

Distribution, sources, and potential toxicological significance of PAHs in drinking water sources within the Pearl River Delta†

Taicheng An,^{*a} Meng Qiao,^{ab} Guiying Li,^a Hongwei Sun,^{ab} Xiangying Zeng^a and Jiamo Fu^a

Received 5th October 2010, Accepted 16th March 2011

DOI: 10.1039/c0em00542h

The Pearl River Delta (PRD) region is one of the most population-dense areas in China. The safety of its drinking source water is essential to human health. Polycyclic aromatic hydrocarbons (PAHs) have attracted attention from the scientific community and the general public due to their toxicity and wide distribution in the global environment. In this work, PAHs pollution levels from the drinking source water in nine main cities within the PRD were investigated. $\sum 15$ PAHs concentrations during the wet season varied from 32.0 to 754.8 ng L⁻¹ in the dissolved phase, and from 13.4 to 3017.8 ng L⁻¹ in the particulate phase. During the dry season, dissolved PAHs ranged from 48.1 to 113.6 ng L⁻¹, and particulate PAHs from 8.6 to 69.6 ng L⁻¹. Overall, $\sum 15$ PAHs concentrations were extremely high in the XC and ZHQ stations during the wet season in 2008 and 2009. In most sites, PAHs originated from mixed sources. Hazard ratios based on non-cancerous and cancerous risks were extremely higher in XC compared with the others during the wet season, though they were much less than 1. Nevertheless, risks caused by the combined toxicity of $\sum 15$ PAHs and other organics should be seriously considered. PAHs toxic equivalent quantities ranged from 0.508 to 177.077 ng L⁻¹.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs) that ubiquitously exist in the global environment,¹ especially in industrialized areas.² They are produced from a large number of sources, including the incomplete combustion of wood, coal, petroleum, and some organic polymers, as well as the discharges from motor vehicles, refined-oil production plants, and petroleum leakages.^{3–8} Over 200 PAH congeners have been detected throughout the world, sixteen of

which were identified as the priority environment pollutants by the United States Environmental Protection Agency (USEPA). Most PAHs have been found to possess teratogenic, mutagenic, and particular carcinogenic properties.⁹ As they are lipophilic, PAHs tend to accumulate in the fatty tissues of animals, and may pose risks to human health through food chains.¹⁰

The Pearl River Delta (PRD) region is situated in Guangdong Province in the southern part of China. Since China's reform and opening up, this area has experienced rapid industrial and economic development. The pollution of PAHs from industrial factories and automobile exhaust has unavoidably increased in recent years. New PAHs can input to the water systems due to a higher run off and a higher load of fresh terrestrial and atmospheric organic matter. Due to their potential risk to human health, much attention has been paid to the pollution levels of PAHs in the water environment. There are four main rivers, the Zhujiang, Beijiang, Dongjiang, and Xijiang in the PRD. The Beijiang and Xijiang converge into Zhujiang in Sanshui, while

^aState Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Resources Utilization and Protection, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China. E-mail: antc99@gig.ac.cn; Fax: +0086-20-85290706; Tel: +0086-20-85291501

^bGraduate School of Chinese Academy of Sciences, Beijing, 100049, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0em00542h

Environmental impact

The Pearl River Delta (PRD) region is one of the most population-dense areas in China. PAHs have attracted attention from both the scientific and general communities due to their toxicity and wide pollution. To date, however, no work has reported the PAH pollution level in the source water within this area. Furthermore, few studies have been carried out regarding potential health risks through water consumption. Hence, this work mainly focuses on the investigation the distribution, sources, and potential risk to human health of PAHs in drinking source waters within the PRD. All these collected information is necessary for the control and management of these kind POPs.

Dongjiang runs directly into the Pearl River Estuary. Some investigations have examined the pollution levels of PAHs in this area. Deng *et al.*¹¹ reported that the concentration of PAHs ranged from 21.7 to 138.0 ng L⁻¹ during the years 2005 and 2006 in Xijiang. PAH concentrations in the water columns were between 987.1 and 2878.5 ng L⁻¹ in Zhujiang, and between 944.0 and 6654.6 ng L⁻¹ at the Macao Harbor.¹² To date, however, no work has reported the PAH pollution level in the drinking source water within this area, although it is very significant in health considerations. The recognition of PAH sources is also necessary for the control and management of these POPs.

Due to the high toxicity of PAHs, it is further necessary to assess the safety of the drinking source water caused by PAH contaminants within the PRD region. Nevertheless, few studies have been carried out regarding potential health risks through water consumption,¹³ although the drinking exposure is the direct and reasonable pathway for drinking water. However, we can only obtain the hazard ratios of five PAHs targets to assess the risk of drinking water with this method, due to the limited availability of benchmark concentrations of PAHs recommended by the USEPA, which may underestimate the real risk of the drinking water. Therefore, the classic method by the toxic equivalence factors (TEFs) was also employed to fully assess the potential toxicity of total PAHs because the TEFs of 16 individual congeners are all available in the references.^{14,15}

The aim of this study was to investigate the distribution and sources of the EPA priority PAHs in fifteen drinking water sources (the special source part of the rivers and reservoir supplying for population drinking) from the nine cities within the Pearl River Delta region. To gain further insight into whether the drinking water is safe or not to drink by the people, the toxicity from the target PAHs in the drinking water was evaluated with both through water consumption and TEFs method in this work.

2. Materials and Methods

2.1. Study site and sample collection

Fifteen sampling sites were selected from the nine cities within the PRD region as indicated by our previous study on organochlorine pesticides.¹³ Zhujiang mainly supplies water to the main part of Guangzhou, Beijiang supplies water to Foshan and a small part of Guangzhou, Dongjiang supplies water to Huizhou, Dongguan, Shenzhen, and Hong Kong, and Xijiang supplies water to Zhaoqing, Jiangmen, Zhongshan, and Zhuhai. Using pre-cleaned glass bottles, at each sampling site, from both the sides and middle of the river, 20 L of water was collected respectively and then combined as 60 L water for later analysis during the wet (from April to July, 2008) and dry seasons (from December 2008 to February 2009). After returning to the laboratory, the samples were added with sodium azide and stored at 4 °C. Suspended particular materials (SPMs) were collected by filtering the samples through 0.7 µm glass fiber filters (GFFs, Whatman), while the filtered dissolved organics were passed through a XAD-2 resin glass column for later analysis. All sample locations and later detailed pre-treatment procedures are identical to those in our previous work.¹³ The detailed physico-chemical parameters of the 15 water samples are listed in Table S1, ESI.†

2.2. Materials

Sixteen PAH standards specified in EPA Methods 610, including naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Dih), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IncdB), dibenzo[*a,h*]anthracene (DiB), and benzo[*g,h,i*]perylene (BghiP) in a mixture solution of 2000 µg mL⁻¹ and surrogate standards (naphthalene-*d*₈, acenaphthylene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and perylene-*d*₁₂) in a mixture solution of 4000 µg mL⁻¹ were purchased from Supelco (Bellefonte, PA, USA). The internal standard, hexamethylbenzene, was acquired from Dr Ehrenstorfer, GmbH (Augsburg, Germany). HPLC-grade hexane and methanol were purchased from Merck, KGaA (Darmstadt, Germany). Analytical-grade dichloromethane (DCM) (Tianjin, China) was re-distilled using a glass system (a round flask, a flat bottom flask and a condenser). GFFs were pre-combusted at 450 °C for 5 h, while XAD-2 resins (Supelco, Bellefonte, USA) were cleaned with methanol and DCM in a Soxhlet extractor for 72 h, and then soaked in methanol. Before use, the resin column was eluted with 500 mL deionized water. Neutral alumina (100–200 mesh, Shanghai, China) and neutral silica gel (80–100 mesh, Qingdao, China) were Soxhlet extracted for 72 h in DCM. After DCM was volatilized from the particles, the alumina and silica gel were baked at 250 °C and 180 °C for 12 h, respectively, deactivated with 3% (w/w) deionized water for 12 h, and then preserved in *n*-hexane until use. Sodium chloride and anhydrous sodium sulfate (Tianjin, China) were baked at 450 °C before use. All glass containers were pre-cleaned with potassium dichromate-sulfuric acid solutions and kilned at 450 °C for 5 h in a muffle furnace.

2.3. Pretreatment procedure

The procedures for extraction and purification were carried out according to a previous study.¹² Briefly, for the dissolved phase, the XAD-2 resin columns absorbed organics, spiked with surrogated standards, were eluted with methanol and DCM. The resins were then extracted with methanol and DCM using an ultrasonic bath. The eluent mixture was successively extracted with the mixture of DCM and saturated sodium chloride solution, and DCM and deionized water. The DCM-phase extract was then concentrated and dehydrated with anhydrous sodium sulfate. The solvent in each extraction was changed into hexane. The hexane-phase extract was concentrated to 1 mL and then purified with an alumina and silica gel (1 : 2) glass column (8 mm diameter, 180 mm height). The first fraction eluted with 10 mL hexane was discarded. The second fraction containing PAHs was eluted with 75 mL hexane and DCM, concentrated to 1 mL with a rotary evaporator, and then to 0.2 mL under a gentle nitrogen stream. A known amount of internal standard was added to each sample before instrument analysis. For the particulate phase, after freeze-drying, the GFFs were spiked with surrogate standards and Soxhlet extracted with 250 mL DCM for 72 h. Activated copper was added to the DCM to remove sulfur. Further treatment of the DCM-phase extracts is the same as described above.

2.4. Instrument analysis

All samples were analyzed using an Agilent Technologies 7890A gas chromatography equipped with a 5795C mass spectrometer detector (GC/MSD) and HP-5MS silica fused capillary column (30 m × 0.25 mm × 0.25 μm). The column temperature was programmed as follows: initially 60 °C for 5 min and increased at a rate of 3 °C min⁻¹ to 295 °C, and held for another 30 min. A 1 μL sample was injected automatically with a splitless mode. Peak identification was as described previously.¹⁶

Dissolved organic carbon (DOC) was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPH, Kyoto) and the particulate organic carbon (POC) was determined by a CHNS elemental analyzer (Vario EL III Elementar, Germany), after the removal of carbonate with acid. The measurement of TOC and DOC were performed on the original water samples.

2.5. Quality control and quality assurance

Quantification was performed using the internal standard method based on a five-point calibration curve for individual components, and Hexamethylbenzene was used as the internal standard for PAHs in GC/MSD analysis. GC/MSD was calibrated daily, and the relative difference between the five-point calibration and daily calibration was below 20%. Measured individual PAH concentrations were normalized by the area of the internal standard, but not corrected with the recoveries of the individual PAHs. The correlation coefficients for all calibration curves for every target compound and surrogate standard were greater than 0.997.

For the chemical analysis, surrogate standards were added to all analyzed samples, including dissolved and particulate samples, the procedural blanks, and the spiked blanks before extraction to quantify the procedural recovery. The last two blanks were conducted for every ten samples. The detection limits of individual PAHs ranged from 0.02 to 0.14 ng L⁻¹ for a 60 L sample. Because of the relatively low recoveries of Nap-*d*₈ in each sample (as shown in Table S2, ESI†) and the high levels of Nap in the blank samples, Nap was excluded and not discussed further in this study.

2.6. Calculations of the hazard ratio and the TEQ

Non-cancer and cancer hazard ratios of PAHs were also calculated according to our previous reference.¹³ If the hazard ratio is greater than the unity, it indicates that the water is posing hazardous risks to humans. The toxic equivalents (TEQ) were also used to assess the risks caused by PAHs to human health according to the standard recommended by the USEPA. It could be calculated from the toxic equivalency factor (TEF), relative to BaP (BaP_{eq}), as documented by Nisbet and Lagoy.¹⁴

3. Results and discussion

3.1. Levels and composition profiles of PAHs

Sixteen PAHs, except Nap, were detected in the 15 water samples, both in the dissolved and particulate phases. ∑15 PAHs concentrations during the wet season varied from 32.0 (YT sample) to 754.8 ng L⁻¹ (ZHQ sample), with a mean value of

126.4 ng L⁻¹ for the dissolved phase, and from 13.4 (HZH sample) to 3017.8 ng L⁻¹ (XC sample), with a mean of 240.8 ng L⁻¹ for the particulate phase (Table S3a, ESI†). During the dry season, the concentrations of the dissolved PAHs ranged from 48.1 (ZHH sample) to 113.6 ng L⁻¹ (JM sample), with a mean value of 78.6 ng L⁻¹, while the concentrations of the particulate PAHs ranged from 8.6 (FSH sample) to 69.6 ng L⁻¹ (XC sample), with a mean of 20.8 ng L⁻¹ (Table S3b, ESI†).

During the wet season, ∑15 PAHs concentrations were extremely high in the XC (3159.9 ng L⁻¹) and ZHQ (770.0 ng L⁻¹) stations (Fig. 1). This maybe due to the new PAHs input in these sites because there is a gasoline boat running across the river to the docks at the ZHQ station at fixed intervals. Therefore, accidental petroleum leaks could occur at this sampling site. As for the XC site, a large number of residential areas and industrial factories were located around the sampling station. Both sides of the river had roads with busy traffic. Reports of accidental contaminations in the river were obtained. All these may have contributed to the high-level of PAHs at the XC site. As for other sampling stations in the PRD region, ∑15 PAHs concentrations were relative low and did not vary significantly between the wet and dry seasons. In general, however, the PAH deposition in the wet season seems to be higher than in the dry season. The possible reason could be new PAHs can input to the water systems due to a higher run off and a higher load of fresh terrestrial and atmospheric organic matter during wet season.

Compared with the contamination of the drinking water sources in other areas of China (Fig. S1, ESI†), the PAH levels in the PRD region (58.8–3159.9 ng L⁻¹) were far lower than those in Daliao River (946.1–13 448.5 ng L⁻¹)¹⁷ and slightly lower than those in Gaoping River in Taiwan Province (nd–9400.0 ng L⁻¹).¹⁸ However, they were also much higher than those in the Three Gorges Reservoir (13.8–97.2 ng L⁻¹),¹⁹ the drinking water sources in Henan Province (15.0–884.0 ng L⁻¹),²⁰ and Xijiang in Guangdong Province (21.7–138.0 ng L⁻¹) in the years 2005 to 2006.¹¹

Generally, to better understand the distribution and sources of PAHs, the sixteen PAHs, except Nap, can be classified into 5 groups based on their numbers of rings. The percentages of different ring numbers in each sample during the wet and dry seasons are illustrated in Figs. 2a and 2b, respectively. On

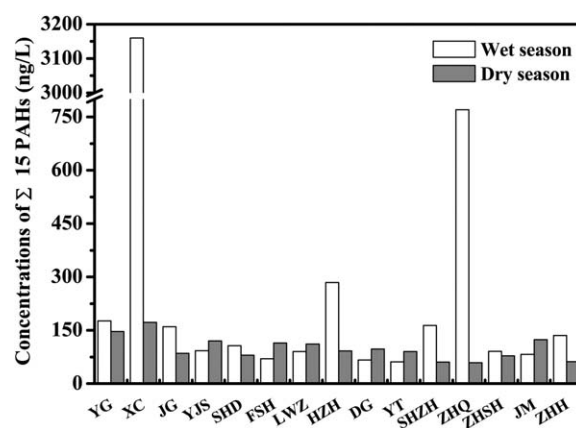


Fig. 1 Comparison of the PAHs levels (particle and dissolved water phase) between wet and dry seasons.

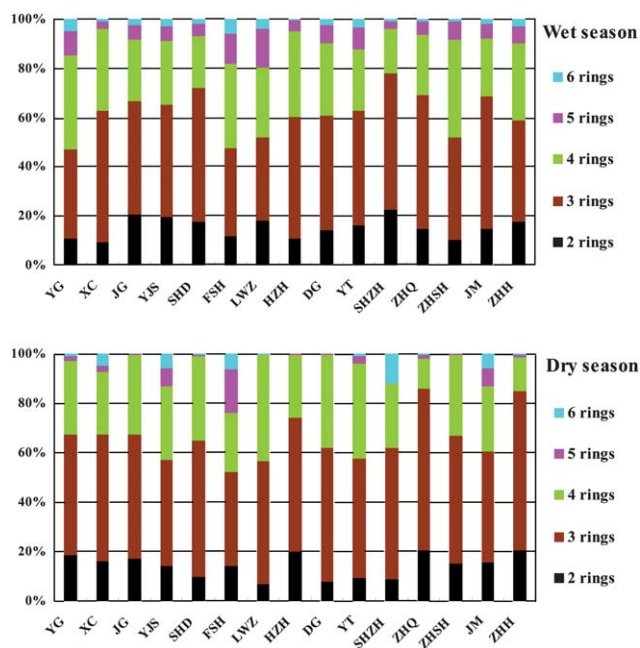


Fig. 2 Participation of different ring number PAHs in the total PAHs.

average, the total concentrations of two-ringed PAHs (Ace, Dih, and Flu) in all samples accounted for 15.23% of the total PAHs during the wet season and 14.33% of the total PAHs during the dry season. Three-ringed PAHs (Phe, Ant, and Flua) made up 46.33% of the total PAHs during the wet season and 51.44% of the total during the dry season. Three-ringed PAHs dominated total PAH compositions. Four-ringed PAHs (Pyr, BaA, Chry, BbF, and BkF) made up 28.94% of the total PAHs during the wet season and 28.71% of the total PAHs during the dry season. These were considered to be the second-dominant components of total PAHs. The proportions of five-ringed (BaP, IncdB and DiB) and six-ringed (BghiP) PAHs were relatively low during both the wet and dry seasons.

3.2. PAH distributions in dissolved and particulate phases

The relationship between PAH levels and TOC were also investigated; the results are shown in Fig. S2, ESI.† The XC sample was excluded due to the high $\sum 15$ PAHs concentration and TOC found in this site. The TOC is determined from the sum of DOC and POC. The PAH levels showed no linear correlations with DOC, both in the wet ($R^2 = 0.0296$) and dry ($R^2 = 0.0015$) seasons. Better linear correlations were obtained with POC in wet ($R^2 = 0.6575$) but not in dry ($R^2 = 0.2590$) seasons. This may be because PAHs are lipophilic, and the adsorption of PAHs on the particulate phase was higher than that in the dissolved phase.²¹ In addition, the quality of organic matter changes during wet seasons is due to a higher run off from and a higher load of fresh terrestrial organic matter, which might be one reason for the increasing PAH levels during wet seasons.

3.3. Source identification

Due to the wide-spread sources of PAHs, the possible sources of PAHs in the drinking source water within this region were also

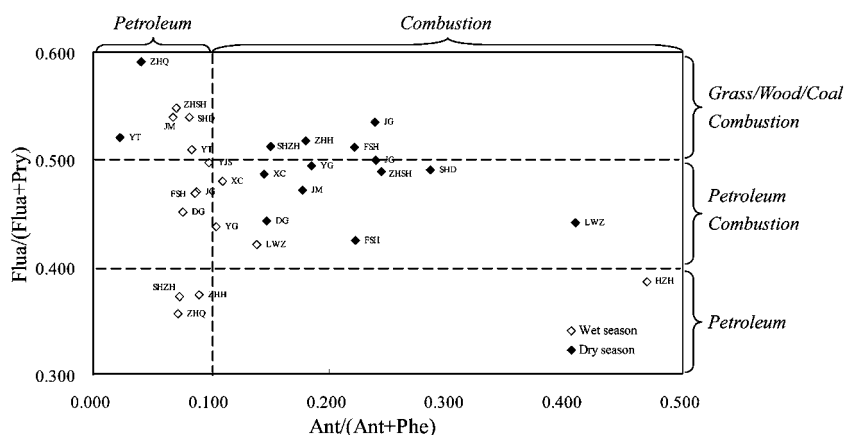
determined *via* conventional reported methods.^{22–26} According to these references, the ratios between pairs of individual PAHs are often employed to determine the sources of PAHs (See ESI for more information, ESI†).

Fig. 3a shows all PAH sources identified *via* the ratios of Ant/(Ant + Phe) and Flua/(Flua + Pyr), indicating that PAH sources originated mainly from petroleum discharges during the wet season and from combustion during the dry season in most samples. In SHZH, ZHH, and ZHQ, PAHs originated mainly from petroleum discharges during the wet season. Passenger ferries passed through ZHH and ZHQ station every day, which might be the main reason for this phenomenon. During the dry season in SHZH, ZHH, JG, PAHs originated mainly from wood/coal combustion. In other stations, PAH sources were likely to be from petroleum discharges, the combustion of wood/coal and the combustion of petroleum. Fig. 3b shows the PAH sources determined from the ratios of BaA/(BaA + Chry) and IncdB/(IncdB + BghiP). PAHs originating from petroleum discharges were found for the SHZH station during the dry season. During the dry season in JG, HZH, ZHSH, LWZ, SHD, JM, FSH, and ZHQ, and the wet season in LWZ, ZHQ, SHZH, ZHSH, and JM, PAHs originated mainly from the combustion of wood/coal. PAHs in other stations came from mixed sources. In summary, based on the results obtained, the sources of PAHs in drinking water within the PRD area originated from petroleum discharges, the combustion of wood/coal and the combustion of petroleum.

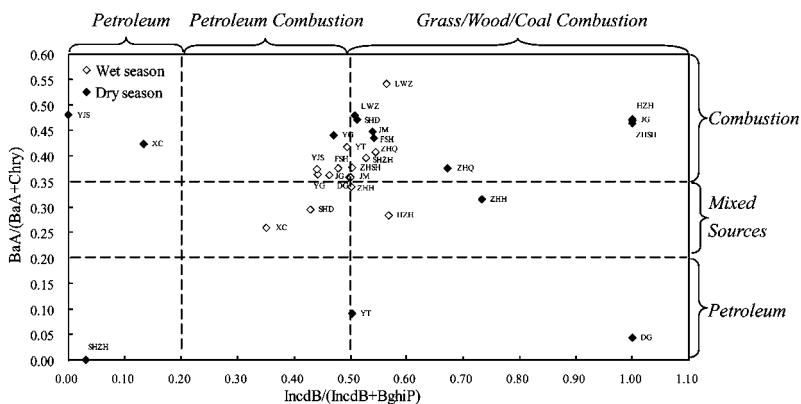
3.4. Risk assessment

The potential health risks of PAHs were examined through water consumption based on both non-cancerous and cancerous hazard ratios. Fig. S3, ESI,† shows the non-cancerous health risks caused by four individual PAHs, including Dih, Flu, Flua, and Pyr, during both wet and dry seasons. The non-cancerous hazard ratios ranged from 1.24×10^{-5} (YT sample) to 1.26×10^{-3} (XC sample) during the wet season, and from 1.24×10^{-5} (ZHQ sample) to 4.81×10^{-5} (YG sample) during the dry season. These are by far below the unity. During the wet season, the hazard ratio of XC was 8 to 100 times higher than that in other samples. During the dry season, the hazard ratios of the samples did not fluctuate significantly. Pyr and Flua were the dominant components in most samples with non-cancerous risks to human health during both wet and dry seasons. The non-cancerous hazard ratios of all the samples in both wet and dry seasons were all below 1.26×10^{-3} , far lower than 1. According to the calculation, the four individual PAHs would not induce non-cancerous hazard risks in all drinking source water samples in this study. However, as the combined effects of all PAHs were not considered, we may not ignore completely the non-cancerous hazard risks caused by total PAHs in the future.

Fig. S4, ESI,† shows the cancerous health risks of BaP during both wet and dry seasons. The cancerous hazard ratios ranged from 2.63×10^{-4} (YT sample) to 6.60×10^{-3} (XC sample) during the wet season, and from 0 (JG, YJS, SHD, PSH, LEZ, DG, SHZH, ZHSH, and JM samples) to 2.46×10^{-4} (XC sample) during the dry season. Conclusions similar to those concerning non-cancerous hazard ratios during the wet season can be drawn from these results; the cancer hazard ratios of the XC sample



a



b

Fig. 3 Sources determination of PAHs by different isomers.

were about 2 to 25 times higher than those of the other samples. During both wet and dry seasons, the cancer hazard ratios of BaP in all samples were far below the unity, demonstrating that no cancerous hazard risks to human health were caused by BaP alone. Still, the cancerous risks caused by the combined effects of all PAHs cannot be determined with certainty. Thus, cancer hazard risks should not be overlooked in future research.

The USEPA Integrated Risk Information System (<http://www.epa.gov/iris>) lists only Dih, Flu, Flua and Pyr, which may cause non-cancerous hazard risks, and BaP, which may cause cancerous hazard risks, as PAHs with risks to human health by water consumption. Thus, the hazard risks caused by total PAH targets could not be evaluated by this method. An alternative method was used to assess the toxicity of the total PAHs based on TEQs. The relative results were calculated by TEFs and are listed in Table S4, ESI.† As is shown in Tables 1a and 1b, the TEQs of total PAHs ranged from 8.379 (JM sample) to 77.058 ng L⁻¹ (ZHQ sample), except at the XC station, which had an extremely high value of 177.077 ng L⁻¹, during the wet season, and from 0.508 (DG sample) to 9.051 ng L⁻¹ (XC sample) during the dry season. Exceptionally high values in FSH (57.389 ng L⁻¹) and CHJ (59.273 ng L⁻¹) were found during this season. The TEQs during the wet season were much higher than those during the dry season. The high TEQ of PAHs in XC, FSH and CHJ resulted mainly from high levels of DiB. Regardless of the

season, 7 carcinogenic PAHs, including DiB, BaA, BaP, BbF, BkF, IncdB, and Chry, contributed significantly to the total TEQs of the 15 (Table 1). PAHs with higher molecular weights possessed higher toxicity than those with lower molecular weights. The TEQs of DiB and BaA were much higher than others during the wet season. This phenomenon was also observed in previous studies.²⁷ The TEQ of XC station was extremely high during the wet season, possibly resulting from the high pollution levels of PAHs and indicating the high risk exposure of the drinking source water in this station. Nevertheless, TEQ calculations can only determine the toxicity orders of the samples. They do not clearly demonstrate the potential risks posed to human health. Thus, human health risks caused by the total PAHs should not be ignored because the combined effects of individual PAHs were not considered in this study.

4. Conclusions

The \sum 15 PAHs concentrations ranged from 58.8 to 3159.9 ng L⁻¹ during wet and dry seasons. Three-ringed PAHs accounted for the majority of the total PAHs, and the concentrations of four- and two-ringed PAHs were lower. Five- and six-ringed PAHs only took up a small portion of the total PAHs. The pollution levels of PAHs in drinking water sources within the PRD region were relatively high compared with those in other parts of China.

Table 1 Toxic equivalents for PAHs during the wet season (ng L⁻¹ BaP_{eq})

BaP _{eq} ng L ⁻¹	YG	XC	JG	YJS	SHD	FSH	LWZ	HZH	DG	YT	SHZH	ZHQ	ZHSH	JM	ZHH
Acenaphthylene	0.004	0.025	0.002	0.003	0.001	0.001	0.004	0.001	0.002	0.003	0.003	0.008	0.002	0.001	0.002
Acenaphthene	0.003	0.052	0.005	0.003	0.001	0.001	0.003	0.005	0.001	0.001	0.007	0.025	0.001	0.002	0.003
Fluorene	0.012	0.220	0.026	0.012	0.017	0.006	0.010	0.025	0.006	0.006	0.027	0.081	0.006	0.009	0.019
Phenanthrene	0.040	0.966	0.052	0.029	0.043	0.017	0.021	0.062	0.022	0.021	0.077	0.349	0.023	0.032	0.040
Anthracene	0.046	1.188	0.050	0.031	0.038	0.016	0.035	0.552	0.018	0.019	0.060	0.270	0.018	0.023	0.039
Fluranthene	0.019	0.594	0.017	0.010	0.012	0.007	0.005	0.023	0.007	0.006	0.008	0.044	0.013	0.010	0.011
Pyrene	0.025	0.643	0.019	0.010	0.010	0.007	0.008	0.037	0.008	0.006	0.014	0.080	0.011	0.009	0.019
Benzo[a]anthracene	0.777	7.506	0.395	0.263	0.174	0.269	0.463	1.088	0.172	0.196	0.437	3.187	0.386	0.165	0.441
Chresene	0.135	2.149	0.070	0.044	0.042	0.045	0.039	0.275	0.031	0.027	0.067	0.464	0.064	0.030	0.086
Benzo[b]fluoranthene	1.243	6.873	0.538	0.375	0.385	0.551	0.473	2.078	0.442	0.328	0.263	1.615	0.829	0.399	0.635
Benzo[k]fluoranthene	0.906	6.420	0.511	0.311	0.277	0.412	0.477	0.303	0.194	0.187	0.179	1.405	0.660	0.214	0.458
Benzo[a]pyrene	7.107	41.55	3.722	2.347	2.448	2.977	5.589	3.385	1.779	1.656	2.126	16.968	4.553	1.675	3.651
Indeno[1,2,3-cd]pyrene	0.672	1.961	0.366	0.198	0.148	0.377	0.431	0.266	0.177	0.206	0.163	1.104	0.078	0.182	0.376
Dibenzo[a,h]anthracene	17.280	106.565	8.135	6.210	5.975	8.495	21.450	32.140	6.545	7.710	7.245	51.365	7.230	5.610	9.120
Benzo[g,h,i]perylene	0.085	0.362	0.042	0.025	0.020	0.041	0.033	0.020	0.018	0.021	0.015	0.092	0.008	0.018	0.037
∑15PAHs	28.355	177.077	13.950	9.872	9.590	13.221	29.042	40.260	9.423	10.392	10.690	77.058	13.881	8.379	14.938
∑7Ca PAHs ^a	28.121	173.027	13.737	9.748	9.449	13.125	28.923	39.535	9.340	10.310	10.479	76.108	13.800	8.275	14.767

^a Carcinogenic PAHs.**Table 2** Toxic equivalents for PAHs during the dry season (ng L⁻¹ BaP_{eq})

BaP _{eq} ng L ⁻¹	YG	XC	JG	YJS	SHD	FSH	LWZ	HZH	DG	YT	SHZH	ZHQ	ZHSH	JM	ZHH	CHJ
Acenaphthylene	0.005	0.001	0.004	0.002	0.001	0.004	0.000	0.006	0.000	0.000	0.000	0.002	0.002	0.006	0.002	0.005
Acenaphthene	0.005	0.005	0.003	0.004	0.002	0.004	0.003	0.003	0.003	0.002	0.002	0.002	0.003	0.003	0.002	0.002
Fluorene	0.017	0.022	0.008	0.011	0.005	0.009	0.005	0.009	0.005	0.006	0.004	0.008	0.008	0.010	0.009	0.006
Phenanthrene	0.040	0.058	0.023	0.028	0.023	0.024	0.023	0.029	0.020	0.024	0.014	0.031	0.021	0.033	0.028	0.025
Anthracene	0.092	0.098	0.072	0.079	0.090	0.068	0.157	0.090	0.157	0.006	0.087	0.013	0.069	0.071	0.046	0.079
Fluranthene	0.022	0.020	0.013	0.016	0.012	0.013	0.017	0.012	0.017	0.019	0.009	0.007	0.012	0.015	0.007	0.014
Pyrene	0.023	0.021	0.013	0.021	0.013	0.012	0.021	0.010	0.022	0.017	0.009	0.005	0.013	0.017	0.006	0.011
Benzo[a]anthracene	0.821	0.909	0.674	0.709	0.671	0.633	1.263	0.608	0.063	0.146	0.000	0.096	0.614	0.677	0.071	0.692
Chresene	0.104	0.124	0.076	0.077	0.076	0.082	0.137	0.068	0.138	0.146	0.069	0.016	0.071	0.084	0.016	0.083
Benzo[b]fluoranthene	0.141	0.127	0.000	0.000	0.042	0.000	0.039	0.000	0.000	0.138	0.000	0.000	0.000	0.042	0.006	0.063
Benzo[k]fluoranthene	0.051	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.000	0.000	0.003	0.000	0.000	0.004	0.097
Benzo[a]pyrene	0.938	1.554	0.000	0.000	0.000	0.000	0.000	0.107	0.000	1.348	0.000	0.148	0.000	0.000	0.043	1.056
Indeno[1,2,3-cd]pyrene	0.128	0.131	0.028	0.832	0.033	0.872	0.034	0.023	0.035	0.101	0.023	0.059	0.024	0.866	0.049	0.910
Dibenzo[a,h]anthracene	4.715	5.895	0.000	0.000	0.000	55.595	0.000	0.000	0.000	0.000	0.000	1.260	0.000	0.000	1.130	56.150
Benzo[g,h,i]perylene	0.014	0.085	0.000	0.072	0.003	0.074	0.003	0.000	0.000	0.010	0.072	0.003	0.000	0.074	0.002	0.079
∑15PAHs	7.116	9.051	0.913	1.850	0.971	57.389	1.700	0.965	0.508	1.964	0.288	1.651	0.835	1.899	1.421	59.273
∑7Ca PAHs ^a	6.897	8.740	0.778	1.618	0.822	57.182	1.472	0.805	0.284	1.880	0.092	1.582	0.709	1.669	1.320	59.051

^a Carcinogenic PAHs.

According to the composition of isomers with molecule weights of 178 and 202, PAH sources might originate from petroleum discharges during the wet season and from the combustion of wood/coal and the combustion of petroleum during the dry season. The ratios of isomers with molecular weights of 228 and 276 indicated that PAHs originated from petroleum discharges, the combustion of wood/coal and the combustion of petroleum during both wet and dry seasons. Risk assessment *via* calculations of the hazard ratios and TEQs suggested that the toxicity caused by PAHs in drinking water sources were extremely high in the XC station, whereas the individual PAHs in all samples within the PRD region did not pose non-cancerous and cancerous hazards to human health. However, risks from the combined effects of individual PAHs to human health require further study.

Acknowledgements

This work is contribution No. IS-1319 from GIGCAS, and was financially supported the Science and Technology Project of

Guangdong Province, China (2007A032400001 and 2006A36803001).

References

- 1 K. C. Jones and P. de Voogt, *Environ. Pollut.*, 1999, **100**, 209–221.
- 2 J. Li, H. R. Cheng, G. Zhang and X. Li, *Environ. Pollut.*, 2009, **157**, 273–279.
- 3 K. Nikolaou, P. Masclat and G. Mouvier, *Sci. Total Environ.*, 1984, **32**, 103–132.
- 4 C. D. Simpson, A. A. Mosi, W. R. Cullen and K. J. Reimer, *Sci. Total Environ.*, 1996, **181**, 265–278.
- 5 M. B. Fernandes, M. A. Sicre, A. Boireau and J. Tronczynski, *Mar. Pollut. Bull.*, 1997, **34**, 857–867.
- 6 E. Manoli, C. Samara, I. Konstantinou and T. Albanis, *Chemosphere*, 2000, **41**, 1845–1855.
- 7 S. O. Baek, R. A. Field, M. E. Goldstone, P. W. Kirk, J. N. Lester and R. Perry, *Water, Air, Soil Pollut.*, 1991, **60**, 279–300.
- 8 A. M. Mastral and M. S. Callén, *Environ. Sci. Technol.*, 2000, **34**, 3051–3057.
- 9 J. A. Ross and S. Nesnow, *Mutat. Res., Fundam. Mol. Mech. Mutagen.*, 1999, **424**, 155–166.

-
- 10 L. Keith and W. Telliard, *Environ. Sci. Technol.*, 1979, **13**, 416–423.
- 11 H. M. Deng, P. A. Peng, W. L. Huang and J. Z. Song, *Chemosphere*, 2006, **64**, 1401–1411.
- 12 X. J. Luo, B. X. Mai, Q. S. Yang, J. M. Fu, G. Y. Sheng and Z. S. Wang, *Mar. Pollut. Bull.*, 2004, **48**, 1102–1115.
- 13 M. Qiao, T. C. An, X. Y. Zeng, D. L. Zhang, G. Y. Li, G. Y. Sheng, J. M. Fu, G. X. Zhang and J. Guo, *J. Environ. Monit.*, 2010, **12**, 1666–1677.
- 14 I. C. T. Nisbet and P. K. Lagoy, *Regul. Toxicol. Pharmacol.*, 1992, **16**, 290–300.
- 15 U. G. Ahlborg, G. C. Becking, L. S. Birnbaum, A. Brouwer, H. Derks, M. Feeley, G. Golor, A. Hanberg, J. C. Larsen, A. K. D. Liem, S. H. Safe, C. Schlatter, F. Waern, M. Younes and E. Yrjänheikki, *Chemosphere*, 1994, **28**, 1049–1067.
- 16 B. X. Mai, H. M. Fu, G. Y. Sheng, Y. H. Kang, Z. Lin, G. Zhang, Y. S. Min and E. Y. Zeng, *Environ. Pollut.*, 2002, **117**, 457–474.
- 17 W. Guo, M. C. He, Z. F. Yang, C. Y. Lin, X. C. Quan and H. Z. Wang, *Chemosphere*, 2007, **68**, 93–104.
- 18 R. A. Doong and Y. T. Lin, *Water Res.*, 2004, **38**, 1733–1744.
- 19 J. X. Wang, Y. H. Bi, G. Pfister, B. Henkelmann, K. X. Zhu and K. W. Schramm, *Chemosphere*, 2009, **75**, 1119–1127.
- 20 Y. G. Ma, J. P. Cheng, F. Jiao, K. X. Duo, Z. Rong, M. Li and W. H. Wang, *Environ. Monit. Assess.*, 2008, **146**, 127–138.
- 21 S. W. Karickhoff, D. S. Brown and T. A. Scott, *Water Res.*, 1979, **13**, 241–248.
- 22 B. A. Benner, S. A. Wise, L. A. Currie, G. A. Klouda, D. B. Klinedinst, R. B. Zweidinger, R. K. Stevens and C. W. Lewis, *Environ. Sci. Technol.*, 1995, **29**, 2382–2389.
- 23 H. Budzinski, I. Jones, J. Bellocq, C. Pierard and P. Garrigues, *Mar. Chem.*, 1997, **58**, 85–97.
- 24 P. M. Gschwend and R. A. Hites, *Geochim. Cosmochim. Acta*, 1981, **45**, 2359–2367.
- 25 E. Lipiatou and A. Saliot, *Mar. Chem.*, 1991, **32**, 51–71.
- 26 M. B. Yunker, R. W. Macdonald, R. Vingarzan, R. H. Mitchell, D. Goyette and S. Sylvestre, *Org. Geochem.*, 2002, **33**, 489–515.
- 27 Y. F. Jiang, X. T. Wang, F. Wang, Y. Jia, M. H. Wu, G. Y. Sheng and J. M. Fu, *Chemosphere*, 2009, **75**, 1112–1118.