PAHs in organic film on glass window surfaces from central Shanghai, China: distribution, sources and risk assessment

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Abstract Polycyclic aromatic hydrocarbons (PAHs) concentrations were analysed in the organic film on the glass surfaces of different functional areas in central Shanghai. Concentration levels of total PAHs in the organic film ranged from 1,348.5 to 4,007.9 ng m^{-2}. The concentration of PAHs was lowest in parks and green spaces (1,348.5 ng m^{-2}) and highest in traffic zones (4,007.9 ng m^{-2}). A concentration gradient of total PAHs was observed as follows: traffic zones > commercial areas > cultural and educational areas > parks and green spaces. The distribution of PAHs was characterised by 3–4 ring PAHs in the study areas. The most abundant PAHs were phenanthrene (20.5 %), fluorene (16.7 %), pyrene (12.4 %) and chrysene (Chry) (11.2 %). The mass of the bulk film was composed of organic and inorganic compounds and ranged from 246 to 1,288 mg m^{-2}. The bulk film thickness varied from 144 to 757 nm in the different functional areas. The ratios of An/178 and Fl/202 and principal component analysis suggested that PAHs came mainly from the mixed sources of fossil fuel, coal and incomplete combustion of biomass. Benzo[a]anthracene (BaA)/ Chry is not suitable for use as a tracer for the transmission process of PAHs because of the rapid depletion of BaA in the organic film by photooxidation during daylight hours. The concentration of benzo[a]-pyrene equivalent (BaPeq) varied from 21 to 701 ng g^{-1}, and the major carcinogenic contributors of the 16 PAHs were BaP, DahA, B[b/k]F and InP, accounting for 83 % of BaPeq.

Keywords PAHs · Glass surface · Organic film · Source apportionment · Shanghai

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic compounds composed of two or more fused aromatic rings. PAHs are formed primarily by incomplete combustion and pyrolysis of organic compounds (Wang et al. 2013). PAHs are ubiquitous in the urban environment; especially in mega-cities, large emissions of PAHs have been observed due to accelerated urbanisation and high-density traffic conditions. PAHs have gained great attention due to their teratogenicity, carcinogenicity and mutagenicity (Castro et al. 2011; Petry et al. 1996). One of the best-known PAHs, benzo[a]pyrene (BaP), is classified by

the International Agency for Research on Cancer (IARC) as carcinogenic to human health (IARC 2010).

Urban impervious surfaces such as glass, pavement and roofs are typical products of high urbanisation. A thin organic film could develop on impervious surfaces from the condensation and deposition of gas- and particle-phase organic contaminants and their transformation products that occur at elevated concentrations in urban air (Diamond et al. 2000). The few existing studies show that the proportion of organic matter in organic film ranges from approximately 5 to 20 %. Organic film on glass windows was suggested to be an effective passive sampler for semivolatile lipophilic air pollutants such as PAHs (Diamond et al. 2000; Law and Diamond 1998). Moreover, organic film can act as a dynamic sink/source for PAHs (Diamond et al. 2000), i.e. gaseous and particulate PAHs, can be adsorbed into the organic film and then transmitted to the atmosphere or into surface water bodies through evaporation or rainfall erosion (Diamond et al. 2001). Thus, organic film plays an important role in the distribution and behaviour of PAHs in the urban environment.

As one of the largest cities in China, Shanghai is an important industrial and economic centre and is intensively urbanised. Impervious surfaces have increased rapidly and formed the city's second physical geographical pattern (Alberti et al. 2006). Due to a significant increase in automobile and construction activities, the city is also under the stress of airborne contaminants such as PAHs. However, until now most studies have focussed on the occurrence and distribution of PAHs in dust, rivers, soils and plants in urban areas (Cheng et al. 2007; Liu et al. 2007; Qiao et al. 2010; Ren et al. 2006). Information on the content of PAHs in the organic film on window glass is lacking. In the present study, fifteen organic film samples were taken from glass window surfaces in different functional areas. The objective of this study was to evaluate the contamination levels and sources of PAHs in organic film on glass surfaces in Shanghai.

Materials and methods

Study area and sample collection

In March 2012, fifteen organic film samples were collected from the exterior of glass surfaces of buildings in parks and green spaces, cultural and educational areas, commercial areas and traffic zones in central Shanghai (including the Jing'an District, Huangpu District, Xuhui District, Changning District, Hongkou District, Yangpu District, Putuo District, Zhabei District) (Fig. 1). The samples were collected by scrubbing the surface of windows with dichloromethane (DCM)-rinsed laboratory tissues. The laboratory tissues were pre-extracted with DCM. A 10-cm border was left around the outside of the window area to minimise contamination from window sealant materials or paints. A sample was collected from approximately 0.1 m^2 of window at each site. Field blanks were prepared at two sites by waving the laboratory tissues that had been wetted with DCM in the air until dry (Butt et al. 2004). Samples covered with aluminium foil were brought back to the laboratory and stored at −20 °C until extraction.

PAHs extraction and clean-up

The procedure for PAHs extraction was modified from the procedure used in Wang et al. (2012). Briefly, samples were extracted with 120 mL of mixed solvent [acetone and DCM (1:1, v/v)] for 20 h using a Soxhlet apparatus. Extracts were concentrated to perform a solvent substitution with n-hexane, and the samples were then purified by passing them through a silica–alumina column (silica: 8 g, 100–200 mesh, activated at 160 °C for 24 h, and deactivated with 10 % water; alumina: 4 g, 50–200 mesh, activated at 400 °C for 4 h, and deactivated with 10 % water). The top of the column was filled with 1 g of anhydrous sodium sulphate (baked at 450 °C for 4 h). The first component, which contained alkanes, was eluted with 15 mL of n-hexane. The second component, which contained the target PAHs, was eluted with 70 mL of mixed solvent (DCM and n-hexane (3:7, v/v)). Finally, the PAH eluent was reduced to 1 mL for gas chromatography/mass spectrometry (GC/MS) analysis.

The samples were detected using a GC equipped with a DB-5 polysiloxane polymer column (30 m × 0.25 mm i.d., film thickness 0.25 μm), with helium as the carrier gas at 1 mL min^{-1} flow. The oven temperature was held at 55 °C for 2 min, heated to 280 °C at a rate of 20 °C min^{-1} and held for 4 min, and then heated to 310 °C at a rate of 10 °C min^{-1} and held for 5 min. The injection volume was 1 μL in splitless mode. In this study, the 16 PAHs prioritised
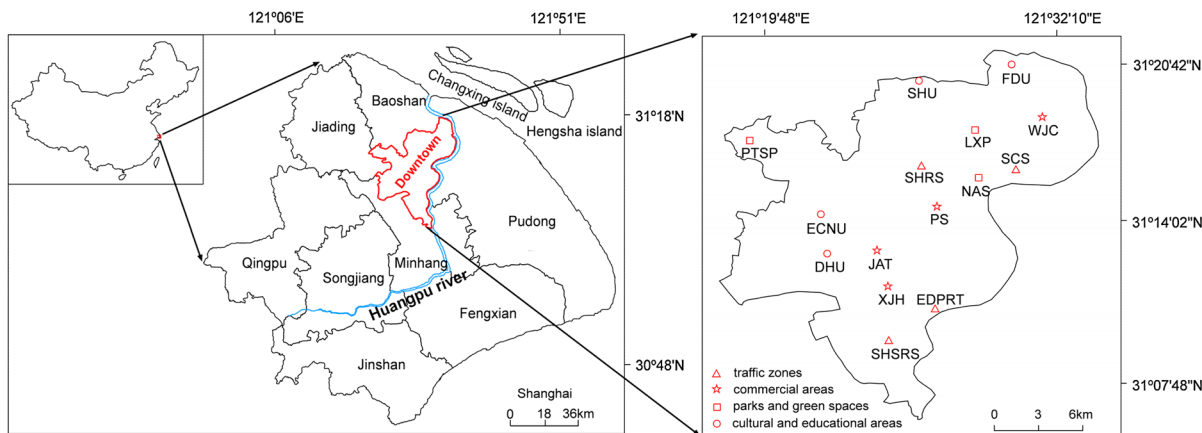
Fig. 1 Map showing the study area and sampling locations

by the United States Environmental Protection Agency (USEPA) were analysed: naphthalene (NaP), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phe), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP). B[b]F and B[k]F were calculated together as B[b/k]F because their peaks overlapped in the chromatographic analysis (Wang et al. 2012).

Quality control and quality assurance (QC/QA)

Field blanks and method blanks were analysed routinely to determine any background contamination. NaP and Phe were detected in some field blank samples (<3 % of the actual content of the sample). The experimental procedure was tested for recoveries by analysing spiked blanks with the 16 PAH standards, and the recoveries of the 16 PAHs ranged from 70 to 110 %. Five surrogate standards were added to the organic film samples to determine the recoveries of the PAHs in the real samples. The recoveries of the surrogate standards were NaP-d_8, ranging from 79.8 to 95.1 %; Ace-d_{10}, ranging from 79.9 to 95.7 %; Phe-d_{10}, ranging from 74.8 to 98.9 %; Chry-d_{12}, ranging from 77.8 to 106.2 % and Per-d_{12}, ranging from 80.1 to 101.7 %. Blanks were deducted from the final results, and the final results were corrected for the recoveries.

Results and discussion

Organic film on glass

The total mass of film and bulk film thickness (Table 1) varied according to how "dirty" the glass was. The mass of organic film for commercial areas ranged from 356 to 3,130 mg m^{-2} (geometric mean is 1,288 mg m^{-2}) and was significantly higher than the mass of organic film for traffic zones (677 mg m^{-2}), cultural and educational areas (563 mg m^{-2}), and parks and green spaces (246 mg m^{-2}) in central Shanghai as well as that for Toronto (100 mg m^{-2}) and Hong Kong (200 mg m^{-2}) (Gingrich and Diamond 2001; Li et al. 2010). The mass of organic film for parks and green spaces was slightly lower than that for Baltimore (306 mg m^{-2}) and Guangzhou (560 mg m^{-2}) (Li et al. 2010; Liu et al. 2003).

Research results have shown that a 10–1,000-nm thickness of organic film may be formed on an urban impervious surface (Law and Diamond 1998). Organic and inorganic compounds can contribute to bulk film thickness. In general, bulk film thickness was calculated according to the formula shown in the following equation:

$$Ft = M\left(mg\,m^{-2}\right) \times 10^9\left(nm\,m^{-1}\right)/1.7 \times 10^9\left(mg\,m^{-3}\right)$$

where M is the total mass of organic film including organic and particulate phases, and 1.7×10^9 (mg m^{-3}) is the density of the atmospheric aerosol (Liu et al. 2003). The bulk film thickness was greater at urban sites than at suburban and rural sites (Liu et al.

Table 1 Thickness and mass of organic film and PAH distribution in organic film

	Parks and green spaces		Cultural and educational areas		Commercial areas		Traffic zones	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Organic film thickness (nm)[a]	132.7–164.7	144.7 ± 17.01	133.4–676.4	331.2 ± 403.9	209.6–1,841.8	757.9 ± 875.5	87.3–609.2	398.4 ± 275.1
Organic film mass (mg/m²)[b]	218–280	246 ± 29	226–1,150	563 ± 238	356–3,130	1,288 ± 1,488	148–1,035	677 ± 468
NaP (ng/m²)	69.4–104	88.7 ± 16	143.2–271.4	222.7 ± 57.1	137.8–289.2	208.4 ± 71.1	62.1–229.9	169.6 ± 93.4
Acy (ng/m²)	19.6–20.3	19.1 ± 1.0	22.4–78.1	42.1 ± 25.4	37.2–80.4	44.8 ± 21.6	13.8–67.7	43.9 ± 27.5
Ace (ng/m²)	15.1–78.9	39.4 ± 28.0	22.9–37.8	29.7 ± 6.3	19.7–45.4	28.8 ± 10.5	7.2–38.2	26.4 ± 16.8
Fluo (ng/m²)	47.3–66.6	57.9 ± 8.1	70.6–141.9	105.1 ± 36.3	75.8–190.2	135.2 ± 48.6	45.8–158.1	115 ± 60.6
Phe (ng/m²)	205.9–461	296.8 ± 113	315.6–859.1	615.3 ± 229.4	340.6–889.4	590 ± 246.4	239.6–933.9	678.3 ± 381.9
An (ng/m²)	19.2–29.5	23.2 ± 4.4	48.5–75.7	63.4 ± 12.7	39.2–88.2	59.8 ± 29.5	21–110.8	74.8 ± 47.5
Fl (ng/m²)	127.8–231.6	191.7 ± 44.8	324–964.6	559 ± 294.2	241.5–1,161	567.2 ± 419.5	350.6–836.4	631 ± 251.4
Py (ng/m²)	109.1–175.1	138.5 ± 33.7	197.5–769.4	441.2 ± 252.1	184.4–923.7	438.4 ± 342.0	189.4–705.6	494.7 ± 270.8
BaA (ng/m²)	21.7–56.7	39.6 ± 14.8	33.1–283.7	150.2 ± 106.6	45.7–263.9	126.7 ± 98.9	35.1–277.8	177.5 ± 126.7
Chry (ng/m²)	89.8–159.1	124.6 ± 32.6	150.8–712.8	373.7 ± 249.1	169.4–996.1	418.6 ± 385.6	164.8–764.5	508.5 ± 309.3
B[b/k]F (ng/m²)	33.3–97.1	68.2 ± 26.9	86–472.3	235.3 ± 169.1	108–548.8	235.9 ± 204.0	76.6–422.4	273.6 ± 177.9
BaP (ng/m²)	17.8–59.8	36.5 ± 17.5	36.3–336.2	168.8 ± 125.7	28.3–327.4	142.4 ± 132.5	32.6–281.8	176.3 ± 129.0
InP (ng/m²)	18.9–48.8	34.1 ± 12.3	45.6–256.8	132.2 ± 91.4	37.2–330.6	131.7 ± 133.9	35.5–250.5	163.6 ± 113.3
DahA (ng/m²)	10.4–18.5	12.8 ± 3.8	13.8–86.1	43.4 ± 31.8	9.1–94.7	40.6 ± 38.7	6.4–78.6	50.9 ± 38.9
BghiP (ng/m²)	25.1–69.7	48 ± 18.6	59.6–371.1	185.9 ± 136.3	49.6–450.8	184.6 ± 183.0	47.6–355.6	225.3 ± 159.3
T-PAH s (ng/m²)	1,159.6–1,512.4	1,348.5 ± 145.1	2,213.7–6,052.3	3,645.9 ± 1,735.1	2,270.9–7,042.2	3,655.6 ± 2,254.3	1,426.1–5,672.5	4,007.9 ± 2,266.9

[a] Organic film thickness = M (mg m^{-2}) $\times 10^9$ (nm m^{-1})/1.7 $\times 10^9$ (mg m^{-3}). M is the quality of an organic film, and 1.7 $\times 10^9$ (mg m^{-3}) is the density of the atmospheric aerosols

[b] Organic film mass was obtained by pre- and post-weighing of gravimetric samples

2003). In this study, the bulk film thickness for parks and green spaces, cultural and educational areas, commercial areas and traffic zones ranged from 132 to 164, 133 to 676, 209 to 1,841 and 87 to 609 nm, respectively, with the average, 144, 331, 757 and 398 nm (Table 1), respectively, which was thicker than that of Guangzhou (330 nm), Hong Kong (120 nm) and Baltimore (181 nm) (Li et al. 2010; Liu et al. 2003). The bulk film thickness was thinnest in parks and green spaces and was similar between cultural and educational areas and traffic zones. The bulk film thickness was much greater in commercial areas than in other functional areas. The film thickness may be affected by ground dust disturbances because commercial areas have a large number of people and vehicles. In addition, fugitive dust from construction sites near the sampling sites was a major factor.

PAHs in organic film

Organic film on the glass surface comprised elemental carbon (0.7 %), organic compounds (5 %), inorganic compounds (94 %), and others (0.3 %). PAHs account for only 0.2 % of the total mass of the film (Lam et al. 2005). The PAH concentrations in glass film can be expressed in two ways, area normalised and mass normalised. Area-normalised concentrations reflect the total concentrations of PAHs in the air, whereas mass-normalised concentrations reflect the amount of PAHs in relation to the available organic glass film (Unger and Gustafsson 2008).

Area-normalised concentrations of PAHs in organic film in the study are shown in Table 1 and are plotted in Fig. 2. The concentrations of total PAHs ranged from 1,348.5 to 4,007.9 ng m^{-2} for the different functional areas in Shanghai. The concentration of PAHs was lowest for parks and green spaces (1,348.5 ng m^{-2}) and highest for traffic zones (4,007.9 ng m^{-2}), followed by commercial areas (3,655.6 ng m^{-2}) and cultural and educational areas (3,645.9 ng m^{-2}). In comparison with other studies, as shown in Table 2, the concentration of PAHs was lower in the different functional areas of central Shanghai than in downtown Baltimore (5,408 ng m^{-2}) (Liu et al. 2003), downtown Toronto (6,100 ng m^{-2}) (Gingrich and Diamond 2001), and the area around the World Trade Center after the September 11 terrorist attacks in New York (38,744 ng m^{-2}) (Butt et al. 2004) and was significantly higher in the different

functional areas of central Shanghai than in suburban Toronto (1,800 ng m^{-2}) and rural Toronto (210 ng m^{-2}) (Gingrich and Diamond 2001), downtown Stockholm (376 ng m^{-2}) (Unger and Gustafsson 2008), Guangzhou (1,290 ng m^{-2}) and Hong Kong (380 ng m^{-2}) (Pan et al. 2012). A concentration gradient of PAHs was observed as follows: traffic zones > commercial areas > cultural and educational areas > parks and green spaces. This difference was mainly due to the decrease in concentrations of particulate and condensable gaseous PAHs in air as the increased distance from pollution sources. This gradient was also observed in soil and vegetation in central Shanghai (Liu and Du, unpublished data). Concentrations of PAHs were higher at DHU (Donghua University) and SHU (Shanghai University) than in other cultural and educational areas because these two university campus are in close proximity to traffic lane featured by heavy traffic flow; thus, vehicle emissions are a major pollution source which agree with the conclusion that PAHs in central Shanghai originated from emissions from traffic rather than from long-distance transmission from remote areas (Liu et al. 2007). In addition, concentrations of PAHs were significantly higher in the commercial area of Wujiaochang (WJC) and at traffic zones such as Shanghai Railway Station (SHRS) and the Entrance of the Dapu Road Tunnel (EDPRT) than at other sampling sites. These results indicate that the PAHs in organic film are associated mainly with vehicle emissions.

The distribution patterns of PAHs are shown in Fig. 3. The highest contributors were Phe (20.5 %), Fluo (16.7 %), Py (12.4 %) and Chry (11.2 %). The pattern is similar to urban air particulate, showing ageing relative to urban air (Gingrich and Diamond 2001). Generally, the patterns of PAHs in this study were similar to those in previous studies like Baltimore (Liu et al. 2003), Guangzhou and Hong Kong (Pan et al. 2012). PAHs of 3–4 rings were the most abundant of the total PAHs, contributing 73.6 % of the total PAHs. The high molecular weight PAHs (4–6 rings) were mostly associated with the particulate phase (Pan et al. 2012). The distribution pattern of 4–6 rings PAHs in the film were similar to the patterns in dust fall and suspended particulate matter from Shanghai (Ren et al. 2006; Yan et al. 2012), suggesting an aged atmospheric sample in the atmospheric particulate matter and organic film including Chry, B[b/k]F and InP.
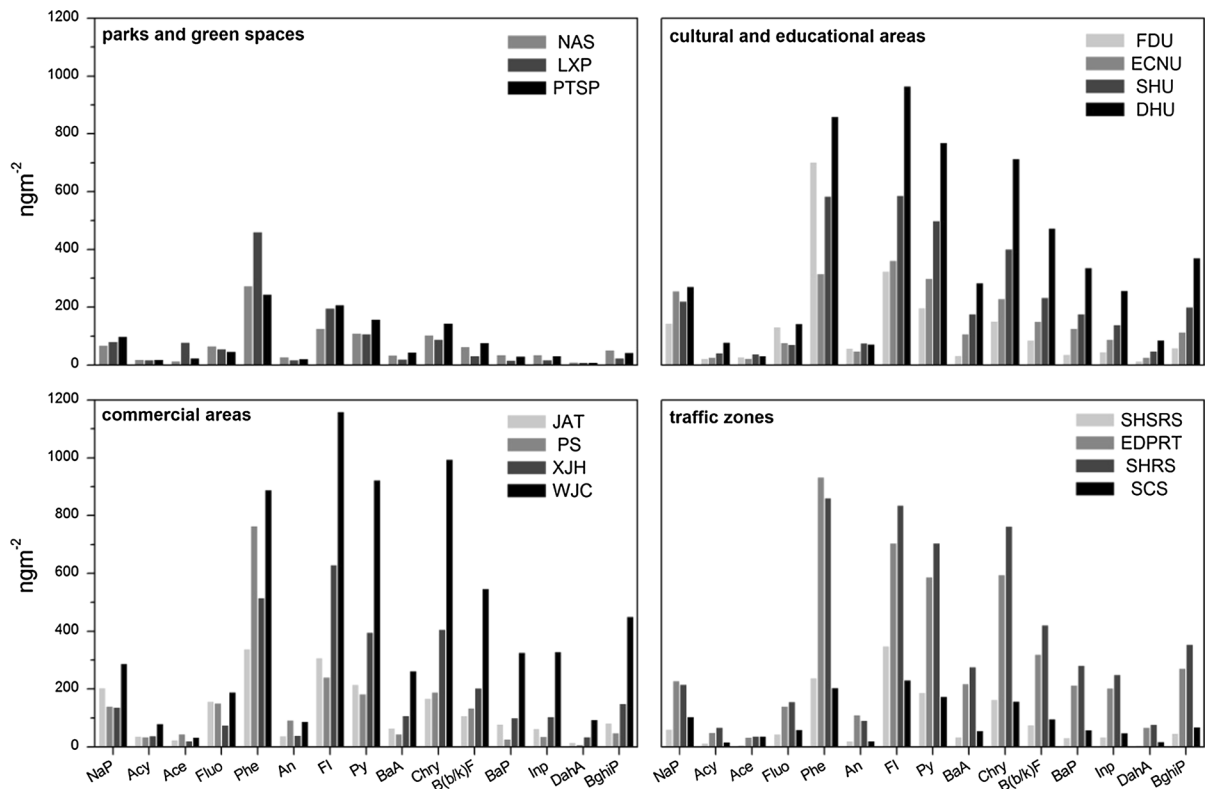
Fig. 2 Contents of PAHs in organic material in the film from different functional areas. Parks and green spaces including *LXP* Lu Xun Park; *PTSP* Putuo Sports Park; *NAS* National Anthem Square; cultural and educational areas including *FDU* Fudan University; *ECNU* East China Normal University; *SHU* Shanghai University; *DHU* Donghua University; commercial areas including *WJC* Wujiaochang; *PS* People's Square; *JAT* Jing'an Temple; *XJH* Xu jiahui; traffic zones including *SCS* Shipping Center Square; *SHRS* Shanghai Railway Station; *EDPRT* Entrance of the Dapu Road Tunnel; *SHSRS* Shanghai South Railway Station

Sources of PAHs

To assess and reduce the environmental and health risks of PAHs, some specific compounds have been widely used to detect the potential sources of PAHs (Yunker et al. 1999). PAHs originate from incomplete combustion of fossil fuels and biomass and natural diagenetic processes (Yunker et al. 1996). Low molecular weight PAHs result from petroleum-derived residues, while high molecular weight PAHs are generated in high temperature combustion processes. LMW/HMW [(Phe + An + Fl + Py)/(BaA + Chry + BbF + BkF + BaP + InP + DahP + BghiP)] could be used as indicators to identify sources of PAHs (Soclo et al. 2000). In this study, the ratios of LMW/HMW in the organic film were all above 1 (Fig. 4), indicating that the dominant sources of PAHs in organic film were petroleum sources (Soclo et al. 2000).

Previous studies showed that the content of BaA was significantly reduced after long-range transport because of the rapid photodegradation rate (Fraser et al. 1998). The ratio of BaA/Chry can be used as a tracer for the diagnostic transmission process. A smaller ratio indicates that the PAHs go through a long-distance atmospheric transmission, while a larger ratio indicates local sources. As shown in Fig. 4, the ratios of BaA/Chry were all less than 1, suggesting that PAHs were derived from long-distance pollution sources. However, BaA/Chry values for road dust in Shanghai were mostly larger than 1, indicating that PAHs mainly come from local emission sources (Liu et al. 2007). This difference may be affected by depletion of PAHs by rapid photooxidation in organic film that was expected to enhance the loss of PAHs through photolysis (Pan et al. 2012). The ratio of BaA/Chry is therefore not suitable for use as a source discriminator in glass film. Degradation mechanisms

Table 2 Comparison of total PAH concentrations in organic film in central Shanghai with others

Area	Description	PAHs numbers analysed	Total PAHs concentrations (ng m^{-2})		Reference
			Mean	Range	
Baltimore (USA)	Urban	20	4,272	1,593–9,453	Liu et al. (2003)
New York (USA)	Urban[a]	43	38,744	1,780–154,050	Butt et al. (2004)
Toronto (Canada)	Urban	47	6,100	900–62,000	Gingrich and Diamond (2001)
Stockholm (Sweden)	Urban	43	376	79–467	Unger and Gustafsson (2008)
Guangzhou (China)	Urban	16	1,290	1,040–1,430	Pan et al. (2012)
Hong Kong (China)	Urban	16	380	210–630	Pan et al. (2012)
Toronto (Canada)	Suburban	47	1,800	1,300–2,600	Gingrich and Diamond (2001)
Toronto (Canada)	Rural	47	210	60–600	Gingrich and Diamond (2001)
Shanghai (China)	Urban[b]	16	1,349	1,160–1,512	This study
Shanghai (China)	Urban[c]	16	3,646	2,214–6,052	This study
Shanghai (China)	Urban[d]	16	3,656	2,271–7,042	This study
Shanghai (China)	Urban[e]	16	4,008	1,426–5,673	This study

[a] Samples were collected after the September 11 terrorist attacks in New York

[b] Samples were collected in parks or green spaces

[c] Samples were collected in cultural and educational areas

[d] Samples were collected in commercial areas

[e] Samples were collected in traffic zones

Fig. 3 Percentages of PAH components in organic film. *DHU* Donghua University; *ECNU* East China Normal University; *EDPRT* Entrance of the Dapu Road Tunnel; *FDU* Fudan University; *JAT* Jing'an Temple; *LXP* Lu Xun Park; *NAS* National Anthem Square; *PS* People's Square; *PTSP* Putuo Sports Park; *SCS* Shipping Center Square; *SHRS* Shanghai Railway Station; *SHSRS* Shanghai South Railway Station; *SHU* Shanghai University; *WJC* Wujiaochang; *XJH* Xu jiahui
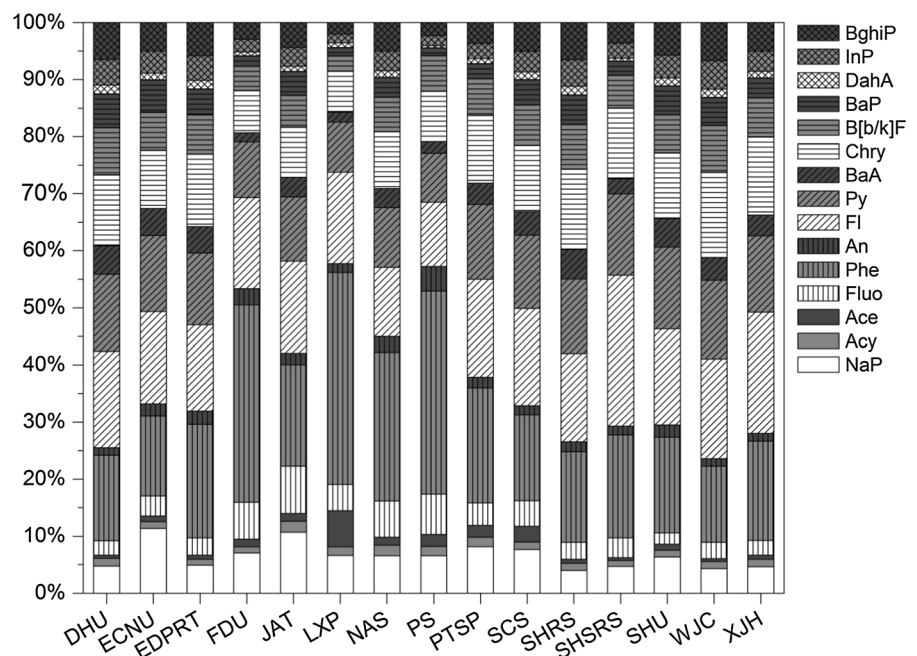
and quantitative analysis of PAHs in organic film can be studied further in future research.

PAH isomers show similar migration and transformation behaviour in the environment, and the ratios of An/178 (An and Phe) and Fl/202 (Fl and Py) were used as a source apportionment indicator to estimate the emission source of PAHs (Yunker et al. 1999). A ratio of An/178 <0.1 implies that the PAHs originate from

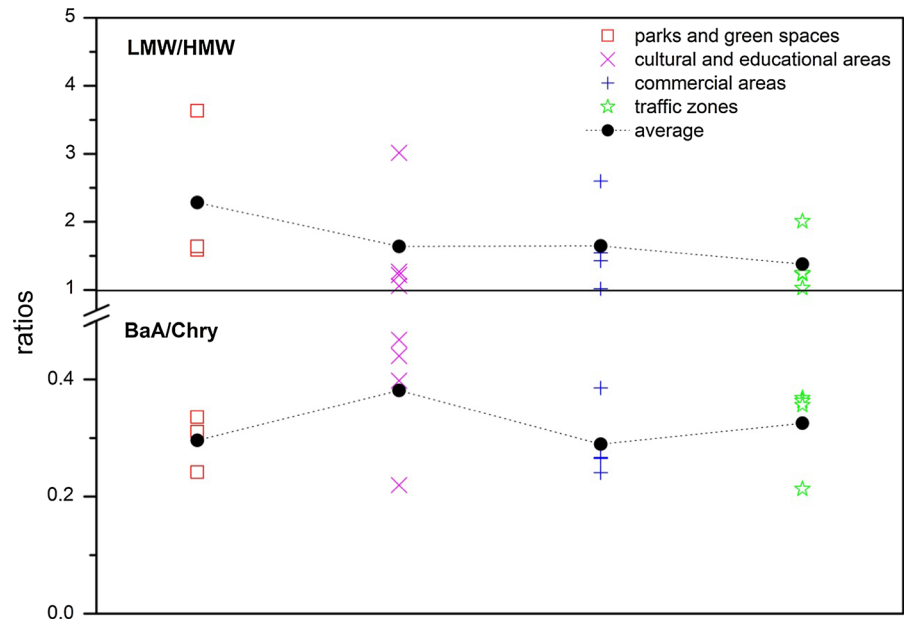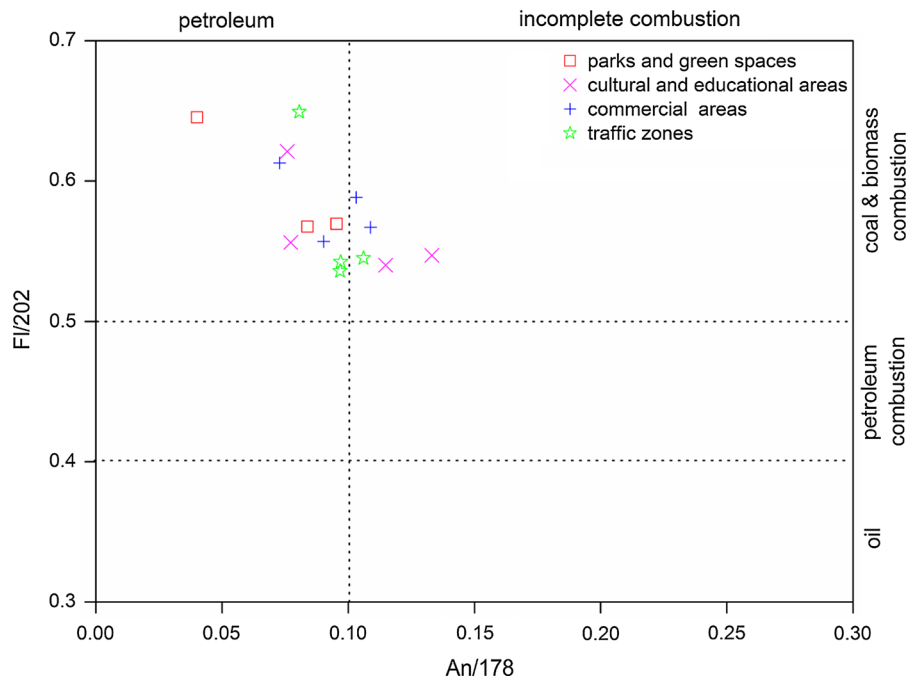**Fig. 4** Distribution ratio of LMW/HMW and BaA/Chry for PAHs in organic film

Fig. 5 Diagnostics for distinguishing pollution sources for PAHs in organic film

petroleum sources, and a ratio >0.1 suggests that PAHs originate from coal and biomass combustion. A ratio of Fl/202 >0.5 indicates coal and biomass combustion, a ratio of Fl/202 between 0.4 and 0.5 is characteristic of oil (vehicle and crude oil) combustion, and a ratio of Fl/202 <0.4 indicates petroleum sources. Based on the source analytical index, the ratio

of PAHs in organic film is shown in Fig. 5. The Fl/202 (Fl + Py) ratio >0.5 for the film indicates that PAHs in film in central Shanghai come mainly from coal and incomplete biomass combustion. However, the ratio of An/178 (An + Phe) was mostly below 0.1, indicating that the PAHs were derived from liquid fossil fuel combustion. A ratio <0.1 is characteristic of coal and

biomass combustion. In summary, PAHs in the organic film originated mainly from mixed sources of liquid fossil fuel, coal and incomplete biomass combustion.

In this study, principal component analysis (PCA) was used to classify and identify the sources of PAHs in organic film from Shanghai. The first principal component (PC1) and second principal component (PC2) were responsible for 72.8 and 16.2 % (Table A.1), respectively, of the total variance of PAHs in organic film (Fig. 6). Some researchers reported that Phe, An, Fl, Pyr, BaA, Chry and BaP are associated with coal combustion (Larsen and Baker 2003; Simcik et al. 1999). B[b/k]F is associated with the combustion of fossil fuels (Kavouras et al. 2001; Rogge et al. 1993). BaA and Chry are products of diesel and natural gas combustion (Khalili et al. 1995; Rogge et al. 1993). InP, BghiP and DahA have been identified as typical tracers of traffic emissions (Fraser et al. 1998). Na and Fluo originate from the leaking or volatilisation of petroleum, and Ace and Acy are indicators for coke oven combustion emissions (Simcik et al. 1999). In this study, two distinct clusters were separated along the PC1. Principal component loading plots revealed that PC1 was coal and traffic emission sources and that PC2 was coke oven combustion (Table A.2). Figure 5 shows that People Square (PS), Luxun Park (LXP), Fudan University (FDU) and National Anthem Square (NAS) are enriched in Fluo and Ace, indicating that the PAHs were derived from the leaking or volatilisation of petroleum and coke oven combustion. The rest of the sampling sites were enriched in Phe, An, Pyr, Fl, Chry, BaP, DahA, InP, BghiP and B[b/k]F, and these components come from mixed sources of petroleum, coal and incomplete biomass combustion. The results from the PCA are consistent with the isomer ratio. The pattern again indicates that the sources of PAHs in the organic film on the glass surfaces were derived mainly from petroleum, coal and incomplete biomass combustion.

Risk assessment of PAHs

The USEPA has classified BaA, Chry, BbF, BkF, BaP, InP and DahA as probable human carcinogens (Qiao et al. 2010). The mass-normalised concentration of these seven carcinogenic PAHs in glass film from central Shanghai ranged from 142 to 2,810 ng g^{-1}. Each PAH has a different carcinogenic activity (Bergvall and Westerholm 2007). To assess the carcinogenic potential of PAHs in film, toxic equivalency factors (TEFs) were used to quantify the benzo[a]pyrene equivalent (BaPeq) concentration. The carcinogenic potency for an organic film sample is calculated by multiplying the concentration of the individual PAHs with their TEFs (Wang et al. 2013). In this study, the concentration of BaPeq varied from 21 to 701 ng g^{-1}. The mean concentrations of BaPeq in parks and green spaces, culture and educational areas, commercial areas and traffic zones were 281,

Fig. 6 Principal component analysis (PCA) of PAHs in organic film from downtown Shanghai. PC1 explained 72.8 % of the variance of the data matrix, and PC2 explained 16.2 % of the rest of the PAHs in organic film
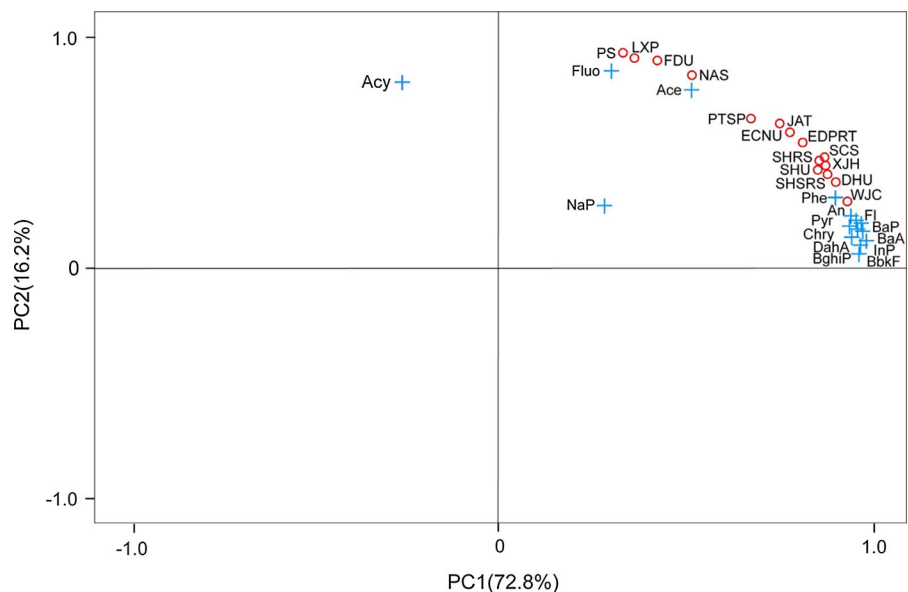
490, 261 and 454 ng g^{-1}, respectively. The BaPeq in organic film was similar to that in soil from Shanghai (Wang et al. 2013). However, the values of BaPeq in organic film were lower than those of the dust in air conditioner filters sampled from different types of room: office (1,010 ng g^{-1}), bedroom (901 ng g^{-1}) and restaurants (782 ng g^{-1}), and higher than the values of BaPeq in conference rooms (153 ng g^{-1}) (Zhou et al. 2010). The main carcinogenic contributors of the 16 PAHs were BaP, DahA, B[b/k]F and InP, accounting for 83 % of the BaPeq in this study. This result is similar to that for soil from Shanghai (Wang et al. 2013). The average value of BaPeq in film from central Shanghai was lower, with a safe BaPeq value of 600 ng g^{-1}, than the Canadian soil guideline [based on an incremental lifetime cancer risk (ILCR) of 10^{-6}] (Wang et al. 2013). However, the carcinogenic potential of PAHs in organic film should be considered because windows are prevalent in everyday life.

Conclusion

Sixteen PAHs in organic film on glass surfaces from central Shanghai were determined systematically. High concentrations of PAHs were observed in the organic film samples, and a concentration gradient was obvious. Organic film samples from traffic zones contained more PAHs than organic film samples from commercial areas, cultural and educational areas, and parks and green spaces. Similar distributions of 3–4 ring PAHs were observed in central Shanghai and other research areas. The PAHs were dominated by Phe, Fluo, Py and Chry. The measured bulk film thickness in the different functional areas was within the ranges reported in previous studies. The results of this study suggest that BaA/Chry is not appropriate to distinguish the transmission process of PAHs in organic film, suggesting that glass surfaces can enhance the rate of photooxidation of PAHs in organic film. PAHs in organic film on surfaces in central Shanghai originated mainly from the mixed sources of fossil fuel and coal/biomass combustion. The average value of BaPeq in film from central Shanghai was lower than that for other environmental media and ILCR.

References

Alberti, M., Redman, C., Wu, J. G., et al. (2006). Urban landscape patterns and global environmental change: Complex dynamics and emergent properties. *IHDP-UGEC Update Newsletter, 2*, 5–7.

Bergvall, C., & Westerholm, R. (2007). Identification and determination of highly carcinogenic dibenzopyrene isomers in air particulate samples from a street canyon, a rooftop, and a subway station in Stockholm. *Environmental Science and Technology, 41*(3), 731–737.

Butt, C. M., Diamond, M. L., Truong, J., Ikonomou, M. G., Helm, P. A., & Stern, G. A. (2004). Semivolatile organic compounds in window films from lower Manhattan after the September 11th World Trade Center attacks. *Environmental Science and Technology, 38*(13), 3514–3524.

Castro, D., Slezakova, K., Delerue-Matos, C., Alvim-Ferraz, M. D., Morais, S., & Pereira, M. D. (2011). Polycyclic aromatic hydrocarbons in gas and particulate phases of indoor environments influenced by tobacco smoke: Levels, phase distributions, and health risks. *Atmospheric Environment, 45*(10), 1799–1808.

Cheng, J. P., Yuan, T., Wu, Q., Zhao, W. C., Xie, H. Y., Ma, Y. G., et al. (2007). PM10-bound polycyclic aromatic hydrocarbons (PAHs) and cancer risk estimation in the atmosphere surrounding an industrial area of Shanghai, China. *Water, Air, and Soil pollution, 183*(1–4), 437–446.

Diamond, M. L., Gingrich, S. E., Fertuck, K., McCarry, B. E., Stern, G. A., Billeck, B., et al. (2000). Evidence for organic film on an impervious urban surface: Characterization and potential teratogenic effects. *Environmental Science and Technology, 34*(14), 2900–2908.

Diamond, M. L., Priemer, D. A., & Law, N. L. (2001). Developing a multimedia model of chemical dynamics in an urban area. *Chemosphere, 44*(7), 1655–1667.

Fraser, M. P., Cass, G. R., & Simoneit, B. R. T. (1998). Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environmental Science and Technology, 32*(14), 2051–2060.

Gingrich, S. E., & Diamond, M. L. (2001). Atmospherically derived organic surface films along an urban-rural gradient. *Environmental Science and Technology, 35*(20), 4031–4037.

IARC. (2010). *Monographs on the evaluation of carcinogenic risks to humans. Volume 92. Some non-heterocyclic aromatic hydrocarbons and some related exposures*. Lyon: IARC Press.

Kavouras, I. G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E. G., Von Baer, D., et al. (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environmental Science and Technology, 35*(11), 2288–2294.

Khalili, H., Mahar, J., Asche, H. P., & Davis, B. (1995). Self-esteem enhancement group in acute psychiatric setting.

Canadian Psychology-Psychologie Canadienne, 36(2A), 227.

Lam, B., Diamond, M. L., Simpson, A. J., Makar, P. A., Truong, J., & Hernandez-Martinez, N. A. (2005). Chemical composition of surface films on glass windows and implications for atmospheric chemistry. *Atmospheric Environment, 39*(35), 6578–6586.

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*(9), 1873–1881.

Law, N. L., & Diamond, M. L. (1998). The role of organic films and the effect on hydrophobic organic compounds in urban areas: An hypothesis. *Chemosphere, 36*(12), 2607–2620.

Li, J., Lin, T. A., Pan, S. H., Xu, Y., Liu, X. A., Zhang, C., et al. (2010). Carbonaceous matter and PBDEs on indoor/outdoor glass window surfaces in Guangzhou and Hong Kong, South China. *Atmospheric Environment, 44*(27), 3254–3260.

Liu, M., Cheng, S. B., Ou, D. N., Hou, L. J., Gao, L., Wang, L. L., et al. (2007). Characterization, identification of road dust PAHs in central Shanghai areas, China. *Atmospheric Environment, 41*(38), 8785–8795.

Liu, Q. T., Diamond, M. L., Gingrich, S. E., Ondov, J. M., Maciejczyk, P., & Stern, G. A. (2003). Accumulation of metals, trace elements and semi-volatile organic compounds on exterior window surfaces in Baltimore. *Environmental Pollution, 122*(1), 51–61.

Pan, S. H., Li, J., Lin, T., Zhang, G., Li, X. D., & Yin, H. (2012). Polycyclic aromatic hydrocarbons on indoor/outdoor glass window surfaces in Guangzhou and Hong Kong, south China. *Environmental Pollution, 169*, 190–195.

Petry, T., Schmid, P., & Schlatter, C. (1996). The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). *Chemosphere, 32*(4), 639–648.

Qiao, M., Cai, C., Huang, Y. Z., Liu, Y. X., Lin, A. J., & Zheng, Y. M. (2010). Characterization of PAHs contamination in soils from metropolitan region of Northern China. *Bulletin of Environmental Contamination and Toxicology, 85*(2), 190–194.

Ren, Y., Lian, J. J., Xue, H. X., Chen, J. M., & Cheng, T. T. (2006). Determination of PAHs in dust from Shanghai by optimized SFE and GC/MS. *Annali di Chimica, 96*(11–12), 669–680.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., & Simoneit, B. R. T. (1993). Sources of fine organic aerosol. 5. Natural-gas home appliances. *Environmental Science and Technology, 27*(13), 2736–2744.

Simcik, M. F., Eisenreich, S. J., & Lioy, P. J. (1999). Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment, 33*(30), 5071–5079.

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*(5), 387–396.

Unger, Maria, & Gustafsson, Örjan. (2008). PAHs in Stockholm window films: Evaluation of the utility of window film content as indicator of PAHs in urban air. *Atmospheric Environment, 42*(22), 5550–5557.

Wang, Z., Liu, Z., Yang, Y., Li, T., & Liu, M. (2012). Distribution of PAHs in tissues of wetland plants and the surrounding sediments in the Chongming wetland, Shanghai, China. *Chemosphere, 89*(3), 221–227.

Wang, X. T., Miao, Y., Zhang, Y., Li, Y. C., Wu, M. H., & Yu, G. (2013). Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: Occurrence, source apportionment and potential human health risk. *Science of the Total Environment, 447*, 80–89.

Yan, L., Li, X., Chen, J., Wang, X., Du, J., & Ma, L. (2012). Source and deposition of polycyclic aromatic hydrocarbons to Shanghai, China. *Journal of Environmental Sciences, 24*(1), 116–123.

Yunker, M. B., Macdonald, R. W., Goyette, D., Paton, D. W., Fowler, B. R., Sullivan, D., et al. (1999). Natural and anthropogenic inputs of hydrocarbons to the Strait of Georgia. *Science of the Total Environment, 225*(3), 181–209.

Yunker, M. B., Snowdon, L. R., MacDonald, R. W., Smith, J. N., Fowler, M. G., Skibo, D. N., et al. (1996). Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environmental Science and Technology, 30*(4), 1310–1320.

Zhou, H. C., Zhang, C. C., Cai, H. X., Song, Y. Y., & Xue, H. B. (2010). The distribution and possible source of polycyclic aromatic hydrocarbons in dust from six air conditioner filters. *China Environmental Science, 30*, 1303–1308.