195
Benzo[a]pyrene	2	12	9	41	390	161
Indeno[1,2,3-c,d]pyrene	<1	9	6	<1	22	11
Dibenzo[a,h]anthracene	<1	12	5	4	22	12
Benzo[g,h,i]perylene	<1	<1	–	<1	<1	–
$\sum$PAH	226	601	352	1765	35210	14066
$\sum$PAH$_{CARC}$	4	43	28	50	695	249

$\sum$PAH$_{CARC}$: benzo[a]anthracene + benzo[b]fluoranthene + benzo[k]fluoranthene + benzo[a]pyrene + indeno[1,2,3-c,d]pyrene + dibenzo[a,h]anthracene (IARC probable and possible human carcinogens).
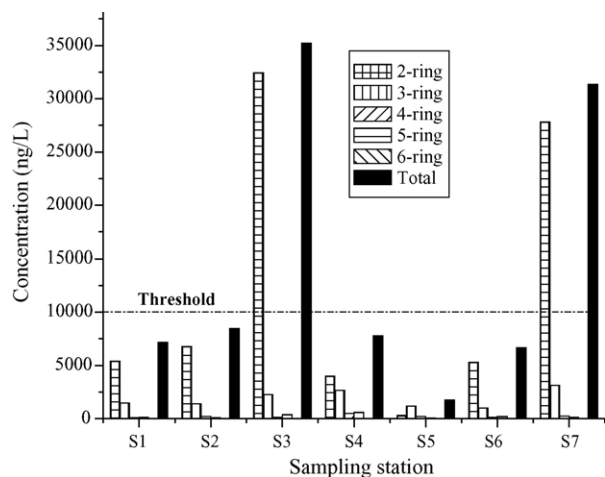
Fig. 4. Concentrations of two-, three-, four-, five-, six-ring and total PAHs in the surface water column of Tianjin. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.

again was at the mouth where both Yueya River and Fuxing River merge into Haihe River, might be associated with the accumulation of sewage discharge. In addition, there were a lot of industries (e.g. chemical, power) around the study area, many of which were discharging waste effluents; hence, there were many non-point sources in the area, contributing to the very high concentrations of PAHs detected. The highest PAH concentration of reclaimed water was observed at station R1, from which the secondary effluent of municipal sewage treatment plant was introduced into recycled water treatment processes (coagulation–flocculation unit, continuous microfiltration unit and ozonation unit) for advanced treatment. As shown in Fig. 3, the total PAH concentrations of reclaimed water were decreased along the treatment train and a total PAH concentration decrease of more than 50% was obtained.

The compositional pattern of PAH by ring size along the contamination gradient is shown in Fig. 5. It is clear that two- and three-ring PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) are the most abundant PAHs, which on average occupied 69 and 24% of total PAHs in surface water and 5 and 76% of total PAHs in reclaimed water. In addition, four- and five-ring PAHs on average occupied 4 and 3% of total PAHs in surface water and 8 and 10% of total PAHs in reclaimed water, respectively. Naphthalene is one of the most frequently detected compounds in almost all surface water samples (except S5, which was collected close to hospital). Higher proportions (about 90% of naphthalene) were observed at stations S3 and S7. However, three-ring PAHs predominated over other PAHs in reclaimed water samples.
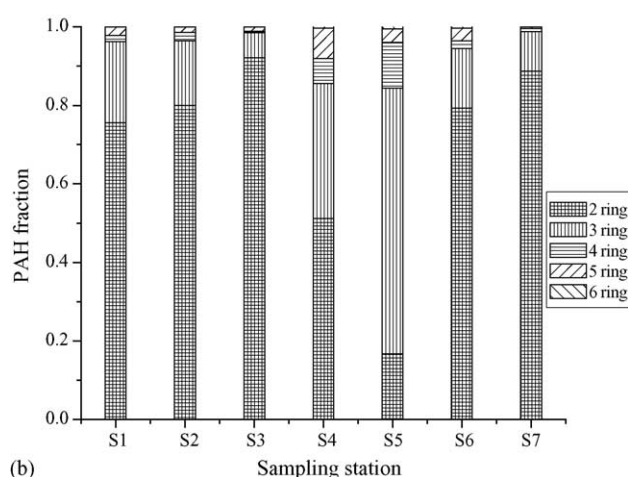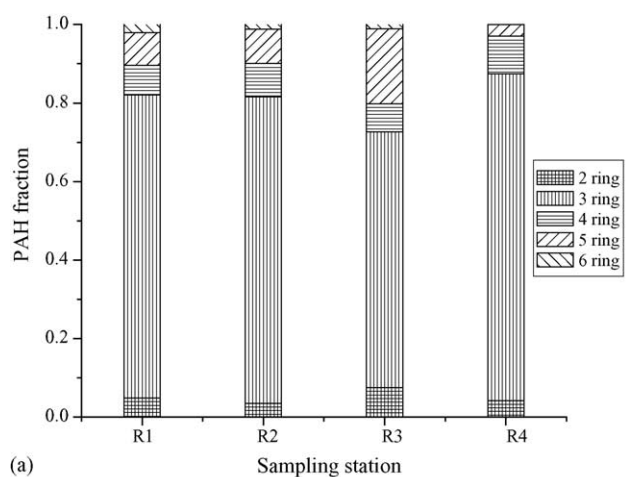

Fig. 5. Composition pattern of parent PAHs in: (a) reclaimed water and (b) surface water of Tianjin. Two-ring PAHs include naphthalene; three-ring PAHs include acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene; four-ring PAHs include fluoranthene, pyrene, benzo[a]anthracene and chrysene; five-ring PAHs include benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; six-ring PAHs include indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene.

Although PAHs do not show extremely high acute toxicity towards aquatic organisms, the low molecular mass PAHs tend to be more toxic than the high molecular mass PAHs [40]. The concentrations of PAHs in waters exceeding 10,000 ng/L suggested that the water was heavily contaminated by PAHs [40]. Lethal concentration (LC_{50}) as low as 10,000 ng/L has been reported for various organisms including *mysid* [41]. It is clear from Fig. 4 that two samples (S3 and S7) had total PAH concentrations exceeding this LC_{50} value, suggesting that certain organisms in the area might have suffered acute toxicity.

Municipal wastewaters are main sources of PAHs in surface waters. Concentrations of total PAHs in raw municipal wastewaters have been found to vary significantly, depending on the amount of industrial effluents possibly co-treated with domestic wastewaters. Treated wastewaters usually contain

Table 2
Summary of total parent PAH concentration (ng/L) in surface water from various sites in the world and China

Location	Date of sampling	N^a	n^b	Range (ng/L)	Reference
Northern Greece	July–August 1996	8	16	184–856	[1]
Aegean Sea (eastern Mediterranean)			14	0.113–0.489	[14]
Baltic Sea	August 1995		14	0.300–0.594	[14]
Danube Estuary	August 1995	2	14	0.183–0.214	[14]
Seawater around England and Wales	June 1993–July 1995	63	15	<1–24821	[17]
Jiulong River Estuary, China	June 1999	19	16	6960–26920	[23]
Daya Bay, China	August 1999	14	16	4228–29325	[24]
Tonghui River, Beijing, China	April 2002	16	16	192.9–2651	[31]
Hangzhou rivers, China	December 2002	17	10	989–9663	[32]
Hangzhou rivers, China	July and November 1999–2002	17	10	34400–67700 (July); 4700–15300 (November)	[33]
Minjiang River Estuary, China	November 1999	13	16	9890–474000	[34]
Tianjin rivers, China		30	16	45.81–1272	[35]
Tianjin rivers, China	April 2004	7	16	1765–35210	This study

    [a] N, number of samples analysed.
    [b] n, number of compounds analyzed.

PAHs at much lower concentrations due to their removal by adsorption on particles, biodegradation or volatilization [25]. Just as Fig. 3 showed, the total PAH concentrations of all reclaimed samples were under of 601 ng/L ($\ll$the threshold 10,000 ng/L). In addition, it can be seen from Figs. 3 and 4 that total PAH concentrations of domestic wastewater after reclamation treatment are one to two orders of magnitude lower than in the rivers.

The total PAH concentrations in water found in the study area are four to five orders of magnitude higher than those found in waters in Danube Estuary [14], Aegean [14] and Baltic Sea [14] (Table 2). Concentrations were also higher than total PAH levels detected in northern Greece [1] and Tonghui River, Beijing, China [31], and Hangzhou rivers, China [32]. Interestingly, similarly high levels were also found in Jiulong River Estuary, China [23], Daya Bay, China [24], Hangzhou rivers, China [33] and some marine sites around England [17]. In addition, it could be seen from Table 2 that the total PAH concentrations of Minjiang River Estuary were higher than those obtained from our study. However, it was strange that the total PAH concentrations of rivers in Tianjin reported by Shia et al. [35] were one to two orders of magnitude lower than our results. As there have been rare studies, it is difficult to assess the temporal variation of PAHs in rivers of Tianjin.

3.2. Sources of PAHs

3.2.1. Ratio analysis

Parent PAHs have both natural sources (oil seeps, bitumen, coal, plant debris and forest and prairie fires) and anthropogenic sources (fossil fuels and combustion). Since the PAH compositions of the two sources overlap, the significance of anthropogenic PAHs in the environment must be evaluated against a dynamic background of natural PAHs. However, in many areas affected by human activities, natural sources are overwhelmed by anthropogenic sources except perylene. Anthropogenic sources include both high and low temperature combustion of fossil fuels and the direct release

of oil and its products. For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable, "kinetic" PAH isomers relative to the more stable, "thermodynamic" isomers and the stability of the lighter PAH isomers has been calculated to support such interpretations [42].

The ratios of Ph/An within the two-ring PAH group and Fl/Py within four-ring PAH group were used to differentiate PAHs of different origins. Ph is more thermochemically stable than An, and therefore at low maturation temperatures much higher molar fraction of Ph is produced compared to An. These molar ratios of Ph/An at petroleum maturation temperatures lead to higher values. These can be as high as 50 at 373 K. To the contrary, high temperature processes (800–1000 K), such as the incomplete combustion of organic materials (coal burning, wood burning, vehicular exhaust emission, waste crankcase oil and asphalt roofing material), are characterized by low Ph/An ratio value (4–10). Thus, Ph/An > 15 for petrogenic sources and Ph/An < 10 for pyrolytic sources. Due to the wide range of values for this index found in the literature, values between 10 and 15 are considered indeterminate relative to source [29,43].

Likewise, discrimination also occurs in the fluoranthene/pyrene (Fl/Py) ratio. In petroleum-derived PAHs, pyrene is more abundant than fluoranthene. At higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. As such, a value grater than 1 is classically related to pyrogenic sources [44]. Hence, in combination, a Ph/An ratio value <10 and Fl/Py ratio >1 indicates that PAHs originate from pyrogenic sources [29]. The ratios of Ph/An, Fl/Py in surface water and reclaimed water were calculated and are listed in Table 3. As shown in Table 3, almost all the ratios of Ph/An > 15 and Fl/Py < 1 tended to indicate that PAHs were coming from petrogenic sources.

3.2.2. Principal component analysis

In order to explore more latent relationships among all the stations investigated, the principal component analysis (PCA) was applied to the results obtained.

Table 3
Ratios of phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py) in reclaimed water samples and surface water samples from Tianjin, China

Station	Ph/An	Fl/Py
R1	>157	1.09
R2	>83	0.78
R3	>78	0.41
R4	>83	0.53
S1	>629	0.30
S2	>1250	0.39
S3	>531	0.52
S4	>1419	0.46
S5	>904	0.58
S6	>745	0.93
S7	>731	0.52

PCA reduces the number of variables in the original data set into fewer factors (or principal components) without significant loss in the total variance of the data. The loading that each variable in the original data contributes to the principal components enables grouping of data with similar behaviors [45,46].

Distribution of the normalized PAHs data of surface water among the primary and secondary principal component axes is shown in Fig. 6. The two principal components selected are able to account for 99.89% of total variance of the original data. The first and second PCs in surface water represented 87.37 and 12.52% of the variability, respectively. There are three groups discriminated on the factor loading plot (Fig. 6a). Group A clusters samples of stations 3 and 7; group B, samples collected from stations 1, 2, 4 and 6; group C only contains one sample, which collected from the station 5. The discrimination in three groups was confirmed by hierarchical clustering analysis (HCA), using complete linkage and Euclidean distances (Fig. 7).

From Fig. 2, we can see both the samples of stations 3 and 7 collected from the Haihe River, probably contain similar contaminants, so they constitute the group A. As shown in Fig. 6a, group A is characterized by the negative axes of both principal components; on the other hand, from Fig. 6b, this quadrant is dominated by naphthalene. This indicated that naphthalene contributed significantly to the samples in group A, and the contribution of naphthalene over the contribution of the other PAHs notability.

The samples of stations 1, 2 and 6 were collected from the places nearby different interchanges, so they cluster together. However, the characteristic of the sample from station 4, where Jinhe River merges into Nanyun River, is similar to that of those samples in group B. The similarity may be caused by their complicated origins of contamination. Nevertheless, the sample of station 4 has some characteristics different from that of the other samples in group B. Contrary to the other samples in group B, the sample of station 4 is characterized by positive loading in the second principal component, so it got more contribution from the acenaphthylene, fluorine, phenanthrene, pyrene than the other samples.
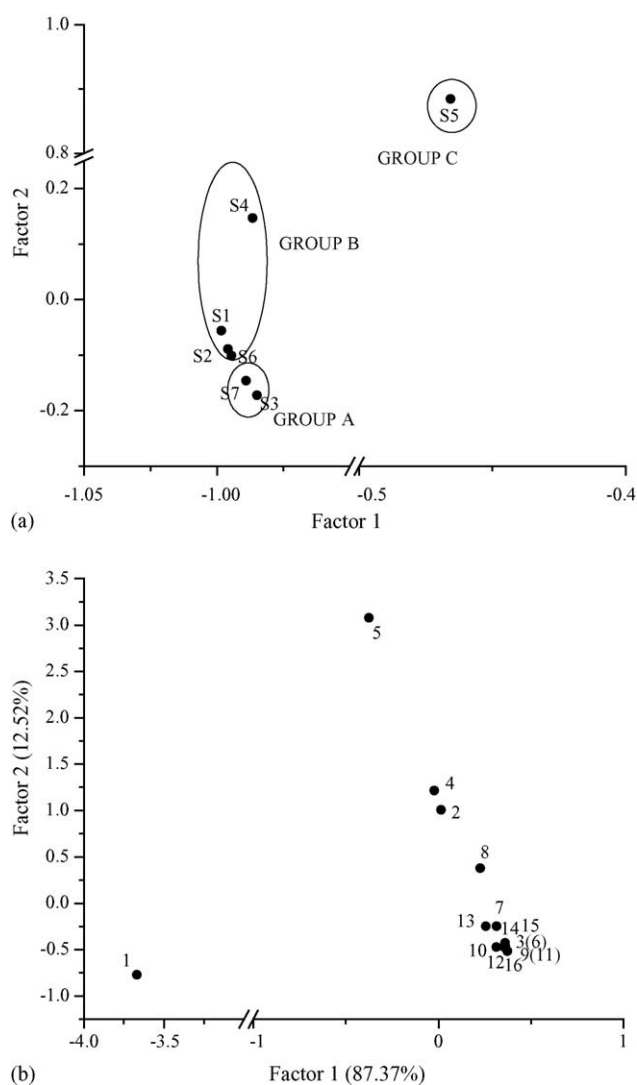

Fig. 6. PCA showing the pattern of PAHs in the surface water: (a) factor loading plot and (b) factor score plot—(1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene, (9) benzo[a]anthracene, (10) chrysene, (11) benzo[b]fluoranthene, (12) benzo[k]fluoranthene, (13) benzo[a]pyrene, (14) dibenzo[a,h]anthracene, (15) indeno[1,2,3-c,d]pyrene and (16) benzo[g,h,i]perylene.

The samples in group B got the contribution from naphthalene mostly among all the PAHs. However, compared with group A, the samples in group B gave a relatively low contribution to factor 2, so they got less contribution from naphthalene than group A. This conclusion can be confirmed by Fig. 4.

The sample of station 5 was collected from Jinhe River, so the characteristic of this sample may be different from the others. As shown in Fig. 6a, the station 5 has a high value of factor 2 and it can be assumed that it is able to get the contribution from something with a high score value of factor 2, which seems to be the phenanthrene, gave the mostly contribution among these PAHs. And the acenaphthylene, fluorene, pyrene also get the positive value, from
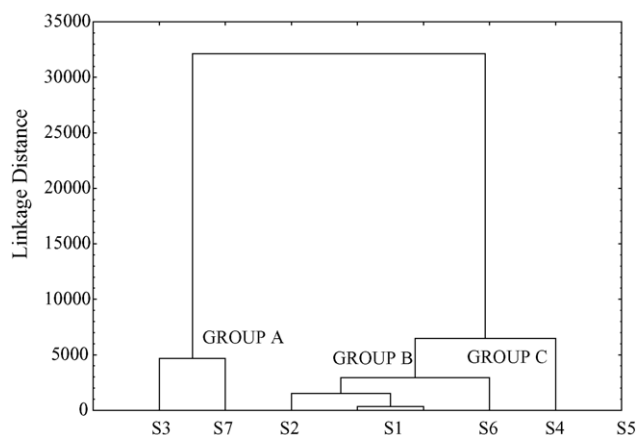
Fig. 7. Hierarchical clustering of the surface water stations (complete linkage, Euclidean distances).

Fig. 6b, so they gave a relatively high contribution to the station 5. Because the station 5 is the only one occupies the region defined by the positive axe of the primary principal component, it got the lowest contribution from the naphthalene.

4. Conclusions

The two PAH profiles of water samples revealed that the dominant PAHs were low molecular weight (two- and three-ring) PAHs in reclaimed water and surface water of Tianjin, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene.

PAH profile in reclaimed water is different from that in surface water. The PAH total concentrations of reclaimed water are usually one to two orders of magnitude lower than those of the river because the PAHs were removed by advanced treatment processes and the PAHs originated from domestic wastewater.

The PAHs in reclaimed water samples and surface water samples originated mainly from petrogenic inputs based on the high proportion of two-ring (naphthalene) and three-ring PAHs. Although the calculated ratios of Ph/An, Fl/Py and principal component analysis are usually performed to analyze the origin of PAHs in sediments, we attempted to apply the ratios and PCA to the surface water in this study. The analysis results showed that the ratios and PCA could be applied to the surface water investigation to some extent.

Oil spill and leakage from boats and ships, vehicular exhaust emission, discharge from municipal and industrial wastewater and runoff might be important sources. These indicate that surface water received anthropogenic PAHs from different sources and although specific sources are known to be responsible for the presence of PAHs in surface waters, their occurrence cannot always be related to a particular source.

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