Occurrence of polycyclic aromatic hydrocarbons in surface sediments of a highly urbanized river system with special reference to energy consumption patterns

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ABSTRACT

Sediment samples collected from downstream of the Dongjiang River, a highly urbanized river network within the Pearl River Delta of South China, were analyzed for 28 polycyclic aromatic hydrocarbons (PAHs). Total concentrations of 28 PAHs, 16 priority PAHs designated by the United States Environmental Protection Agency (USEPA) and the seven carcinogenic PAHs classified by the USEPA ranged from 480 to 4600, 100 to 3400 and 10 to 1700 ng/g dry weight, respectively. Principal component analysis-based stepwise multivariate linear regression showed that sediment PAHs were predominantly derived from coal combustion, refined fossil fuel combustion and oil spills, accounting for 37%, 32% and 23%, respectively, of the total loading. The levels of sediment PAHs remained steady from 2002 to 2008, during which fossil fuel consumption had doubled, probably reflecting efforts to control PAH emissions from fossil fuel combustion. Finally, use of natural gas and liquefied petroleum gas in automobiles should be encouraged to improve environmental quality.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of organic pollutants ubiquitous in the environment, mainly originate from petrogenic sources (crude oil, oil refined products and coals) and incomplete combustion of coal, fossil fuel and biomass etc. (Neff, 1979). Extensive attention has been paid to the environmental levels, origins and behavior of PAHs due to their potential toxicity, carcinogenicity, mutagenicity, and potential for long-range transport (Gusstafson and Dickhut, 1997; Yunker et al., 1999). Emissions of PAHs from developed countries have been greatly reduced since the 1990s (U.S. Environmental Protection Agency, 1998; 2001), yet the ice core record of PAH deposition in Greenland indicated no decrease of PAH levels in the past hundred years (Masclet et al., 1995). Therefore, increased energy consumption as a result of rapid industrialization in developing countries has been pinpointed as the leading factor to slow the reduction of global PAH emissions (Xu et al., 2006).

As one of the fastest growing economies in the world, China also has to deal with a variety of environmental issues. For example, the annual PAH emission from China reached 116,000 tons in 2003 (Zhang et al., 2008), which is obviously a serious threat to the ecological and human health. Recognizing the potentially harsh consequences of no action, China has been adjusting its energy consumption patterns among other things (National Development and Reform Commission, 2007) in an attempt to balance its economic growth and environmental protection.

Because PAHs tend to sorb onto the surface of suspended organic matter when released into aquatic systems and eventually accumulate in sediments, a comparison of the temporal change in sediment PAH levels with fossil fuel consumption patterns may shed lights into the effectiveness of environmental protection measures. In this regard, the Dongjiang River basin, which is located in the eastern part of the Pearl River Delta (PRD) in South China (Fig. 1) and a typical economic zone in China where rapid economic growth has accelerated fossil fuel consumption and aggravated the ambient burden of certain pollutants such as PAHs, is an ideal candidate for conducting such an assessment. Although the PRD region has been recognized as one of the most significant sources of PAHs globally (Lang et al., 2007), the occurrence of PAHs in the Dongjiang River watershed, an important part of the PRD, has not been adequately examined. Luo et al. (2005, 2008) reported the levels of PAHs in surface sediments from various tributaries of the PRD including the

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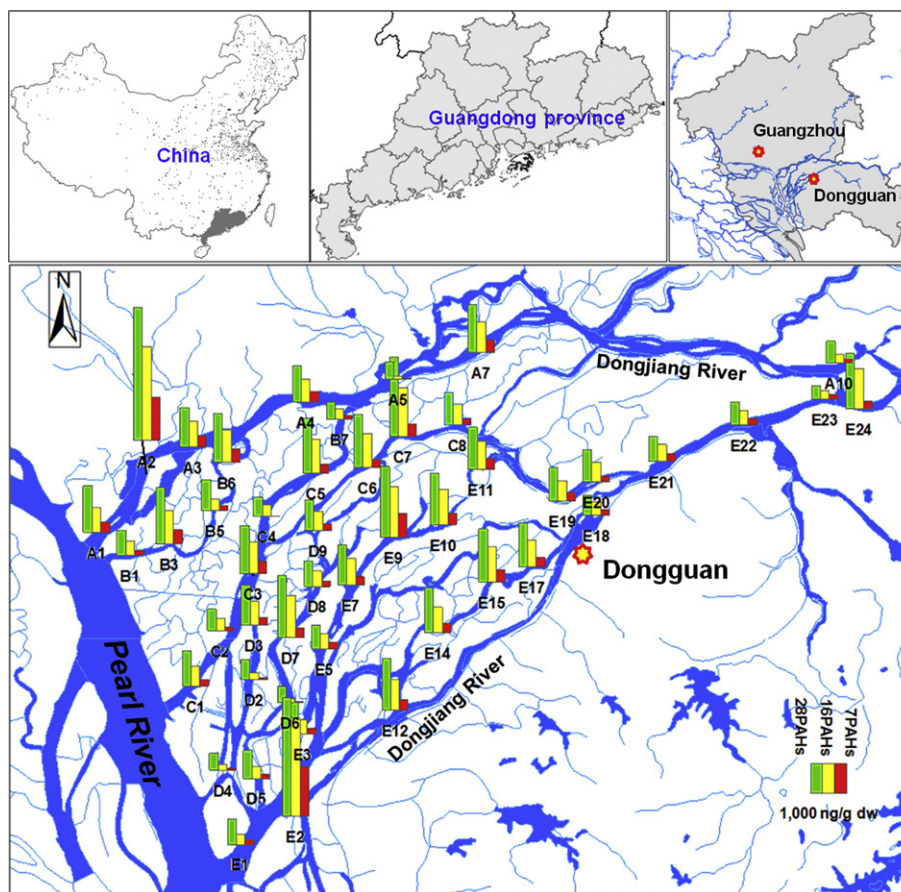E-mail address: eddyzeng@gig.ac.cn (E.Y. Zeng).

Fig. 1. Locality of sampling sites and spatial distribution of PAH levels. 28 PAHs: sum of 28 target PAHs; 16PAHs: sum of 16 priority PAHs designated by the United States Environmental Protection Agency (USEPA); and 7PAHs: sum of the seven carcinogenic PAHs classified by the USEPA.

Dongjiang River, but conducted source diagnostics based on 11 samples only.

The objectives of the present study, based on the analysis of a large number of samples, were to examine the occurrence of sediment PAHs in downstream of the Dongjiang River, to quantitatively apportion the sources of PAHs, and to evaluate the effectiveness of energy consumption efficiency by comparing the temporal change in sediment PAH levels. Several ratios of paired PAH isomers with similar physicochemical properties have been widely used in diagnosing emission sources of PAHs in various environmental compartments (Yunker et al., 1999, 2002a, 2002b), but their application has been largely qualitative. To best ensure the reliability of source apportionment, a statistical approach, i.e., principal component analysis (PCA)-based stepwise multivariate linear regression (PCA-SMLR), was utilized in the present study.

2. Materials and methods

2.1. Materials

A standard mixture of 28 PAH analytes was obtained from AccuStandard (New Haven, CT, USA) for qualitative and quantitative analyses. The nomenclature of these PAHs is listed in Table S1 of the Supplementary material ("S" represents figures and tables in the Supplementary material thereafter). Six deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, and benzo(g,h,i)perylene-d_{12}) purchased from Cambridge Isotope Laboratories (Andover, MA, USA) were employed as surrogate standards. Another three PAHs including 2-fluoro-1,1-biphenyl, p-terhenyl-d_{14} and dibenzo(a,h)anthracene-d_{14} also acquired from Cambridge Isotope Laboratories were used as internal standards.

2.2. Sample collection and extraction

A total of 60 sediment samples including duplicates (0–5 cm) were collected in July 2009 from 47 locations around downstream areas of the Dongjiang River (Fig. 1), with detailed longitude and latitude information listed in Table S2. Sediment samples collected with a grab bucket were cooled immediately with ice and stored at −4 °C upon transport to the laboratory.

Thawed samples were freeze-dried, milled, sorted with an 80–mesh sieve, and stored at −4 °C until extraction. Each sample of approximately 25 g was spiked with the surrogate standards and Soxhlet-extracted for 72 h with 250 mL of a mixture of hexane:acetone (1:1 in volume) and with sufficient copper sheets to remove sulfur. The extract was concentrated with a Zymark TurboVap 500 (Zymark, Hopkinton, MA, USA), solvent-exchanged to hexane (hexane was added to the extract during the concentration process), and further reduced to 1 mL. A glass column (40 cm × 1 cm-id) packed with alumina:silica gel (6 and 12 cm in length, respectively) was used to fractionate the extract. The fraction containing PAHs was eluted with 70 mL of a mixture of hexane:methylene chloride (7:3 in volume). This fraction was transferred to a special glass vial (about 2 mL in volume), concentrated to 0.5 mL and spiked with the internal standards prior to instrumental analysis.

2.3. Instrumental analysis

A Shimadzu GC/MS-QP2010 was used for measurements of PAHs operated in the electron impact and selective ion monitoring modes, and equipped with a 60 m × 0.25 mm-i.d. (0.25 μm film thickness) DB-5MS column (J&W Scientific, Folsom, CA, USA). Column temperature was programmed from 60 °C to 200 °C at 10 °C/min, raised to 250 °C at a rate of 2 °C/min, and then raised to 290 °C at a rate of 20 °C/min (held for 5 min). Injection temperature was programmed from 100 to 280 °C at a rate of 200 °C/min and held for 10 min. Extract was injected in the splitless mode with a split time at 2 min. The ion source and interface temperatures were both maintained at 250 °C. All the samples were analyzed in the full-scan mode, and PAHs were quantified in the selected ion monitoring mode.

2.4. Quality assurance and quality control

Quantification was conducted with an internal calibration method based on seven-point (20, 50, 100, 200, 500, 1000, and 2000 ng/mL) calibration curves for individual compounds. A standard solution was analyzed every day and the difference between this daily calibration and the initial calibration must be less than 20% for individual PAHs before other samples were analyzed. Procedural blank was analyzed for every 15 samples, and no concentration of any target analyte was higher than the lowest concentration (20 ng/mL) of the calibration curve. With an average dry sample weight of 24.4 g and a final extract volume of 0.5 mL, the reporting limit was 0.41 ng/g (20 ng/mL × 0.5 mL/24.4 g) for all target analytes. The recoveries of the surrogate standards, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}, from field samples were 43 ± 8%, 66 ± 11%, 75 ± 12%, 89 ± 12% and 92 ± 21%, respectively. None of the reported PAH concentrations was corrected with the surrogate standard recoveries. All concentrations were normalized to dry sample weights unless specified otherwise.

2.5. Data analysis

Several previous studies (Harrison et al., 1996; Larsen and Baker, 2003; Zuo et al., 2007) have reported the implications of multivariate linear regression (MLR) for source apportionment of PAHs in various environmental matrices. Stepwise MLR is a special form of MLR with stepwise parameter introduction, ensuring that only the parameters that have been demonstrated to significantly affect the regression result are retained before another parameter is introduced, while parameters without significant influences on the regression result are rejected. The computing framework of MLR is detailed elsewhere (Larsen and Baker, 2003), and can be expressed as

$$\begin{bmatrix} PAH_{1,1} & \cdots & PAH_{1,28} \\ \vdots & \ddots & \vdots \\ PAH_{47,1} & \cdots & PAH_{47,28} \end{bmatrix} = \begin{bmatrix} B_{1,1} & \cdots & B_{1,5} \\ \vdots & \ddots & \vdots \\ B_{47,1} & \cdots & B_{47,5} \end{bmatrix} \cdot \begin{bmatrix} FS_{1,1} & \cdots & FS_{1,28} \\ \vdots & \ddots & \vdots \\ FS_{5,1} & \cdots & FS_{5,28} \end{bmatrix} \quad (1)$$

where $PAH_{i,j}$ is the standardized normal deviation of the log-transformed concentration of PAH i at sampling site j, $B_{j,k}$ is the regression coefficient for factor k at sampling site j, and $FS_{k,i}$ is the factor score for factor k on PAH i. Therefore, the contribution of source k to the log-transformed concentration of PAH i at site j ($\varphi_{i,j,k}$) can be calculated by

$$\varphi_{i,j,k} = \frac{B_{j,k}}{\sum_{t=1}^{5} B_{j,t}} \times 100\% \quad (2)$$

which is equivalent to the contribution of source k to PAH i at site j.

3. Results and discussion

3.1. Occurrence of polycyclic aromatic hydrocarbons

The concentration ranges of individual PAHs, as well as the sums of 28 PAHs (Σ_{28}PAH), 16 priority PAHs (Σ_{16}PAH) designated by the United States Environmental Protection Agency (USEPA) and the seven carcinogenic PAHs (Σ_7PAH) classified by the USEPA, are listed in Table S1. The distribution of these concentrations did not fit a normal distribution (predominantly $p < 0.05$), but a log-transformation of the data fulfilled the normality test (predominantly $p > 0.05$) (Table S1). The concentrations of Σ_{28}PAH, Σ_{16}PAH, and Σ_7PAH ranged from 480 to 4600 ng/g (mean: 1410 ng/g), 100–3400 ng/g (mean: 880 ng/g), and 10–1700 ng/g (mean: 330 ng/g), respectively, with higher levels all found in the center of the sampling area, except for E2 and A2 (Fig. 1). Luo et al. (2008) collected 11 sediment samples from the same general area in July and October 2002, and reported a concentration range of 220–2500 ng/g for Σ_{16}PAH without giving an average value or individual concentrations. If the PAH levels from Luo et al. (2008) fit a lognormal distribution and the reported range stands for the 95% confidence interval of the real range, the average level for Σ_{16}PAH would be 980 ng/g. The basically same ranges of Σ_{16}PAH concentrations between the two sampling periods imply that the anthropogenic influences on Dongjiang River sediments may have been steady. Principal component analysis on compositions of PAHs yielded excellent correlations among all sampling sites for Σ_{28}PAH except perylene (Fig. S1). The consistent compositional profiles of Σ_{27}PAH (Σ_{28}PAHs minus perylene) may point to similar sources for these PAHs in the sampling region. In freshwater sediment, perylene was believed to stem from early diagenesis of organic matter

(Hites et al., 1980). The predominance of odd numbered extended n-alkanes in the same sediment samples also corroborated the predominance of terrestrial higher plants as the input source (unpublished data). On the other hand, these results may also implicate different input mechanisms and/or environmental behaviors of sediment Σ_{27}PAH and perylene in downstream of the Dongjiang River. To elaborate this notion, an independent-samples t-test on the relative abundances of Σ_{15}PAH (Σ_{16}PAH minus naphthalene) in sediment acquired in the present study and airborne particles from Guangzhou (Fig. 1) (Bi et al., 2003) in 2002 was conducted; the result showed no difference between the two ($p > 0.05$). In addition, a good linear relationship between the PAH compositions in sediment and airborne particles (Fig. 2) further confirms that sediment PAHs in the Dongjiang River are mainly derived from similar sources with those in air particles.

3.2. Source diagnostics

The compositional profiles of Σ_{28}PAH were dominated by 4- and 5-ring PAHs, with moderate contributions from 2- and 3-ring PAHs (Fig. S2). Occurrence of 4-ring PAHs has often been attributed to combustion of materials with low-ignition point, e.g., coal and biomass fuels, while that of 5-ring PAHs is due to combustion of materials with high-ignition points, such as purified oil (Levendis et al., 1998; Larsen and Baker, 2003; Robinson et al., 2006). High relative abundances of 2- and 3-ring PAHs have been believed to result from petroleum derived residues (Sporstol et al., 1983). As a result, sediment PAHs in the study area may have been mainly resulted from incomplete combustion of fossil fuel and biomass, with minor contributions from petroleum spills.

Ratios of several PAH isomers, such as anthracene/(anthracene + phenanthrene) (Ant/(Ant + Phe)), fluoranthene/(fluoranthene + pyrene) (Flu/(Flu + Pyr)), benz(a)anthracene/(benz(a)anthracene + chrysene) (BaA/(BaA + Chr)), and indeno(l,2,3-cd)pyrene/(ideno(1,2,3-cd)pyrene + benzo(g,h,i)perylene) (IcdP/(IcdP + BghiP)) have been widely used as diagnostic tools to assess possible emission sources. The values of these ratios below 0.10, 0.40, 0.50, and 0.20, respectively, are indicative of petrogenic sources; otherwise, they suggest pyrogenic origins (Yunker et al., 1996, 2002a, 2002b; Soclo et al., 2000). The congested cluster in the Ant/(Ant + Phe) versus Flu/(Flu + Pyr) plot (Fig. 3a) indicates that sediment PAHs in the Dongjiang River were primarily generated from pyrogenic sources. However, the BaA/(BaA + Chr) versus IcdP/
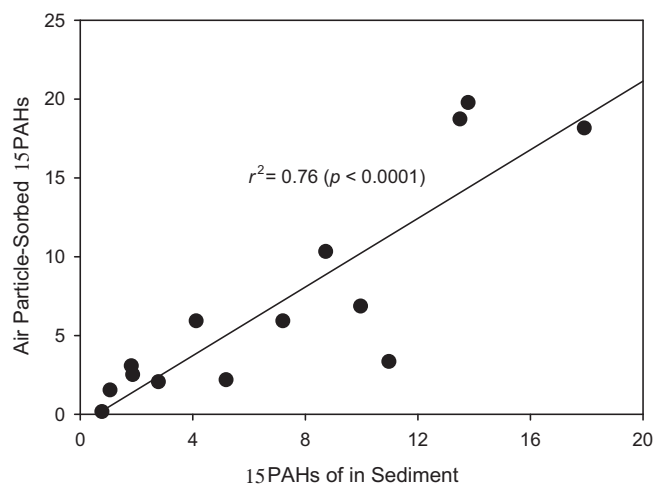

Fig. 2. Comparison of relative individual abundances of 15PAHs in sediment from downstream of the Dongjiang River and particle-sorbed PAHs in Guangzhou. 15PAHs: 16 priority PAHs designated by the United States Environmental Protection Agency minus naphthalene.
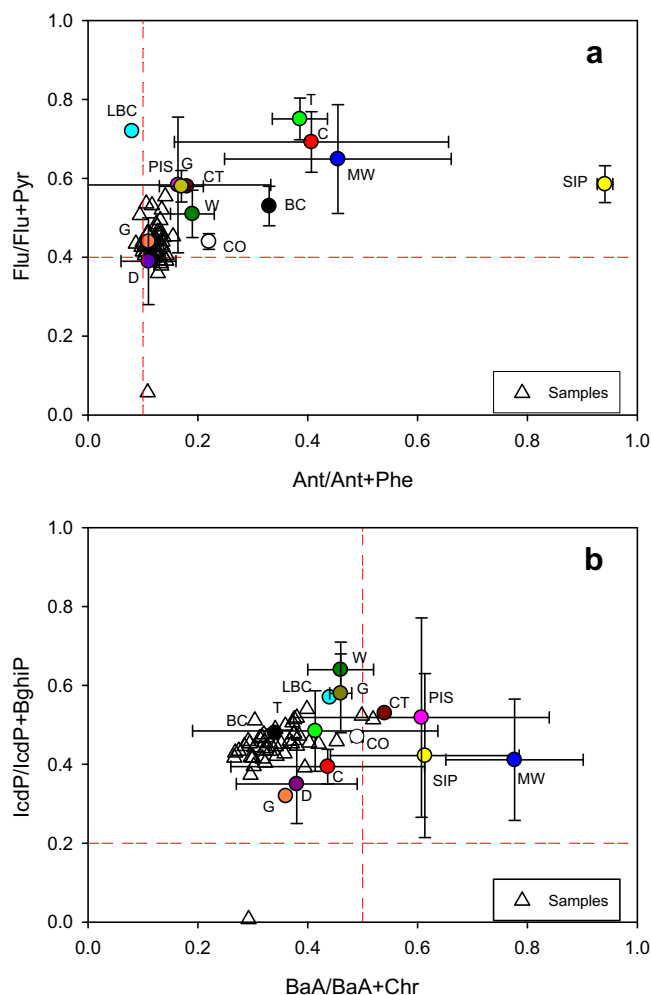
Fig. 3. Cross plots for PAH isomeric ratios in sediment from downstream of the Dongjiang River and for several pyrogenic sources including lignite and brown coal (LBC), coal tar (CT), medical waste (MW), steel and iron plants (SIP), bituminous coal (BC), crude oil (CO), petrochemical industrial sludge (PIS), gasoline (G), cooking (C), grasses (G), diesel (D), tobacco (T), and wood (W). (a) anthracene/(anthracene + phenanthrene) (Ant/(Ant + Phe)) versus fluoranthene/(fluoranthene + pyrene) (Flu/(Flu + Pyr)) and (b) benz(a)anthracene/(benz(a)anthracene + chrysene) (BaA/(BaA + Chr)) versus indeno(123-cd) pyrene/(indeno(123-cd)pyrene + benzo(ghi)perylene) (IcdP/(IcdP + BghiP)).

3.3. Apportionment of PAH sources with stepwise multivariate linear regression integrated principal components analysis

The log-transformed concentrations of individual PAHs were subject to PCA, resulting in four factors accounting for 90% of the variance in the surface sediment data (Table S4). The first factor responsible for 34.4% of the total variance is heavily weighted in 3 and 4-ring PAHs, including acenaphthylene, acenaphthene, 2,3,5-trimethynaphthalene, fluorene, phenanthrene, anthracene, 2-methylphenanthrene, 1-methylphenanthrene, 3,6-dimethylphenanthrene, pyrene and chrysene, along with lower loadings of 5 and 6-ring PAHs. Similar PAH profile was reported for PAHs from combustion of pulverized coal at 1000 °C (Levendis et al., 1998). Elevated levels of acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene have been generally attributed to coal combustion (Chen et al., 2005), whereas pyrene and chrysene have been regarded as markers of coal combustion-derived PAHs (Larsen and Baker, 2003). It should be noted that coal is the most important energy source in the Pearl River Delta, accounting for 50.8% of the energy consumption in 2008, widely employed for industrial production and domestic utility, especially for steel and power industries (Statistical Bureau of Guangdong Province, 2010). Therefore, this factor is rationally assigned to coal combustion.

The second factor, accounting for 33.5% of the total variance, is predominantly reinforced by 5 and 6-ring PAHs consisting of benz(a) anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e) pyrene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene and benzo(g,h,i)perylene. Although benz(a)anthracene has been suggested as a marker of coal combustion, it may be related to coal tar. Enriched benzo(a)pyrene and benzo(g,h,i)perylene have been related to vehicular emissions (Harrison et al., 1996; Larsen and Baker, 2003; Robinson et al., 2006; Boonyatumanond et al., 2007). A higher relative abundance of benzo(k)fluoranthene, compared to other PAHs was proposed to indicate diesel-powered vehicle exhausts (Larsen and Baker, 2003; Robinson et al., 2006). In addition, indeno(1,2,3-cd)pyrene, has also been found in both diesel and gas engine emissions (May and Wise, 1984; Larsen and Baker, 2003; Robinson et al., 2006) and gasoline-powered vehicle soot (Boonyatumanond et al., 2007). In summary, this factor appears to be largely related to combustion of refined petroleum products.

The third factor, responsible for 16.1% of the total variance, is highly weighted with naphthalene and its methylated derivatives which have been applied as indicators of vaporization or leakage of petroleum-associated products (Page et al., 1988; Yunker et al., 1996; Marr et al., 1999; Zakaria et al., 2002). Hence, this factor can be classified as an indicator of PAHs from oil spill.

The fourth factor, contributing 6% of the variance, is enriched with perylene and 9,10-diphenylanthracene. This distribution is considered unusual, because perylene is a natural compound formed from biogenic precursors during early diagenesis (Hites et al., 1980) while 9,10-diphenylanthracene is an anthropogenic chemical. As discussed in section 3.1, the input mechanisms for perylene and other PAHs were different in the study region. Therefore this factor is attributed to unknown sources.

From the above PCA analysis, contributions of the major input sources to PAHs in Dongjiang River sediments were estimated with SMLR. The contribution of PAH i from source k in a given sample j (ng/g) can be calculated by multiplying the concentration of PAH i at site j with $\varphi_{i,j,k}$. As shown in Figs. S3a–c, the predicted levels of PAHs correlate nicely with the measured concentrations. However, PCA-SMLR results indicate that 12 out of the 47 samples contained negative source contributions (Table S5), which is practically impossible and probably associated with point source interferences such as the high concentrations of 9,10-diphenylanthracene detected at C4 and E14. For this reason, the negative source contributions

(IcdP + BghiP) plot (Fig. 3b) suggests a combined pyrolytic and petrogenic source of PAHs. Fig. 3 further compares the diagnostic indices from the present study and those representing PAHs of typical pyrogenic sources, with numerical values listed in Table S3. A few notions can be made from this comparison. First, all the diagnostic indices for the sediment PAHs are similar to those for PAHs generated from gasoline and diesel exhausts. Second, the Flu/(Flu + Pyr) and IcdP/(IcdP + BghiP) values indicate the similarity between the sediment PAHs and those from combustion of crude oil, bituminous coal, coal tar and grass, and furnaces of steel and iron plants and petrochemical industrial sludge incinerators. Third, the sediment PAHs are similar to PAHs from cooking emissions or combustion of tobacco based on BaA/(BaA + Chr) and IcdP/(IcdP + BghiP), and identical to PAHs from combustion of lignite and brown coal based on Ant/(Ant + Phe) and IcdP/(IcdP + BghiP). Finally, the sediment PAHs appear to be different from PAHs derived from medical waste incineration. In general, source diagnostics based on simple PAH ratios could not obtain definite conclusions about the input sources of sediment PAHs, but the above analyses suggested fossil fuel combustion may be the dominant source of PAHs.

were replaced with the homologous average values of other positive contributions for the purpose of evaluating the average source contributions. Average concentrations of different PAHs from the four sources illustrate that sediment PAHs in the Dongjiang River were predominated by coal combustion, followed by combustion of refined fossil fuel, oil spill and other sources (Fig. 4). The concentration-weighted contribution proportions of these four sources were 37%, 32%, 23% and 8%, respectively.

3.4. Correlation between the occurrence of sediment PAHs and energy consumption patterns

The above analyses indicate that the majority of PAHs in downstream sediment of the Dongjiang River were largely (92%) attributed to fossil fuel related sources. It should be emphasized that coal and petroleum are still the primary types of energy used in Guangdong Province (Beijing Traffic Management Bureau, 2010), and the amounts of coal and petroleum consumed have drastically increased from 2002 to 2008 in Guangdong Province (Figs. 5 and 6). Therefore, a temporal comparison of sediment PAH levels and source contributions with fossil fuel consumption may give hints on the effectiveness of control measures, such as increased fuel efficiency and enhanced cleaner fuel consumption, in mitigating PAH contamination.

Fig. 6 shows that the daily average consumption of both coal and refined petroleum products had doubled from 2002 to 2008 in Guangdong Province (Beijing Traffic Management Bureau, 2010). However, the concentration range of Σ_{16}PAH in Dongjiang River sediments has remained basically unchanged, i.e., 220–2500 ng/g (mean: 980) in 2002 (Luo et al., 2008) versus 100–3400 ng/g (mean: 880) from the present study. A sampling in July and October 2002 (Luo et al., 2008) estimated that the mean contributions of coal and wood combustion and refined fossil fuel combustion to sediment PAHs in the PRD, including the Dongjiang River, were 36% and 25%, respectively. Multiplying the concentrations of sediment Σ_{16}PAH with the relative contributions from various sources mentioned above yielded that combustion of coal and wood contributed approximately 80–900 ng/g (mean: 350 ng/g) to the sediment Σ_{16}PAH concentrations, whereas combustion of refined fossil fuel contributed 60–630 ng/g (mean: 240 ng/g) in 2002. On the other hand, combustions of coal and refined fossil fuel contributed 40–1300 ng/g (mean: 330 ng/g) and 30–1100 ng/g (mean: 280 ng/g),
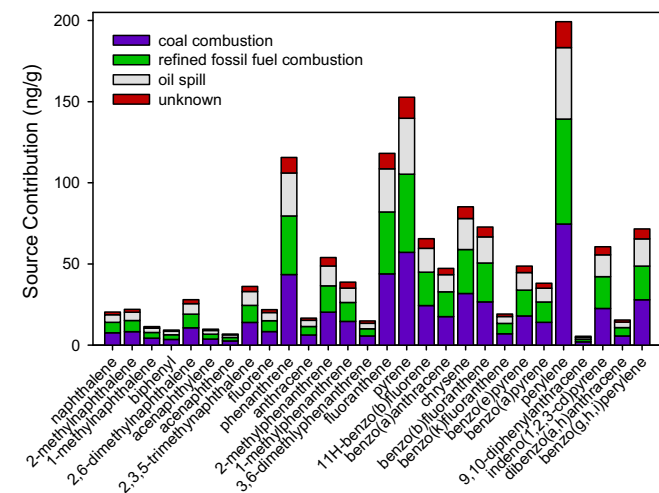

Fig. 5. Amounts of primary energy types, including coal, crude oil and natural gas, consumed from 2002 to 2008 in Guangdong Province (Statistical Bureau of Guangdong Province, 2010).

respectively, in 2008. Clearly, doubling of coal consumption from 2002 to 2008 did not double the sediment PAHs levels, probably due to improved coal combustion efficiency and reduced use of coal for generating electricity (Statistical Bureau of Guangdong Province, 2010). The slight increase of PAH concentrations resulted from refined fossil fuel combustion during the same time period was far slower than the increase of the average consumption amount, which might be attributed to more stringent standards on automobile emissions since the number of civilian vehicles in Guangdong Province increased from 1.7 million in 2000 to 6.6 million in 2009 (Statistical Bureau of Guangdong Province, 2010).

Apparently, better technology such as coal gasification may increase industrial combustion efficiency, but it does not help to lower PAH emissions from domestic and traffic-related sources. Although household use accounts for a tiny fraction of the amount of coal used as fuel, e.g., 0.44 million tons/year versus 44.6 million tons/year in Guangdong Province (Statistical Bureau of Guangdong Province, 2010), their contribution to total PAHs can not be overlooked.

Fig. 4. Average contributions to the concentrations of different PAHs in sediment from downstream of the Dongjiang River from coal combustion, refined fossil fuel combustion, oil spill, and unknown sources.
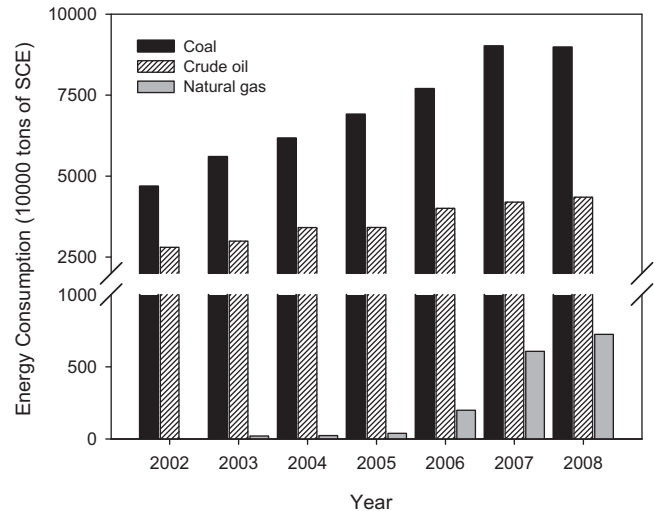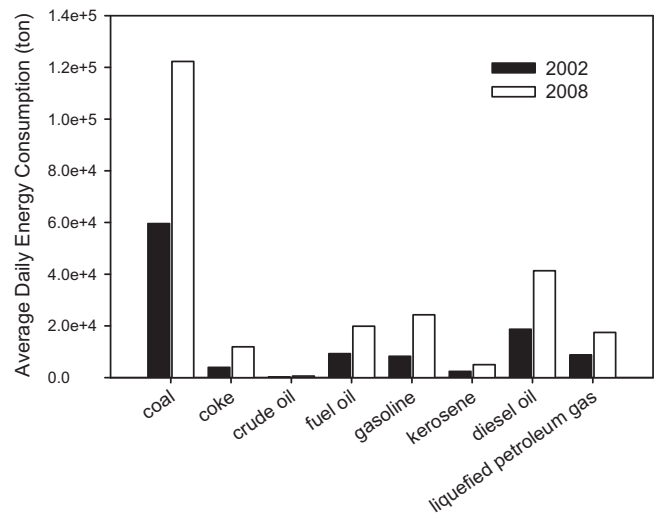

Fig. 6. Average daily consumption of coal, coke, crude oil, fuel oil, gasoline, kerosene, diesel and liquefied petroleum gas in 2002 and 2008 in Guangdong Province (Statistical Bureau of Guangdong Province, 2010).

Because the combustion efficiency of household coal burning is generally low, PAHs from household coal burning has been confirmed to contribute a considerable portion of the urban PAHs in China (Liu et al., 2007). On the other hand, gasoline- and diesel-powered vehicular exhausts have remained the major contributors of petroleum-related PAHs. Because automobile fuel efficiency can hardly be improved in a short period of time, PAH emissions are expected to increase with increasing number of vehicles. Consequently, adoption of more environmentally friendly energy types is the ultimate step toward reduction or elimination of PAH emissions from domestic and vehicular sources. Natural gas and liquefied petroleum gas are cleaner energy forms than other conventional types under the current economic conditions, and more importantly they are almost free of PAHs (Rom, 2007). However, the amounts of natural gas and liquefied petroleum gas, though increasing rapidly in recent years, still constitute only a small portion of the total amount of fuel used in Guangdong Province (Figs. 5 and 6). In reality, liquefied petroleum gas has been mostly confined to residential consumption, i.e., nearly 4.1 out of 6.4 million tons in the entire Guangdong Province annually (Statistical Bureau of Guangdong Province, 2010). Furthermore, there were only 450,000 gas-fueled vehicles out of a total of 176 million in 2009 in China (International Association for Natural Gas Vehicles; Beijing Traffic Management Bureau, 2010). In comparison, Pakistan possessed 2,300,000 gas-powered vehicles at the same time (International Association for Natural Gas Vehicles). Clearly, widening the use of natural gas and liquefied petroleum gas in automobiles is highly desirable in Guangdong Province and China, in an effort to balance economic growth and control of environmental pollution.

Acknowledgments

Appendix. Supplementary material

Supplementary material related to this article can be found at doi:10.1016/j.envpol.2011.03.010.

References

Beijing Traffic Management Bureau, 2010. Statistical Analysis on China's Vehicles and Drivers in the First Half of 2009. http://www.bjjtgl.gov.cn/publish/portal1/ (accessed September 2010).

Bi, X., Sheng, G., Peng, P.A., Chen, Y., Zhang, Z., Fu, J., 2003. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. Atmospheric Environment 37, 289–298.

Boonyatumanond, R., Murakami, M., Wattayakorn, G., Togo, A., Takada, H., 2007. Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. Science of the Total Environment 384, 420–432.

Chen, Y., Sheng, G., Bi, X., Feng, Y., Mai, B., Fu, J., 2005. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. Environmental Science and Technology 39, 1861–1867.

Gusstafson, K., Dickhut, R., 1997. Particle/gas concentrations and distributions of PAHs in the atmosphere of southern Chesapeake Bay. Environmental Science and Technology 31, 140–147.

Harrison, R.M., Smith, D.J.T., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environmental Science and Technology 30, 825–832.

Hites, R.A., Laflamme, R.E., Windsor Jr., J.G., Farrington, J.W., Deuser, W.G., 1980. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, U.S.A. Geochimica et Cosmochimica Acta 44, 873–878.

International Association for Natural Gas Vehicles, 2010. Natural Gas Vehicle Statistics: NGV Count–ranked Numerically as at December 2009. http://www.iangv.org/tools-resources/statistics.html, (accessed September 2010).

Lang, C., Tao, S., Zhang, G., Fu, J., Simonich, S., 2007. Outflow of polycyclic aromatic hydrocarbons from Guangdong, southern China. Environmental Science and Technology 41, 8370–8375.

Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science and Technology 37, 1873–1881.

Levendis, Y.A., Atal, A., Carlson, J.B., 1998. On the correlation of CO and PAH emissions from the combustion of pulverized coal and waste tires. Environmental Science and Technology 32, 3767–3777.

Liu, X., Zhang, G., Li, J., Cheng, H.-R., Qi, S.-H., Li, X.-D., Jones, K.C., 2007. Polycyclic aromatic hydrocarbons (PAHs) in the air of Chinese cities. Journal of Environmental Monitoring 9, 1092–1098.

Luo, X.-J., Chen, S.-J., Mai, B.-X., Zeng, Y.-P., Sheng, G.-Y., Fu, J.-M., 2005. Distribution and sources of polycyclic aromatic hydrocarbons in sediments from rivers of Pearl River Delta and its nearby South China Sea. China Environmental Science 26, 129–134 (in Chinese).

Luo, X.-J., Chen, S.-J., Mai, B.-X., Sheng, G.-Y., Fu, J.-M., Zeng, E., 2008. Distribution, source apportionment, and transport of PAHs in sediments from the Pearl River Delta and the northern South China Sea. Archives of Environmental Contamination and Toxicology 55, 11–20.

Marr, L.C., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V., Hammond, S.K., 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. Environmental Science and Technology 33, 3091–3099.

Masclet, P., Hoyau, V., Jaffrezo, J.L., Legrand, M., 1995. Evidence for the presence of polycyclic aromatic hydrocarbons in the polar atmosphere and in the polar ice of Greenland. Analusis 23, 250–252.

May, W.E., Wise, S.A., 1984. Liquid chromatographic determination of polycyclic aromatic hydrocarbons in air particulate extracts. Analytical Chemistry 56, 225–232.

National Development and Reform Commission, 2007. The Eleventh-five-year Energy Development Planning. National Development and Reform Commission, Beijing, People's Republic of China (in Chinese).

Neff, J.M., 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Applied Science Publishers, London.

Page, D.S., Foster, J.C., Fickett, P.M., Gilfillan, E.S., 1988. Identification of petroleum sources in an area impacted by the Amoco Cadiz oil spill. Marine Pollution Bulletin 19, 107–115.

Robinson, A.L., Subramanian, R., Donahue, N.M., Rogge, W.F., 2006. Source apportionment of molecular markers and organic aerosol1. polycyclic aromatic hydrocarbons and methodology for data visualization. Environmental Science and Technology 40, 7803–7810.

Rom, W.N., 2007. Polycyclic Aromatic Hydrocarbons and Petroleum Industry, Environmental and Occupational Medicine, fourth ed.. Lippincott Williams & Wilkins, p. 1884.

Soclo, H.H., Garrigues, P., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Marine Pollution Bulletin 40, 387–396.

Sporstol, S., Gjos, N., Lichtenthaler, R.G., Gustavsen, K.O., Urdal, K., Oreld, F., Skei, J., 1983. Source identification of aromatic hydrocarbons in sediments using GC/MS. Environmental Science and Technology 17, 282–286.

Statistical Bureau of Guangdong Province, 2010. Guangdong Statistical Yearbook (2009). http://www.gdstats.gov.cn/tjnj/ml_c.htm (accessed September 2010).

U.S. Environmental Protection Agency, 1998. 1990 Emissions Inventory of Section 112(c)(6) Pollutants: Polycyclic Organic Matter (POM), TCDD, TCDF, PCBs, Hexachlorobenzene, Mercury, and Alkylated Lead.

U.S. Environmental Protection Agency, 2001. Technology Transfer Network National Air Toxics Assessment Washington, DC.

Xu, S., Liu, W., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. Environmental Science and Technology 40, 702–708.

Yunker, M.B., Snowdon, L.R., Macdonald, R.W., Smith, J.N., Fowler, M.G., Skibo, D.N., Mclaughlin, F.A., Danyushevskaya, A.I., Petrova, V.I., Ivanov, G.I., 1996. Polycyclic aromatic hydrocarbons composition and potential sources for sediment samples from the Beaufort and Batents Sea. Environmental Science and Technology 30, 1310–1320.

Yunker, M.B., Macdonald, R.W., Goyette, D., Paton, D.W., Fowler, B.R., Sullivan, D., Boyd, J., 1999. Natural and anthropogenic inputs of hydrocarbons to the Strait of Georgia. Science of the Total Environment 225, 181–209.

Yunker, M.B., Backus, S.M., Pannatier, G.E., Jeffries, D.S., Macdonald, R.W., 2002a. Sources and significance of alkane and PAH hydrocarbons in Canadian arctic rivers. Estuarine. Coastal and Shelf Science 55, 1–31.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002b. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489–515.

Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., Kumata, H., 2002. Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in malaysia: a widespread input of petrogenic PAHs. Environmental Science and Technology 36, 1907–1918.

Zhang, Y., Dou, H., Chang, B., Wei, Z., Qiu, W., Liu, S., Liu, W., Tao, S., 2008. Emission of polycyclic aromatic hydrocarbons from indoor straw burning and emission inventory updating in China. Annals of the New York Academy of Sciences 1140, 218–227.

Zuo, Q., Duan, Y.H., Yang, Y., Wang, X.J., Tao, S., 2007. Source apportionment of polycyclic aromatic hydrocarbons in surface soil in Tianjin, China. Environmental Pollution 147, 303–310.