Environ Sci Pollut Res (2012) 19:1352–1363
DOI 10.1007/s11356-011-0623-0

URBANIZATION IN CHINA AND ITS ENVIRONMENTAL IMPACT

Impacts of urbanization on surface sediment quality: evidence from polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) contaminations in the Grand Canal of China

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Received: 28 May 2011 / Accepted: 14 September 2011

Abstract
Introduction Organic pollutants, especially synthetic organic compounds, can indicate paces of anthropogenic activities. Effects of urbanization on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) distributions in surface sediment were conducted in urban sections of the Grand Canal, China, consisting of a four-level urbanization gradient.
Materials and methods The four-level urbanization gradients include three countryside towns, two small-size cities, three medium-size cities, and a large-size city. Diagnostic ratio analysis and factor analysis–multiple linear regression model were used for source apportionment of PAHs. Sediment quality guidelines (SQGs) of USA and Canada were employed to assess ecological risks of PAHs and PCBs in surface sediments of the Canal.
Results and discussion Ranges of PAH and PCB concentrations in surface sediments were 0.66–22 mg/kg and 0.5–93 μg/kg, respectively. Coal-related sources were primary PAH sources and followed by vehicular emission. Total concentration, composition, and source apportionment of PAHs exhibited urbanization gradient effects. Total PCB concentrations increased with the urbanization gradient, while total PAHs concentration in surface sediments presented an inverted U Kuznets curve with the urbanization gradient. Elevated concentrations of both PAHs and PCBs ranged at effect range low levels or interim SQG, assessed by USA and Canadian SQGs.
Conclusions PAHs and PCBs in surface sediments of the Grand Canal showed urbanization gradient effects and low ecological risks.

Keywords PAHs · PCBs · Surface sediment · Urbanization · Source apportionment · Ecological risk

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are well-documented anthropogenic contaminants owing to bio-accumulative ability and potential adverse (carcinogenic and mutagenic) impacts on human and wildlife health (Mai et al. 2002; Boonyatumanond et al. 2006; Shi et al. 2007; Neamtu et al. 2009; Hu et al. 2011; Erickson and Kaley 2011).

PAHs are enriched with petroleum and coal-derived liquids and are also derived from combustions of biomass and fossil fuels. Between 1970s and 1980s, sedimentary PAHs showed a decreasing trend (Hites et al. 1977; Yamashita et al. 2000) worldwide because of the successful transition of home heating from coal to oil and natural gas and of the improved combustion efficiency for power generation. PAHs in surface sediments can be originated from various anthropogenic sources, including the "point" source, such as spills/seeps of petroleum or coal-derived liquids, associated with definable acute or long-term

Responsible editor: Philippe Garrigues

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industrial activities, and "non-point" sources, such as atmospheric deposition of combustion-derived particles and surface runoffs from the surrounding urban and industrial areas (Jiang et al. 2000; Zakaria et al. 2002; Stout et al. 2004; Li et al. 2006; Sofowote et al. 2008). However, in the past decades, sedimentary PAHs increased in some developing regions since the energy demands dramatically increased with the rapid urbanization (Van Metre et al. 2000; Lima et al. 2003; Liu et al. 2009).

PCBs are a class of persistent organic pollutants, consisting of a wide variety of synthetic compounds, used as dielectric fluids in capacitors and transformers, print inks, paints, or pesticides due to their physical and chemical stability. PCB production has been banned worldwide since late 1970s except those remaining in use in some closed systems. Because of their high stability, considerable high PCB concentrations remained in sediments in industrialized and urbanized coastal zones (Mai et al. 2002; Hong et al. 2005; Urbaniak et al. 2008; Martinez et al. 2010) and were even detected in Arctic sediments transported via atmospheric transportation (Carrizo and Gustafsson 2011).

Given that PAHs and PCBs were tightly related to human activities in the past decades, we hypothesize that their type and concentration might indicatively associate with urbanization process in environmental matrices. Few rural–urban gradient studies incidated that PAHs and PCBs in sediments exhibited urbanization gradient effects at different levels (Foster and Cui 2008; Wong et al. 2009). But urbanization gradient consists of individual urban areas has not been tested for its effects on distribution of PAHs and PCBs in sediment.

The southern section of the ancient Grand Canal (shortened as "the Canal" thereafter) connects the Yangtze River in the north and the Qiantang River in the south (Fig. 1). The Canal runs through the Yangtze River Delta (YRD) city cluster, the largest one in China, comprising towns and cities with diverse development levels. The Canal receives water from local water network without fixed flow direction and has served as an important waterway in the region since it dug back to the seventh century. Before the industrial development alongside the Canal, it was used as water resources for drinking, living, and agricultural irrigation. With the fast economic development and following rapid urbanization, a large volume of untreated industrial and living wastewater discharged directly or indirectly with stormwater into the Canal, especially in the early 1980s. This led to a serious impairment of surface water and sediment quality (Chen et al. 2004). Our previous study also found that metals (Cr, Cu, Hg, and Fe) in surface water from urban sections of the Canal were closely associated with local industrial activities, and gross domestic products (GDPs) of primary and tertiary industries (Yu et al. 2011). But, organic pollution in urban sections of the Canal remains unknown (Zhu et al. 2005). In order to testify the hypothesis, i.e., the presence of PAHs and PCBs in environmental matrices might relate to the urbanization process, we designed to investigate distribution (type and concentration) of PAHs and PCBs in surface sediments in urban sections along the Canal, transecting the YRD city cluster. The urban sections of the Canal located in nine towns and cities consisting of a serial urbanization gradient from towns to small-size cities, medium-size cities, and a large-size city. Sources and ecological risks of PAHs and PCBs in surface sediments from the Canal were analyzed as well.

2 Materials and methods

2.1 Surface sediment sample collection

Nine urban sections of the Canal were selected to undertake the study in May, 2008, consisting of three countryside towns (labeled as "Town-#"), two small-size cities ("SSC-#"), three medium-size cities ("MSC-#"), and one large-size city ("LSC") (Fig. 1). An agriculture section was sampled as a reference in the rural region of SSC-1. Sampling sites and its urbanization level were described previously by Yu et al. (2011). A Peterson grabber was used to grab surface sediment samples from each section with an approximate interval of 500 m. The top 10-cm layer of the sediment was carefully collected and placed into a polyethylene bag using a stainless steel spoon. The collected samples were stored in a −20°C car freezer (CF-110DC, WAECO, Germany) and transported back to the lab. After deeply frozen at −20°C for a week, the frozen samples were lyophilized in a freeze dryer (FD-1C-50, Boyikang, Beijing, China). The freeze-dried samples were ground to pass a 100-mesh nylon sieve (<0.147 mm) and stored in a −20°C freezer prior to chemical analyses.

At least four surface sediment samples were collected each section to meet the statistical requirement. The agricultural section has 4 sampling points, while there were 13, 12, 44, and 14 sampling points for three Towns, two SSCs, three MSCs, and one LSC sections, respectively. In total, 87 surface sediment samples were collected from nine urban sections and one agricultural section in the Canal. The urbanization gradient consisting of these individual urban areas was classified by population and economic indices (including GDP and its constitution and per capita) (Yu et al. 2011).

2.2 Physicochemical properties of surface sediments

Total organic carbon (TOC) analysis was performed with a TOC analyzer (TOC-Vcpn, Shimadzu, Japan) with a solid

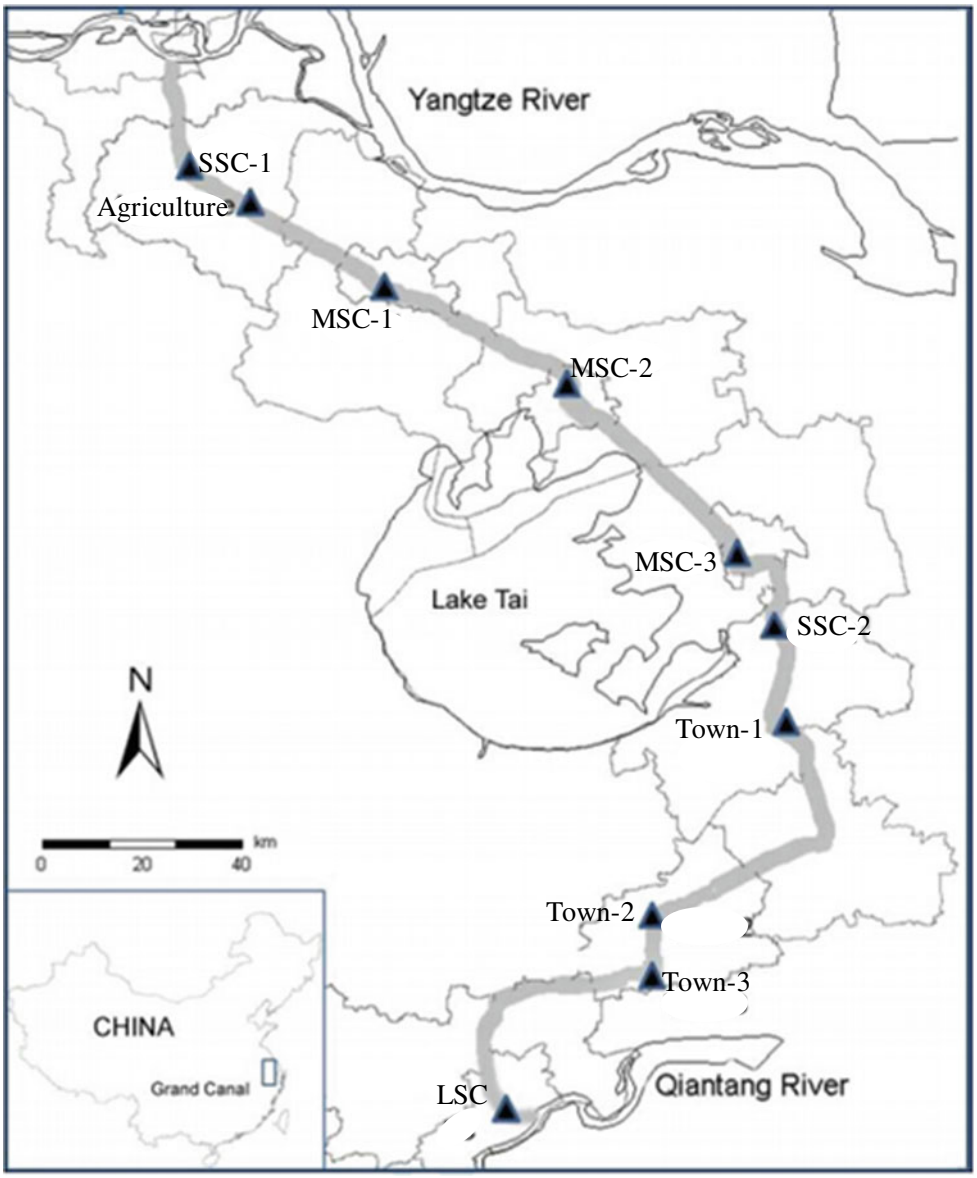

Fig. 1 Spatial locations of investigated urban sections of towns and cities along the south section of the Grand Canal in China. The urbanization gradient consisted of one agricultural section (4 points), three town urban sections (Town, 13 points), two small-size city (SSC, 12 points) urban sections, three medium-size city (MSC, 44 points) urban sections, and one large-size city (LSC, 14 points) urban sections

sample module (SSM-5000A, Shimadzu, Japan). pH and EC were measured at a ratio of 1:5 (sediment/deionized water) using a pH–EC meter (Accumet Excel XL60, Fisher Scientific Inc., USA).

2.3 PAH and PCB measurements

2.3.1 Chemicals and reagents

Standard solutions of 16 US EPA priority PAHs, 16 common PCB congeners (PCB Mix 77), internal standards (pyrene-d10 for PAHs and 2,4,5,6-tetracholo-m-xylene (TCMX) for PCBs), and surrogate standards (a mixture solution of perdeuterated PAHs (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12), 4-4′-dibromo-octafluoro-biphenyl (DBOFB), and PCB-103) were purchased from the Ehrenstorfer GmbH Co. (Augsburg, Germany). The 16 US EPA priority PAHs include naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BgP). The 16 common PCB congeners (PCB Mix 77) include PCB-28, PCB-52, PCB-101, PCB-77, PCB-123, PCB-118, PCB-114, PCB-153, PCB-105, PCB-138, PCB-126, PCB-167, PCB-156, PCB-180, PCB-169, and PCB-189.

All solvents (dichloromethane, acetone, and hexane) used for sample processing and analyses were of HPLC grade from Tedia Co. (USA). Pure water was taken from a

Milli-Q water system (Thermo Fisher Scientific Inc., USA). Anhydrous sodium sulfate, silica gel, and alumina were of analytical grade from Sinopharm Chemical Reagent Co. (Shanghai, China). The silica gel (100–200 mesh) and alumina (100–200 mesh) were extracted for 48 h using a Soxhlet apparatus, activated in the oven at 170°C for 8 h and at 450°C for 4 h, and then deactivated with distilled water at a ratio of 5% and 1% (m/m), respectively (Hong et al. 2009).

2.3.2 Extraction procedure

Sample extraction and cleanup followed the US EPA Method 3540C. Briefly, sediment samples were Soxhlet-extracted for 48 h with acetone/hexane (1:1, *v*/*v*) for PAHs and PCBs. The extracts were purified with a silica/alumina column. After extraction and cleanup, samples were concentrated and adjusted to 1 mL by volume for gas chromatography with a mass spectroscopy (GC–MS) analysis (Yuan et al. 2001).

2.3.3 GC–MS analysis

PAH and PCB analysis was conducted using a gas chromatography (Hewlett-Packard 7890, Agilent Co., USA) equipped with a mass spectroscopy detector (HP5975C, Agilent Co., USA), and a HP-5MS column (30 m long with internal diameter at 0.25 mm and film thickness at 0.25 μm, Agilent Co., USA). For the PAHs analysis, the column temperature was programmed to rise from 60°C to 150°C at a rate of 15°C/min, and increase to 220°C at 5°C/min and to 300°C at 10°C/min, and then hold at 300°C for 5 min. For the PCB analysis, the temperature was programmed to hold at 120°C for 2 min, rise from 120°C to 160°C at a rate of 10°C/min and hold for 3 min at 160°C, then increase to 190°C at 1.5°C/min and then to 240°C at 2°C/min, and finally increase to 280°C at 10°C/min and hold at 280°C for 2 min. Helium was used as a carrier gas. The injector and detector temperatures were 280°C and 300°C, respectively. The electron-impact energy was 70 eV and the mass-to-charge ratio scan (*m*/*z*) was from 50 to 500 amu. The selected ion mode was chosen.

2.3.4 Quality control and quality assurance

All analytical data were subjected to strict quality control. Method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spike (standards spiked into matrix), and sample duplicates were processed. PAHs and PCBs were quantified using internal calibration based on five-point calibration curves for individual compounds. Reported results were corrected by recoveries of the surrogate standards, i.e., 63.7±10.4% with acenaphthene-d10, 81.8±10.0% with phenanthrene-d10, 81.6±10.9% with chrysene-d12, 78.2±11.5% with perylene-d12, 73.6±9.5% with DBOFB, and 87.0±10.7% with PCB103, respectively. Concentrations of PAHs were presented as milligram per kilogram and PCBs as microgram per kilogram on the basis of dry weight.

2.4 Statistical analysis

Since the field sampling strategy was not an evenly design, a general linear model (Proc GLM) was applied for the analysis of variance (ANOVA) to compare differences of total PAHs, total PCBs, detected PCBs number, and physicochemical properties (pH, electrical conductivity, and total organic carbon) in the surface sediments from investigated sections of the Grand Canal. The Duncan's multiple range test was conducted following the GLM–ANOVA as a post hoc test. Linear regression (Proc REG) was employed to explore correlations between total concentrations of PAHs or PCBs and physicochemical properties (pH, EC, and TOC). To source the PAHs in surface sediments from the Canal, a factor analysis (Proc Factor) was applied with Kaiser's normalization and varimax rotation (Hopke 1985). The generated factor scores

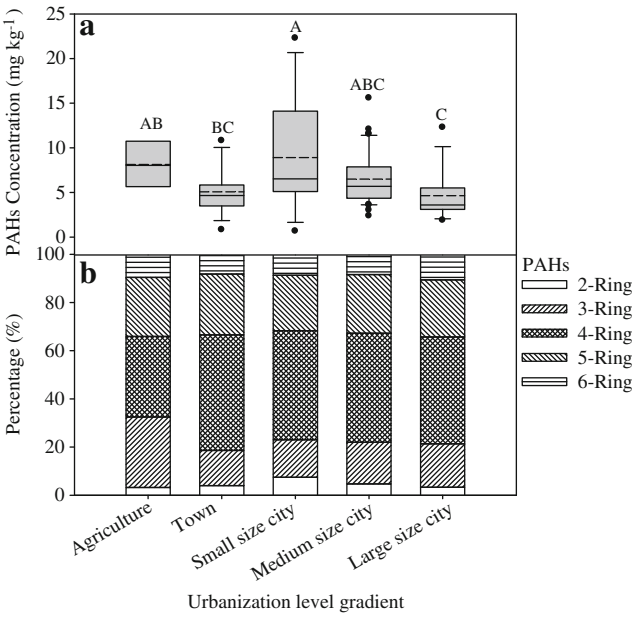

Fig. 2 Total PAHs (**a**) and composition (**b**, by median) in surface sediments from agricultural and urban sections of the Grand Canal along an urbanization gradient. The urbanization gradient consisted of one agricultural section (4 points), three town urban sections (Town, 13 points), two small-size city (SSC, 12 points) urban sections, three medium-size city (MSC, 44 points) urban sections, and one large-size city (LSC, 14 points) urban sections. *Different letters above the bars* indicated significant difference between the two urbanization levels ($p<0.05$) which was tested by a Duncan's Multiple Range Test following a GLM–ANOVA. In the *boxplots*, the *dash line* represents the mean, while the *solid line* showed the median

were carried out a multiple linear regression analysis (Proc Reg) against standard deviates of total 16 priority PAHs at different urbanization levels. The relative contributions of different sources to PAHs in surface sediments from Town, SSC, MSC, and LSC urban sections were calculated based on the regressed linear model (Larsen and Baker 2003). All statistical analyses were implemented using the SAS software (Ver. 9.1.3 for Windows®, SAS Institute Inc., Cary, NC, USA).

3 Results and discussion

3.1 Urbanization effects on concentration and composition of PAHs and PCBs in surface sediments of the Canal

Total 16 priority PAHs' concentration ranged from 0.66 to 22 mg/kg in surface sediments from nine urban sections and an agricultural section along the Canal (Fig. 2a). In comparison with other urban areas in the world, surface sediments from urban sections of the Canal had compatible ranges of total 16 priority PAH's concentration except surface sediments from heavily contaminated waters, like waterways in Tacoma, WA, USA and Sydney Harbour, Australia (Table 1). Grouped by the four-level urbanization gradient (i.e., Town, SSC, MSC, and LSC), the total 16 PAH concentration, regardless of mean or median, increased from town to SSC and then decreased from SSC to MSC, and to LSC (Fig. 2a). This significant trend ($p<0.05$) right fits into the inverted U environmental Kuznets Curve (Orubu and Omotor 2011), suggesting that PAHs in sediments might record urbanization effects on environmental changes. Although there are few studies on urbanization level gradient from town to large city like this study, a PAH gradient was also found along a rural–urban transect in a Mid-Atlantic coastal river basin (USA), which correlated to population density in the nearby sub-basins (Forster and Cui 2008). But, Wong et al. (2009) found a weak rural–urban gradient for PAHs in surface sediments from the Greater Toronto Area, Ontario, Canada. The composition of 16 priority PAHs (grouped by the ring number in compounds) was at similar percentages for five- and six-ring compounds in surface sediments from agricultural and urban sections (Fig. 2b). However, the four-ring PAHs portions were considerably higher in surface sediments from urban sections from the agricultural sections, while the three-ring PAHs portions were reverse (Fig. 2b). Similarly, four-ring PAH compounds

Table 1 Total 16 priority PAHs and total PCBs in surface sediments from urban water in the world

Pollutant	Location	Site	Population[a] (×1,000)	Urban type	Range	Reference
PAHs (mg/kg)	Norfolk, VA, USA	Urban wetland	233	SSC	1.2–22	Kimbrough and Dickhut 2006
	Tacoma, WA, USA	Waterways	198	SSC	15–3,594	Stout et al. 2003
	Wuxi, China	Urban bay in Lake Tai	2,359	MSC	1.2–4.8	Qiao et al. 2006
	Sydney, Australia	Harbour	4,575	LSC	0.1–380	McCready et al. 2000
	Naples, Italy	Harbour	4,996	LSC	0.01–31	Sprovieri et al. 2007
	Hanoi, Vietnam	Urban lakes	6,500	LSC	1.6–2.3	Kishida et al. 2007
	Ho Chi Minh, Vietnam	Urban channels	>9,000	LSC	4.3–6.4	
	Bangkok, Thailand	Canals	9,100	LSC	0.5-8.4	Boonyatumanond et al. 2006
	Beijing, China	Urban rivers	14,930	LSC	0.2–8.7	Shen et al. 2009
	Yangtze River Delta, China	South section of the Grand Canal	53–101	Town	0.82–11	This study
			104–251	SSC	0.66–22	
			2,353–3,068	MSC	2.4–16	
			4,227	LSC	1.9–12	
PCBs (μg/kg)	Naples, Italy	Harbour	4,996	LSC	1–899	Sprovieri et al. 2007
	Hanoi, Vietnam	Urban lakes	6,500	LSC	21	Kishida et al. 2007
	Ho Chi Minh, Vietnam	Urban channels	>9,000	LSC	44–110	
	Wuhan, China	Streams and tributaries	9,785	LSC	1.2–45	Yang et al. 2009a, b
		Urban lakes			0.9–46	
	Yangtze River Delta, China	South section of the Grand Canal	53–101	Town	0.5–60	This study
			104–251	SSC	3.8–33	
			2,353–3,068	MSC	4.7–49	
			4,227	LSC	12–93	

[a] Data of population for most international cities were mainly extracted from wikipeida.org. Some were from the reference if available. Population of studied cities was extracted from local yearbooks in 2007

predominated in surface sediments from urban rivers in Beijing, China (Shen et al. 2009), Sydney Harbour, Australia (McCready et al. 2000), and riverine, estuarine, and marine sediments in Thailand (Boonyatumanond et al. 2006). Therefore, the distribution and composition of 16 priority PAHs in surface sediments of this study had an urbanization gradient from Agricultural section to Town, SSC, MSC, and LSC urban sections.

PCBs ought to relate to urbanization process because PCB congeners had been widely used in urban livings since 1920s. In other words, PCB congeners become a point pollutant with urban characteristics and historic records since its worldwide ban. Sum of the tested 16 PCB congeners was from 0.5 to 93 μg/kg in the surface sediments from the Canal (Fig. 3a) and PCB-126 was completely not determined in all sections of the Canal.

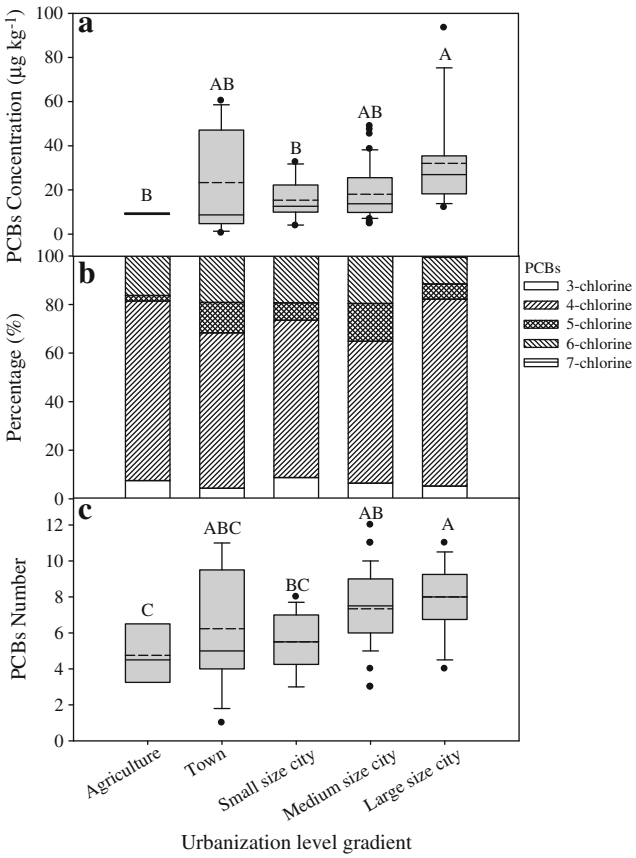

Fig. 3 Total concentrations (**a**), constitution (**b**, median in percentage), and detected number (**c**) of 16 common PCBs in surface sediments from agricultural and urban sections of the Grand Canal along an urbanization gradient. The urbanization gradient consisted of one agricultural section (4 points), three town urban sections (Town, 13 points), two small-size city (SSC, 12 points) urban sections, three medium-size city (MSC, 44 points) urban sections, and one large-size city (LSC, 14 points) urban sections. *Different letters above the bars* indicated significant difference between the two urbanization levels ($p<0.05$) which was tested by a Duncan's Multiple Range Test following a GLM–ANOVA. In the *boxplots*, the *dash line* represents the mean, while the *solid line* showed the median

Regardless of urban type, PCB pollution in the Canal of this study was relatively low in comparison with Naples Harbour, Italy and urban channels of Ho Chi Minh, Vietnam (Table 1). The lowest concentrations of total detected PCBs were found in surface sediments from the Agricultural section, averagely 9.26±0.32 μg/kg (the median is same). Both median and mean concentrations of total detected PCBs in surface sediments from urban sections increased with the urbanization level gradient from Town to LSC except the mean concentrations in the Town sections were larger than in the SSC urban sections but not significant ($p<0.05$, Fig. 3a). The LSC urban surface sediments had significant greater concentrations of total detected PCBs than both SMC and agricultural surface sediments ($p<0.05$, Fig. 3a). This trend pointed out that PCBs have urban characteristics as we hypothesized. In terms of composition of PCB congeners, surface sediments from both agricultural and urban sections of the Canal were dominated by four-chlorine PCB congeners and seven-chlorine PCB congeners were scarcely detected in the surface sediments (Fig. 3b). The urban sections of the Canal had much larger portions of five-chloride PCBs in the surface sediments than the Agricultural section (Fig. 3b). The surface sediments from streams in Wuhan, China were also dominated by four- and five-chlorine PCB congeners (Yang et al. 2009a). Interestingly, not all 16 PCB congeners were detected in surface sediments (Fig. 3c) and the number of detected PCB congeners in surface sediments significantly increased with the urbanization level gradient, especially by median, i.e., LSC>MSC>SSC= Town>Agricultural sections ($p<0.05$, Fig. 3c). This result further confirmed that the developed urban areas used more PCB congeners in species than the developing urban areas, i.e., the urbanization effect. A weak urban–rural gradient effect was found on PCBs in surface sediments of the Greater Toronto Area, Canada (Wong et al. 2009). Urbaniak et al. (2008) also found that an urban catchment discharged higher PCBs amounts into the reservoir sediments than an agricultural and urban mixed catchment. However, Forster and Cui (2008) did not find a close correlation between PCBs in surface sediments and population density of sub-basins in the Mid-Atlantic coastal river basin (USA).

On the other hand, physicochemical properties of surface sediments play an important role to redistribute PAHs and PCBs between water and sediment and in a spatial dimension (Hong et al. 2005; Cavalcante et al. 2009). It might shade urbanization gradient effects on PAHs and PCBs distribution in surface sediments, especially in this study whose surface sediments were collected from different sections of the Canal. The regression analysis exhibited that the sum PCB congeners' concentration had significant correlations with pH, EC, and TOC in surface sediments ($p<0.05$, $n=87$), while the total 16 priority PAHs did not show any statistically significant correlations with

Table 2 Linear regression of total 16 priority PAHs and detected PCBs concentrations with surface sediment physico-chemical properties

Compound	Sediment property	Number of observations	*F* value	*P* value	Adjusted R^2
PAHs	pH	87	3.44	0.0672	0.0275
	EC	87	2.17	0.1449	0.0134
	TOC	87	1.80	0.1835	0.0092
PCBs	pH	87	3.95	0.0502	0.0331
	EC	87	62.67	<0.0001	0.4176
	TOC	87	17.03	<0.0001	0.1571

physicochemical properties of the surface sediments (Table 2). Previous study pointed out that distribution of PAHs in sediment might relate to input sources rather than sediment properties (Tam et al. 2001). Therefore, in this study, PAHs showed a clear environmental Kuznets curve with the urbanization gradient (Fig. 2a) suggesting PAH inputs derived from various sources and sediment properties did not shade the urbanization gradient effects. However, PCBs present a different urbanization gradient pattern, i.e., a positive linear trend with the urbanization gradient. It hints that the limited PCBs by the ban on sale and production in 1979 worldwide recorded the urbanization history due to their remarkable stability in the environment (Fig. 3a) and high correlation with sediment abiotic properties (Table 2).

Furthermore, we employed population and economic indices (GDP and its constituents and corresponding per capita indices) and reduced these indices to one by principle component analysis (PCA) to quantify urbanization level instead of by sole population index (data not shown here). But no correlations between quantitative urbanization level (PCA 1) and total PAH/PCB concentrations in surface sediments were observed. Van Metre et al. (2000) used urban land uses as the urbanization level index and did not found significant relationships between PAHs concentrations in urban lake surface sediments and urban land uses. It might be true that both their and our studies employed indices to quantify urbanization level which do not relate to PAH sources although these indices are overwhelmingly used to quantify urbanization levels. Our previous study indicated that economic indices had strong correlations with surface water quality (nitrogen, phosphorus, and metals) in the Canal (Yu et al. 2011).

3.2 Source apportionment of PAHs and PCBs in surface sediments of the Canal

Sources of PAHs have been identified deriving from incomplete combustion processes or pyrolysis of organic matter, spillage of petrogenic hydrocarbons, and biogenesis (Forster and Cui 2008). Vehicles, coal/oil combustion power generation, heating, and cooking, etc., were considered as anthropogenic activities for pyrolytic PAH sources. Of anthropogenic PAHs, low-molecular-weight PAHs originate from both petrogenic and combustion (low-temperature pyrolysis) sources, while high-molecular-weight PAHs are predominately from pyrolytic source (Mai et al. 2002). Previous studies found that ratios of certain PAHs can distinguish their possible sources, like isomer ratios of Ant/Ant+Phe, Flu/Flu+Pyr, BaA/BaA+Chr, and InP/InP+BgP (Yunker et al. 2002; Katsoyiannis et al. 2007;

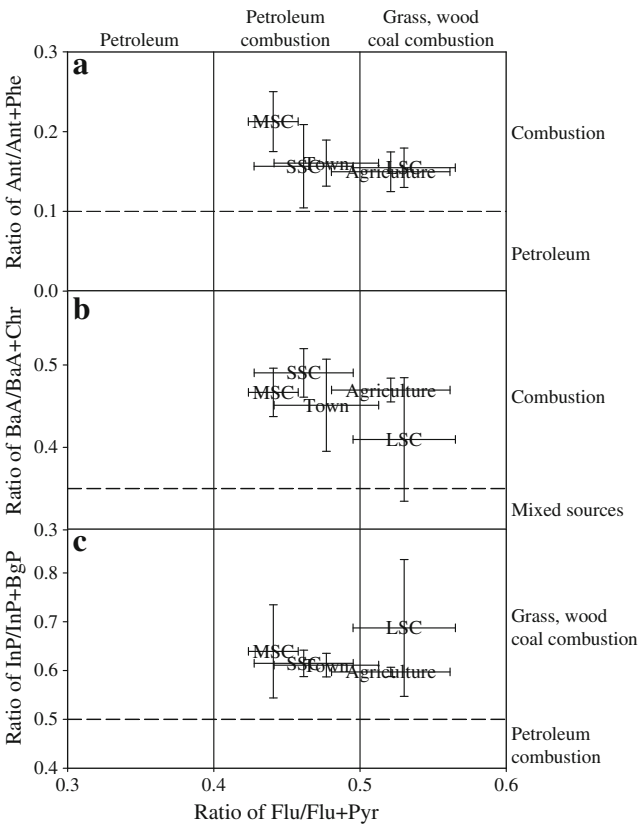

Fig. 4 Source apportionment of PAHs by ratios of fluoranthene (Flu)/Flu+pyrene (Pyr), anthracene (Ant)/178 (**a**), benzo[a]anthracene (BaA)/228 (**b**), and indeno[1,2,3-c,d]pyrene (InP)/InP+benzo[g,h,i]perylene (BgP) (**c**) in surface sediments from agricultural and urban sections of the Grand Canal along an urbanization gradient. The urbanization gradient consisted of one agricultural section (4 points), three town urban sections (Town, 13 points), two small-size city (SSC, 12 points) urban sections, three medium-size city (MSC, 44 points) urban sections, and one large-size city (LSC, 14 points) urban sections

Brandli et al. 2007). In this study, we further hypothesized that possible sources of surface sediment PAHs might differ from urban sections with various urbanization levels, i.e., urbanization effects on PAH sources. Biplots of Ant/Ant+Phe, BaA/BaA+Chr, and InP/InP+BgP ratios against Flu/Flu+Pyr ratio indicated that both surface sediments from agricultural and LSC urban sections were dominated by grass, wood, and coal combustion source PAHs, while Town, SSC, and MSC urban sections might receive PAHs in surface sediments predominantly from petroleum combustion (Fig. 4). It might be true because agricultural sections received PAHs from local biomass combustion, while the LSC urban sections received PAHs from massive coal combustion for power generation, like in Shanghai (Guo et al. 2009).

Contributions of various sources to PAHs in surface sediments of the Canal, calculated by the Factor Analysis-Multiple Linear Regression approach (FA-MLR, Hopke 1985; Larsen and Baker 2003), pointed out that the Town sections mainly received PAHs from coal and vehicular mixed sources (58.8%) and vehicular emission (30.1%) sources; the SSC urban sections were dominated by vehicular emission source (49.7%) and followed by mixed sources (22.6%) and coal combustion source (20.5%); the MSC urban sections had PAHs mainly from both mixed (30.7%) and coal combustion (34.5%) sources; and the LSC urban sections got PAHs predominantly from coal combustion (37.5%) but less from vehicular emission (9.1%) sources (Table 3). This pattern is quite different from other sites, like mangrove sediments in Shantou coastal zone, China (Cao et al. 2011), sediments from Beijing urban river system (Shen et al. 2009), and surface sediments from Black River and Ashtabula River, OH, USA (Christensen and Bzdusek 2005). The Canal has been served as a waterway in the Yangtze River Delta city cluster since it was dug thousands of years ago. Bargo traffics are very heavy everyday even nowadays, especially in the Town and SSC sections, because of cheap costs. It can be

Table 3 PAH source apportionment and relative contributions in surface sediments of the Canal using a factor analysis with varimax rotation and Kaiser's normalization and multiple linear regression

PAH	Ring	Factor1	Factor2	Factor3	Factor4	Factor5
Naphthalene (Nap)	2	0.369	0.130	0.134	**0.886**	0.194
Acenaphthylene (Acy)	3	0.321	0.194	0.420	0.341	**0.738**
Acenaphthene (Ace)	3	0.130	0.090	**0.970**	0.060	0.038
Fluorine (Fl)	3	0.105	0.102	**0.974**	0.068	0.121
Phenanthrene (Phe)	3	0.270	0.157	**0.921**	0.053	0.151
Anthracene (Ant)	3	**0.634**	0.249	**0.571**	0.258	0.200
Pyrene (Pyr)	4	**0.823**	0.309	0.296	0.221	0.173
Fluoranthene (Flu)	4	**0.753**	0.317	0.306	0.178	0.413
Benzo[a]anthracene (BaA)	4	**0.895**	0.336	0.135	0.194	0.041
Chrysene (Chr)	4	**0.894**	0.263	0.170	0.102	0.181
Benzo[b]fluoranthene (BbF)	5	**0.911**	0.320	0.127	0.100	0.037
Benzo[k]fluoranthene (BkF)	5	**0.897**	0.302	0.107	0.132	0.037
Benzo[a]pyrene (BaP)	5	0.369	**0.895**	0.073	0.079	−0.061
Dibenzo[a,h] anthracene (DBA)	5	0.187	**0.868**	0.209	0.077	0.209
Indeno[1,2,3-c,d]pyrene (InP)	6	0.429	**0.856**	0.111	0.153	0.053
Benzo[g,h,i]perylene (BgP)	6	0.374	**0.873**	0.139	0.011	0.152
Variance explained (%)		62.7	15.6	9.6	5.1	2.3
Cumulative (%)		62.7	78.3	87.9	93.0	95.3
Possible source	Number of sample	Coal and vehicular mixed source Contribution (%)	Vehicular emission	Coal combustion	Unburned petroleum	Coal tar
Agricultural section	4	–	–	–	–	–
Town section	13	58.8	30.1	5.1	6.2	–
Small-size city section	12	22.6	49.7	20.5	7.3	–
Medium-size city section	44	30.7	18.0	34.5	8.0	8.8
Large-size city section	14	21.9	9.1	37.5	6.7	24.8

Correlation efficients larger than 0.5 are stated in bold

Table 4 Percentage of sampling points with 9 PAHs (individual and sum) exceeding the threshold effect concentration (TEC) (Swartz 1999; Vinas et al. 2010)

Section	Number of sampling site	3-Ring		4-Ring				5-Ring			Sum
		Phe	Ant	Pyr	Flu	BaA	Chr	BbF	BkF	BaP	
Agriculture	4	100	75	50	75	100	25	100	25	75	100
Town-1	4	25	0	0	0	50	25	50	0	50	25
Town-2	4	0	0	0	0	0	0	25	0	0	0
Town-3	5	60	0	0	0	20	0	20	0	0	0
SSC-1	5	100	80	80	80	100	80	100	40	60	80
SSC-2	7	71	0	29	29	86	57	86	14	71	43
MSC-1	11	64	9	36	18	45	36	64	9	9	36
MSC-2	17	94	12	53	47	82	53	88	6	53	100
MSC-3	16	81	44	56	56	100	63	100	38	63	56
LSC	14	36	7	14	21	29	29	43	14	14	21
Threshold of effect concentration (mg/kg organic carbon)		25	13	51	59	20	30	26	23	31	278

Phe phenanthrene, *Ant* anthracene, *Pyr* pyrene, *Flu* fluoranthene, *BaA* benzo[a]anthracene, *Chr* chrysene, *BbF* benzo[b]fluoranthene, *BkF* benzo[k]fluoranthene, *BaP* benzo[a]pyrene

confirmed by a constant contribution of the unburned petroleum source and vehicular emission to sedimentary PHAs regardless of urbanization gradient. Petroleum leaking is very common for bargo operation and consistent in all urban sections regardless of urbanization level (Table 3). Higher contributions of vehicular-emitted PAHs in the Town and SSC urban sections possibly exhibit heavier bargo traffics than in the MSC and LSC urban sections are mainly for sightseeing boats in the ancient Grand Canal. Coal combustion sources (including the coal tar source) of PAHs in surface sediments increased with the urbanization gradient from 5.1% in the Town sections to 37.5% in the LSC section (from 8.8% in the MSC sections to 24.8% in the LSC section for the coal tar source) (Table 3). The increasing contribution of coal sources with the urbanization gradient further confirmed the above ratio analysis, i.e., medium- and large-size cities annually consumed a large amount of coal for power generation. Therefore, both source apportionment approaches confirmed urbanization gradient effects on PAH sources, suggesting that PAHs might act as a tracer for environmental quality shifts under the urbanization process.

PCBs pollution in environmental matrices is quite different from PAHs pollution. PCBs were banned on production in late 1970s worldwide. The environment does not receive PCB congeners continuously from various sources like PAHs. But, PCBs' stable biochemical property makes them still spreading throughout the global environment, especially in water systems (Carrizo and Gustafsson 2011). Since there is no more PCBs produced and used nowadays, places and facilities used or contained PCBs become sources of PCBs contamination, like electrical transformers and capacitors, and paints. Of China-produced PCBs in 1965–1975, 10% were used as paint additive (Kang et al. 2000). Recently, a study reported PCB distribution and inventories in the north polar (Carrizo and Gustafsson 2011). However, so far, we are unable to apportionment PCB sources in different environmental matrices.

3.3 Ecological risk assessment of PAHs and PCBs in surface sediments from urban sections of the Canal

Risks of PAHs and PCBs in surface sediments from urban sections of the Canal are very important to publics since urban dwellers, especially kids and youths, have numerous opportunities to contact the polluted water and sediments. On the other hand, to assess ecological risks of PAHs and

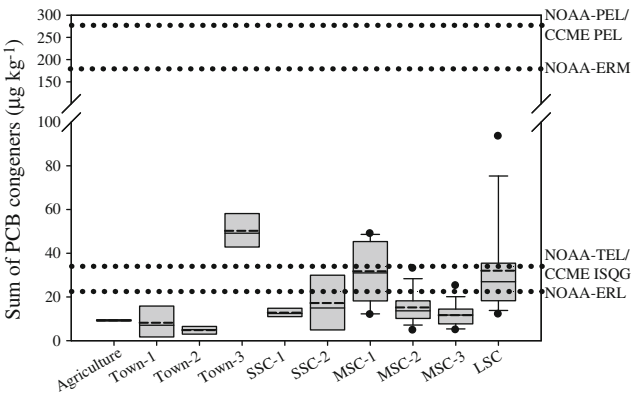

Fig. 5 Ecological risk assessment for PCBs in surface sediments from urban and agricultural sections of the Canal by US-NOAA and CCME sediment quality guidelines. *ERL* effect range low (22.7 μg/kg), *ERM* effect range median (180 μg/kg), *TEL* threshold effect level (34.1 μg/kg), *PEL* probable effect level (277 μg/kg), *ISQG* interim sediment quality guideline (34.1 μg/kg), cited from Burton (2002)

PCBs in surface sediments might provide a basis of management practices for local governments.

Ecological risk assessment of nine PAHs (Phe, Ant, Pyr, Flu, BaA, Chr, BbF, BkF, and Bap) in surface sediments employed the consensus-based sediment quality guidelines (Swartz 1999) and the threshold effect concentration (TEC) of the total nine PAHs used the result of Vinas et al. (2010). Results indicated that sampling sites from SSC, MSC, and LSC urban sections and agricultural section had nine PAHs in surface sediments exceeding individual PAH TECs except the sampling sites from the Town urban sections (Table 4). There was only in the SSC-1 section that four out of five sampling sites had Phe over the probable effect concentration (PEC, 127 μg/kg), but no sections were detected over the toxic effect concentrations (TECs) (Swartz 1999). For the total nine PAHs, all sections, except Town-2 and Town-3 urban sections, had surface sediments over TEC set by Vinas et al. (2010). Of the nine specific PAHs, BbF, Phe, and BaA were priority PAHs possibly contaminating the whole area. BbF was found in all sections of the Canal over its TEC and nine out of ten sections had Phe and BaA exceeding their TECs (Table 4).

Adapting the sediment quality guidelines from the US National Oceanic and Atmospheric Administration (US-NOAA) and Canadian Council of Ministers of the Environment (CCME) (Burton 2002), surface sediments from agricultural and urban sections of the Canal situated at a low risk level of PCB contamination (Fig. 5). Most sections had the sum of PCBs ranging round the effect range low (NOAA-ERL, 22.7 μg/kg) and threshold effect level (NOAA-TEL)/interim sediment quality guidelines (CCME-ISQG)(34.1 μg/kg). Agricultural section, Town-1 and Town-2, and SSC-1 urban sections even had the sum of PCBs below the NOAA-ERL while only the Town-3 urban section was slightly above the NOAA-TEL/CCME-ISQG (Fig. 5). All surface sediments were far away from the effect range median (NOAA-ERM, 180 μg/kg) and the probable effect level (NOAA/CCME-PEL, 277 μg/kg) (Fig. 5).

Overall, surface sediments from agricultural and urban sections of the Canal were slightly contaminated by PAHs and PCBs. But cautions should be taken for further contaminations of PAHs since the increasing demands of energy might lead to massive coal consumption. On the other hand, PCB-contained facilities in the watershed should be well-managed avoiding further contamination.

4 Conclusions

Surface sediments from agricultural and urban sections of the Grand Canal, China were slightly contaminated by PAHs and PCBs. But both concentration and composition of PAHs and PCBs in surface sediments indicated an urbanization gradient. Since PAHs and PCBs quite differ in source, their urbanization gradient effect patterns varied accordingly in surface sediments of the Canal. Total PAHs showed an inverted U environmental Kuznets Curve with the urbanization gradient, while PCBs present a linear increasing trend with the urbanization gradient for both total amount and number of PCBs detected. For the composition, PAHs were dominated by four-ring compounds in surface sediments from urban section and PCBs were by four-chlorine congeners regardless of agricultural and urban sections. Both PAHs and PCBs in surface sediments from the Canal ranged at a trigging concentration of ecological risk. Efficient input source control and management should be taken into account for preventing further organic contamination in the Canal. With the source apportionment, PAHs in surface sediments of the Canal mainly derived from combustion sources identified by ratios and FA-MLR model. Coal-related combustion contribution showed a clear urbanization gradient effect. Both ratio plotting and FA-MLR model indicated that coal combustion was a predominant source for surface sediment PAHs in the LSC urban section, suggesting coal combustion power generation need to be considered for avoiding further PAHs contamination in the region. In short, both PAHs and PCBs in surface sediments showed urbanization gradient effects even though their patterns varied. It confirmed the hypothesis that PAHs and PCBs can act as tracers for urbanization process among individual urban areas as well as the rural–urban gradient.

Acknowledgments This study was financially supported by "Knowledge Innovation Program" (KZCX2-YW-Q02-02) and "Hundred Talent Program" (No. A0815) of Chinese Academy of Sciences. Authors gratefully thank Prof. Max Häggblom from Rutgers University for his valuable comments, Dr. Beth Ravit for English polishing, and Dr. Xian Zhang in Institute of Urban Environment, Chinese Academy of Sciences for kindly help in GC–MS analysis. Authors appreciate valuable comments from two anonymous reviewers.

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