Published in final edited form as:
Environ Pollut. 2010 May ; 158(5): 1245–1251. doi:10.1016/j.envpol.2010.01.021.

Concentrations, sources and spatial distribution of polycyclic aromatic hydrocarbons in soils from Beijing, Tianjin and surrounding areas, North China

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Abstract

The concentrations, profiles, sources and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) were determined in 40 surface soil samples collected from Beijing, Tianjin and surrounding areas, North China in 2007, and all sampling sites were far from industrial areas, roadsides and other pollution sources, and across a range of soil types in remote, rural villages and urban areas. The total concentrations of 16 PAHs ranged from 31.6 to 1475.0 ng/g, with an arithmetic average of 336.4 ng/g. The highest PAH concentrations were measured in urban soils, followed by rural village soils and soils from remote locations. The remote–rural village–urban PAH concentration gradient was related to population density, gross domestic product (GDP), long-range atmospheric transport and different types of land use. In addition, the PAH concentration was well correlated with the total organic carbon (TOC) concentration of the soil. The PAH profile suggested that coal combustion and biomass burning were primary PAH sources.

Keywords

Soil; PAHs; Source diagnostics; Beijing; Tianjin

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants emitted from both natural (forest fires and volcanic activity) and anthropogenic sources (incomplete combustion of fossil fuels, coke production, many industrial processes, and so on). Because of the mutagenic and carcinogenic potential of some PAHs, the U.S. Environmental Protection Agency (EPA) listed 16 PAHs as priority pollutants and seven of these are considered carcinogenic, i.e. benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene (Harvey, 1991).

Soil is the primary environmental reservoir and sink for semi-volatile organic compounds such as PAHs in the terrestrial environment. It has been estimated that soil contains the vast

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majority of PAHs in the Pearl River Delta area (Lang et al., 2008) and Tianjin area of China (Zuo et al., 2007) using fugacity modeling. In addition, PAH contamination of soil can have a direct effect on public health because soil can be easily transferred to humans via ingestion, inhalation or dermal contact. China suffers serious PAH contamination from combustion of fossil fuel and biomass, and the emission of PAHs in China contributed to over 20% of the global total PAH emission (Zhang and Tao, 2008). The PAH contamination issue in China is of particular concern to local authorities and scientists, and several investigations on PAH concentrations and distribution in soil have been carried out (Ma et al., 2005; Tang et al., 2005; Zhang et al., 2006; Cai et al., 2007; Ping et al., 2007; Wang et al., 2007a; Zuo et al., 2007; Li et al., 2008; Yin et al., 2008; Jiang et al., 2009), showing that the concentration of PAHs in surface soil vary markedly along the remote–rural–urban–industrial gradient, similar to those observed in the other countries (Wilcke, 2000; Mielke et al., 2004; Agarwal et al., 2009; Holoubek et al., 2009; Maliszewska-Kordybach et al., 2009a, b).

Beijing and Tianjin are two of the largest cities in northern China. The high population growth and rapid industrialization and urbanization during the last decades have resulted in significant environmental problems, including severe soil PAH contamination (Tao et al., 2004; Ma et al., 2005; Tang et al., 2005; Zuo et al., 2007). In addition, the PAH emission density in the North China Plain is among the highest in China (Zhang et al., 2007) and domestic coal combustion, biomass burning, and coking industry are the major contributors to PAH emissions in this area (Zhang et al., 2007; Zuo et al, 2007). However, most of the studies regarding soil PAHs contamination in Beijing and Tianjin concentrate on polluted areas or “hotspots”, like roadside or traffic area, industrial area and agricultural filed after long-term wastewater irrigation (Tao et al, 2004; Chen et al, 2005; Ma et al, 2005; Tang et al, 2005; Zuo et al., 2007), while researches on uncontaminated agricultural fields and school grasslands or large parks in the urban, are scarce.

So the objectives of this study were to investigate the concentration, profile, and spatial distribution of PAHs in remote (background), rural village and urban soils collected from Beijing, Tianjin and surrounding areas, and all the sampling sites are far from traffic, industrial area and other pollution sources. This was done in order to compare the current PAH contamination levels with regulations and previous studies; to determine the primary sources of PAHs; to compare the PAH concentration in background, rural village and urban areas.

2. Materials and methods

2.1. Chemicals and materials

A mixture of 16 PAHs [naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a, h]anthracene (DahA), indeno[1, 2, 3-cd]pyrene (IcdP), and benzo[ghi]perylene (BghiP)] was purchased from J&K chemical Ltd., USA. The surrogate standards for these PAHs were deuterated PAHs (NAP-d_8, ACE-d_{10}, ANT-d_{10}, CHR-d_{12}, and Perelyne-d_{12}) (J&K chemical Ltd., USA). The internal standards for these PAHs was 2-Fluoro-1,1′-biphenyl and *p*-terphenyl-d_{14} (J&K chemical Ltd., USA).

The solvents used included n-hexane, acetone and dichloromethane (DCM) (analytical grade, Beijing Chemical Reagent Co.). These solvents were purified by redistillation. Silica gel (100–200 mesh) was obtained from Beijing Chemical Reagent Co. and was heated at 450 °C for 4 h, kept in a sealed desiccator, and reactivated at 130 °C for 16 h immediately prior to use. Granular anhydrous sodium sulfate was baked at 650 °C in a furnace for 6 h and stored in the sealed desiccator prior to use. All glassware was cleaned in an ultrasonic cleaner (KQ-500B, Kunshan Ultrasonic Instrument) and heated at 400 °C for 6 h.

2.2. Study area description and soil sampling

A total of 40 composite soil samples were collected in September 2007 at various locations in Beijing, Tianjin and surrounding areas (Fig. 1) after vegetation season. All sampling sites were selected far from industrial areas, roadsides and other point pollution sources, and across a range of soil types in remote, rural villages and urban areas. Furthermore, all remote sites are mountain forests, and the land use types for rural villages sites include agricultural cornfield, vegetable field, orchard and maize filed, and them for urban sites are school and government grasslands. Detailed sampling sites information is provided in Supplementary material (Table S1). When sampling, surface soils (0–5 cm depth) were collected by using a stainless steel soil corer after the upper organic vegetative materials were removed. Five soil samples were pooled and homogenized to provide a composite sample after their collection from a 100 m^2 area.

The soil samples were air-dried at room temperature, sieved through a 70-mesh sieve after removing stones and residual roots, and stored in desiccators prior to analysis. The total organic carbon (TOC) concentration of the soil samples was determined using a TOC analyzer (Shimadzu 5000-A).

2.3. Sample extraction and cleanup

Detailed information on the soils sample extraction and cleanup can be found in the literature (Wang et al., 2007b). Five gram of soil were Soxhlet extracted using 100 ml portions of n-hexane and acetone (1:1, v/v) for 15 h. Twenty percent of the samples were spiked with a range of deuterated PAHs (NAP-d_8, ACE-d_{10}, ANT-d_{10}, CHR-d_{12} and Perelyne-d_{12}) before extraction in order to monitor the efficiency of the extraction and cleanup procedures. After extraction, the samples were purified using a silica gel column. The final volume was adjusted to 1 ml under a gentle stream of N_2, and an appropriate volume (125 μl) of 2-Fluoro-1,1′-biphenyl and *p*-terphenyl-d_{14} (J&K chemical Ltd. USA) were spiked into the vial as internal standards prior to analysis by GC/MS.

2.4. GC-MS analysis and quantification

The PAHs were quantified by GC/MS (Agilent GC6890/5973MSD) using the internal standards. An HP-5 MS column (Agilent, length 30 m, i.d. 0.25 mm, film thickness 0.25 μm) was used with the following temperature program: 60–280 °C at 6 °C/min, isothermal holding at 280 °C for 20 min using helium as the carrier gas. All PAH concentrations were determined using selected ion monitoring (SIM) (Wang et al., 2007b).

2.5. Quality control and quality assurance

The soil samples were analyzed in duplicate to check for reproducibility. The average coefficients of variation for the duplicate samples were 18% (6–31%) for 16 PAHs. The analytical procedural blanks were more than one order of magnitude lower in concentration than the soil samples. The soil PAH concentrations were blank corrected using the arithmetic mean of the procedural blanks. The method detection limits were 0.29 (PHE)-1.02 (BghiP) ng/g. Method recoveries were determined by spiking soil with a working standard (the standard mixture of 16 PAHs from J&K chemical Ltd., USA). For the 16 spiked individual PAHs, the recoveries from NAP to BghiP were from 66% to 114%. The recoveries for the deuterated PAHs were from 85% to 110%.

3. Results and discussion

3.1. PAH concentrations

PAHs were measured in all soil samples and the Kolmogorov–Smirnov (K–S) test results indicated that the individual PAH and TOC concentrations were log-normally distributed in soils (Supplementary material, Table S2). The concentrations of the 16 individual PAHs and 7 carcinogenic PAHs (ΣPAH_{7c}) in soil samples are given in Table 1. The total concentrations of the 16 PAHs (ΣPAH_{16}) varied from 31.6 to 1475.0 ng/g, with an arithmetic mean of 336.4 ng/g and a geometric mean of 184.7 ng/g. This concentration was much higher than the total PAH concentrations (1–10 ng/g) measured intypical endogenous soils resulting from plant synthesis and natural fires (Wilcke, 2000). The highest PAH concentration (1475.0 ng/g) was measured at the Tangshan, an industrial city in Hebei province, while the lowest PAH concentration (31.6 ng/g) was measured in a national parkin Chicheng county, Hebei province. The ΣPAH_{7c} concentration accounted for 18–49% of ΣPAH_{16}. Moreover, BaP concentrations, one of the most potent carcinogenic PAHs, varied from 7.2 to 102.6 ng/g, with an arithmetic mean of 16.9 ng/g. BaP concentration in soil from Beijing, Tianjin and surrounding areas was higher than the urban soils from Hong Kong (9.9 ng/g, Zhang et al., 2006), vegetable soils from Nanjing, China (0.5–11 ng/g, Yin et al., 2008), agricultural soils from Shunde, China (3.4 ng/g, Li et al., 2008). However, it was lower than the vegetable soils from the Yangtze River Delta, east China (36 ng/g, Ping et al., 2007), the suburban Beijing soil (55 ng/g; Ma et al., 2005), Tianjin soils (46 ng/g, Zuo et al., 2007) and agricultural soils from Poland (30 ng/g, Maliszewska-Kordybach et al., 2009a) and Delhi, India (49 ng/g, Agarwal et al., 2009). In addition, it was so similar with vegetable soils from South Korea (16.3 ng/g, Nam et al., 2003).

The PAH concentration of soils is not yet regulated in China and few recommendations or guidelines exist worldwide. Maliszewska-Kordybach (1996) suggested a soil contamination classification system based on ΣPAH_{16} as follows: non-contaminated soil (< 200 ng/g), weakly contaminated soil (200–600 ng/g), contaminated soil (600–1000 ng/g) and heavily contaminated soil (> 1000 ng/g). According to this classification system, 10% of the samples in this study were heavily contaminated, 10% were contaminated, 23% were weakly contaminated and 58% were not contaminated. Over half of sampling sites are remote areas and agricultural fields in this study, so the assessment results from this classification system were expected.

The PAH concentration in soil samples collected from different areas around the world vary significantly (Table 2). The soil ΣPAH_{16} concentrations in this study were comparable to agricultural and grassland soils from the Yangtze River Delta, China (397 ng/g, Ping et al., 2007) and Poland (264 ng/g, Maliszewska-Kordybach, 1996; 423 ng/g, Maliszewska-Kordybach et al., 2009a; 252 ng/g, Maliszewska-Kordybach et al., 2009b), and all these studies were under similar sampling soil types and sampling method. And the soil ΣPAH_{16} concentration in this study was higher than soils from urban and rural areas in Hong Kong (54.6 ng/g, Zhang et al., 2006), in Welsh (187 ng/g, Jones et al., 1989), and agricultural soils from Nanjing, China (178 ng/g, Yin et al., 2008), from Shunde, China (144 ng/g, Li et al., 2008), from Korea (236 ng/g, Nam et al., 2003). However, soil PAH concentrations in this study were much lower than agricultural soils in Delhi, India (830 ng/g, Agarwal et al., 2009), Guangzhou, China (1503 ng/g, Cai et al., 2007), Czech Republic (847 ng/g, Holoubek et al., 2009), and urban areas in New Orleans, United States (2927 ng/g, Mielke et al., 2004), in Shanghai, China (3290 ng/g, Jiang et al., 2009), in Dalian, China (1104 ng/g, Wang et al., 2007a), and all the urban soils from other studies were collected near the polluted roadsides and industrial areas, but soil samples in urban area in this study were collected from school and government grassland, a relatively background location in the large city. So the soil PAHs concentration in this study is on middle level or a little higher level when compared with other researches, even our sampling sites are far from any polluted sources. In addition, the soil PAH concentrations reported in other studies from Beijing and Tianjin were a little higher than this study, for example, urban soils in Beijing (3917 ng/g, Tang et al., 2005), suburban soils in Beijing (1347 ng/g, Ma et al., 2005), urban and rural soils from Tianjin (818 ng/g, Zuo et al., 2007), and the major reason is also the different sampling soil types.

In addition, the BaP-equivalent concentrations (BaP_{eq}) were calculated for this region, and the calculation method was reported by other studies (Agarwal et al., 2009; Jiang et al., 2009). The results were shown in Supplementary material (Table S3), and the BaP_{eq} concentration in soils was 27.75 ng/g for Beijing, Tianjin and surrounding areas, and the seven carcinogenic PAHs contribute the most to the total carcinogenic potency of the soils. Furthermore, the accumulative probabilistic risk frequency of BaP_{eq} concentration for the research area is shown in Supplementary material (Fig. S1), and 82% of this study area for exposure risk was less than 40 ng/g–BaP_{eq}.

3.2. The relationship between PAH and TOC concentration

Some studies have shown that soil TOC is a key property influencing the PAH concentration in urban and contaminated soils (Wilcke, 2000; Tang et al., 2005; Nam et al., 2008; Agarwal et al., 2009), and a few studies have reported a good correlation between soil PAH concentration and TOC concentration for highly contaminated soils (Wilcke, 2000; Tang et al., 2005; Agarwal et al., 2009). However, a poor correlation has also been reported (Zhang et al., 2006; Cai et al., 2007; Wang et al., 2007a; Yin et al., 2008; Jiang et al., 2009). Nam et al. (2008) reported that, in an environment where there is continuous input of fresh PAH contamination, a lack of correlation should be expected, at least until equilibrium is reached. In this study, the soil TOC concentration varied from 0.63% to 4.01% (Supplementary material, Table S1). The correlation scatter plot between ΣPAH_{16} concentration and TOC concentration, the correlation coefficients between individual PAHs and TOC concentration were shown in Fig. 2 and Table 3, respectively. A significant correlation exists between PAHs concentrations and TOC concentration except NAP, but the correlation coefficients were not high, ranging from 0.36 to 0.46. The good correlation between PAH and TOC concentration suggests that the geographic distribution pattern of these compounds is close to steady-state and in equilibrium with soil properties.

3.3. PAH profiles and source identification

Higher proportions of individual PAHs with 4 rings (41.7%) and 3 rings (34.0%) were measured in the soil samples, followed by 2 rings (11.4%), 5 rings (8.9%) and 6 rings PAHs (4.0%) (Table 1). Generally speaking, the PAH profile was characterized by high molecular weight PAHs. PHE, FLA, PYR and BbF were the PAHs in highest concentration in the soil samples, accounting for 16.3%, 16.1%, 10.4% and 8.1% of ΣPAH_{16}, respectively, followed by NAP and BkF (7.7% and 5.9%, respectively). From the PAH emission profile in China (Xu et al., 2006), two to three ring PAHs, four ring PAHs and five to six ring PAHs accounted for 70%, 19% and 11%, respectively, and PHE (13.1%), FLA (8.0%), PYR (6.0%) and ACY (5.7%) were the major PAHs. Based on this, the soil PAH composition profile is different from the PAH emission profile, with higher molecular weight PAHs accounting for a higher proportion of ΣPAH_{16} in soils (Supplementary material, Fig. S2). The differences in these PAH profiles are due to different physiochemical properties (and transport and deposition potential) of the PAHs. Lower molecular weight PAHs are more volatile, exist in the gas phase in the atmosphere and undergo photochemical degradation after emission to atmosphere. However, the higher molecular weight PAHs exist in the particulate phase in the atmosphere due to gas/particle partitioning theory (Bidleman, 1988). Because more than 90% of the PAH burden in surface soil is from dry and wet deposition of particulate matter from the atmosphere (Wild and Jones, 1995), a higher percentage of higher molecular weight PAHs is expected in soil relative to the PAH emission profile.

Two and three-ring PAHs contributed more than 50% of ΣPAH_{16} in tropical and sub-tropical areas, such as Delhi, India and Hong Kong because of high temperatures and this profile is similar to the China's PAH emission profile (Xu et al., 2006). In temperate areas, including Tianjin and Shanghai, China, Korea 4–5 ring PAHs make up a larger portion of the PAH profile in soils due to global fractionation.

In this study, the ratio of low molecular weight (≤ 3 rings) PAH concentration to high molecular weight (≥ 4 rings) PAH concentration ($R_{\leq 3/\geq 4}$) did not vary significantly. The mean $R_{\leq 3/\geq 4}$ was 1.2, ranging from 0.5 to 2.5 (Table 1). For our 40 sites, 23 sites had a ratio greater than 1 and 17 had a ratio less than 1. The results indicate the presence of combustion products from low temperature pyrolytic processes, such as biomass burning and/or petrogenic sources, and high temperature combustion in these soils (Yunker et al., 2002). Because lower molecular weight PAHs are more biodegradable and less lipophilic than higher molecular weight PAHs, in the sites of predominance of low ring PAH with high ratio values, recent pollution can be indicated.

PAH diagnostic ratios (i.e. ANT/(PHE + ANT), FLA/(PYR + FLA), BaA/(CHR + BaA), IcdP/(BghiP + IcdP)) and principal component analysis (PCA) are used to determine the source of PAHs in soils (Zhang et al., 2006; Cai et al., 2007; Ping et al., 2007; Wang et al., 2007a; Yin et al., 2008; Agarwal et al., 2009; Jiang et al., 2009). Based on the PAH isomer ratios compiled by Yunker et al. (2002), the ratio of ANT/(PHE + ANT) < 0.1 suggests petroleum as a PAH source, while a ratio > 0.1 suggests combustion as a source. In addition, an FLA/(PYR + FLA) ratio < 0.4 implies petroleum, 0.4–0.5 implies petroleum (liquid fossil fuel, vehicle and crude oil) combustion, and > 0.5 implies combustion of coal, grass and wood (Yunker et al., 2002). When PAH ratios are used to determine the source of an emission, it is assumed that the ratios remain constant from sources to receptors. However, these ratios can be altered significantly during the transport of the PAH compounds in a multimedia environment because the physicochemical properties of the paired PAH species are not identical (Zhang et al., 2005; Lang et al., 2008). Zhang et al. (2005) reported the calibration factors for the ratio values of PAHs from source to receptor by using fugacity model, and verified it by comparing model calculations with the actual changes in ratio of PAHs as PAHs moved from the sources of the emissions to the surface soils in Tianjin area, part area of this study. So in this study, the ratio of ANT/(PHE + ANT) and FLA/(PYR + FLA) was calibrated using a calibration factor from Zhang et al. (2005). The cross plot of ANT/(PHE + ANT) and FLA/(PYR + FLA) is shown in Fig. 3. For the FLA/(PYR + FLA) ratio, all soil samples had a ratio greater than 0.5 before and after calibration. This suggests that the main PAH sources are coal, grass and wood combustion. However, the ANT/(PHE + ANT) ratio changed significantly after calibration because of faster degradation of ANT during transport compared with PHE. For the majority of soils, this ratio suggested PAHs emissions from combustion processes, with only a few cases of PAH emissions from petrogenic sources. So for soils from Beijing, Tianjin and surrounding areas, the preliminary analysis shows that the PAHs were primarily from coal combustion and biomass burning, and these results are consistent with previous research in Beijing and Tianjin (Ma et al., 2005; Tang et al., 2005; Zuo et al., 2007).

3.4. Spatial distribution of PAHs

A wide range of PAH concentrations were measured in soil from background, rural village and urban areas. The differences in soil individual and total PAH concentrations and profile percent among the three different areas were investigated using one-way ANOVA (Supplementary material, Table S4). The results indicated that significant differences existed between background area soil and rural village and urban area soil for total PAHs concentrations ($p < 0.05$), and between rural village concentrations and urban soil concentrations ($p < 0.05$). The ΣPAH_{16} soil concentrations in rural villages (195.3 ng/g) and urban soils (622.4 ng/g) were 3 times and 9 times higher than background sites (67.8 ng/g) (Table 4), which indicate that local source emissions have a direct contribution to rural and urban soils. In Beijing, Tianjin and surrounding areas, the dominant PAH emission sources are coal combustion and indoor biomass burning for cooking and heating and are mainly found in urban and rural villages. Actually significant differences existed between remote area and urban area, rural village and urban area for all individual compounds, However, there are not significant differences for some PAHs compounds, like ACE, ACY, FLO, PHE, ANT, BaP, DahA, IcdP, between remote area and rural village area.

The geographic distribution of ΣPAH_{16} concentrations in soil is shown in Fig. 1. The most contaminated areas are urban Beijing and Tianjin city, east and southwest of Hebei province, and a number of large cities, e.g. Tangshan, Baoding, Cangzhou and Langfang. The areas with the lowest PAH concentrations are mountain area northwest of Hebei province (Zhangjiakou) and north of Beijing (Huairou) with relatively low population density. A positive correlation between soil ΣPAH_{16} concentration and population density and gross domestic product (GDP) was found ($p < 0.01$, Fig. 4 and Table 3) in rural villages and urban sites. The correlation coefficients ranged from 0.38 to 0.60, from 0.51 to 0.66, between individual PAH and population density, between individual PAH and GDP, respectively. These results suggest that local anthropogenic activities greatly influence soil PAH concentrations. However, if compared with TOC effects ($r^2 = 0.25$), the population ($r^2 = 0.54$) and GDP ($r^2 = 0.47$) are more important for explaining the spatial distribution of soil PAHs concentrations in Beijing, Tianjin and surrounding areas.

For the PAH profiles in background, rural villages, and urban soils, only NAP, ACE, FLO, PHE, BaA, CHR, BkF and BaP were significantly different between three different areas (Fig. 5 and Supplementary material Table S4). Concentrations of BkF and BaP in urban soils were significantly higher than rural village and remote areas, and concentrations of NAP and PHE in remote soils were significantly lower than urban and rural village area. In addition, there are more PAHs compounds which are significantly different between remote area and urban area, than between remote area and rural village, between rural village and urban area. Furthermore, 2–3 ring PAH concentrations were dominant in background soils, while 4–6 ring PAH concentrations were dominant in urban soils. Significant difference for $\text{ratio}_{\leq 3\ \text{ring}/\geq 4\ \text{ing}}$ value existed between three different areas, and there are more low ring PAHs in remote areas. In background soils, PHE (24.1%), NAP (16.5%), FLA (12.5%) and PYR (9.8%) dominated the PAH profile. This was similar to rural soils, PHE (18.9%), FLA (13.4%), BbF (11.5%) and PYR (10.5%). However, in urban soils, FLA (17.3%), PHE (15.0%), PYR (13.1%), and BbF (10.2%) contributed more to ΣPAH_{16}. There are many factors influencing the spatial distribution of different PAHs, such as physicochemical properties of PAHs, TOC concentration in soil, emission density of PAHs, and photochemical degradation of atmospheric PAHs, and so on. Generally two to three ring PAHs are subject to atmospheric transport to remote areas and considered “multi-hop” chemicals, while higher ring PAHs are associated with particles and undergo “single hop” transport behavior, and higher ring PAHs are prone to rapid deposition and retention close to source regions. Due to their different physicochemical properties, emission sources, photochemical degradation and transport potential, PAHs may become fractionated from source regions to remote regions during atmospheric transport. In addition, the sequestration of PAHs in the soils is important when soil samples are extracted by solvent, however, there are more sequestration in the soils for high ring PAH than low ring PAH (Yang et al., 2009), so it can’t explain the lower concentration for 2,3-ring PAHs in urban soils and higher concentration for 2,3-ring PAHs in remote soils. Furthermore, in rural villages, coal and biomass combustion are the major sources of PAH contamination, and the emission factors for low ring PAH from biomass burning are higher than coal combustion (Zhang et al., 2007), and there are more photochemical degradation for low ring PAH in urban than in rural villages because of OH radical (Wang et al., 2009), so that's the reason why high 2,3-ring PAH existed in rural village area than urban area.

4. Conclusion

The concentrations of 16 PAHs (ΣPAH_{16}) in Beijing, Tianjin and surrounding areas ranged from 31.6 to1475.0 ng/g (dry wt), with an arithmetic average of 336.4 ng/g, and the seven carcinogenic PAHs accounted for 18–49% of the $\Sigma PPAH_{16}$ concentration. The 3–4 rings PAHs, phenanthrene, fluoranthene, pyrene and benzo(b)-fluoranthene, were in highest concentration. The most contaminated areas are urban Beijing and Tianjin city, east and southwest of Hebei province, however, the areas with the lowest PAH concentrations are mountain area northwest of Hebei province (Zhangjiakou) with relatively low population density. The background–rural village–urban PAH concentration gradient was related to the PAH emission source intensity, population density, GDP, long-range atmospheric transport and different types of land use. In addition, the PAH concentration was well correlated with the TOC concentration of the soil, however, the population density and GDP are more important for explaining the spatial distribution of soil PAHs concentrations in Beijing, Tianjin and surrounding areas than TOC concentration. The present results suggested that coal combustion and biomass burning were primary PAH sources in Beijing, Tianjin and surrounding areas.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This study is supported by National Basic Research Program (2007CB407301), National Science Foundation of China (Grant 140710019001 and 40730737) and China Scholarship Council (to Wentao Wang). The project described was also supported by Award Number P42ES016465 and P30ES00210 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institute of Environmental Health Sciences or the National Institutes of Health. We are also grateful to two anonymous reviewers for constructive comments.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.envpol.2010.01.021.

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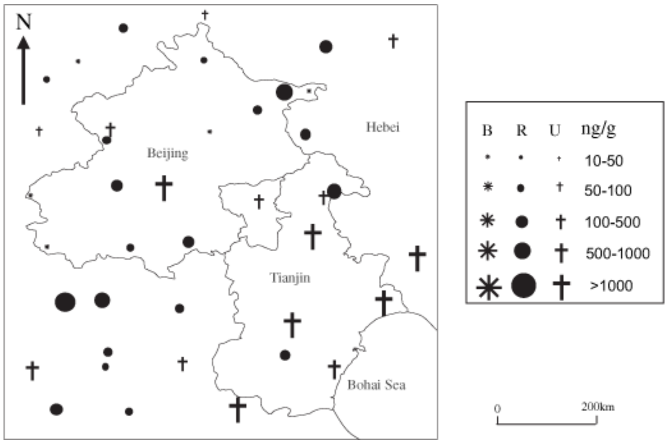

Fig. 1.

Map of sampling sites and ΣPAH_{16} concentrations in soil. Three categories of sampling sites: urban (U), rural village (R) and background areas (B).

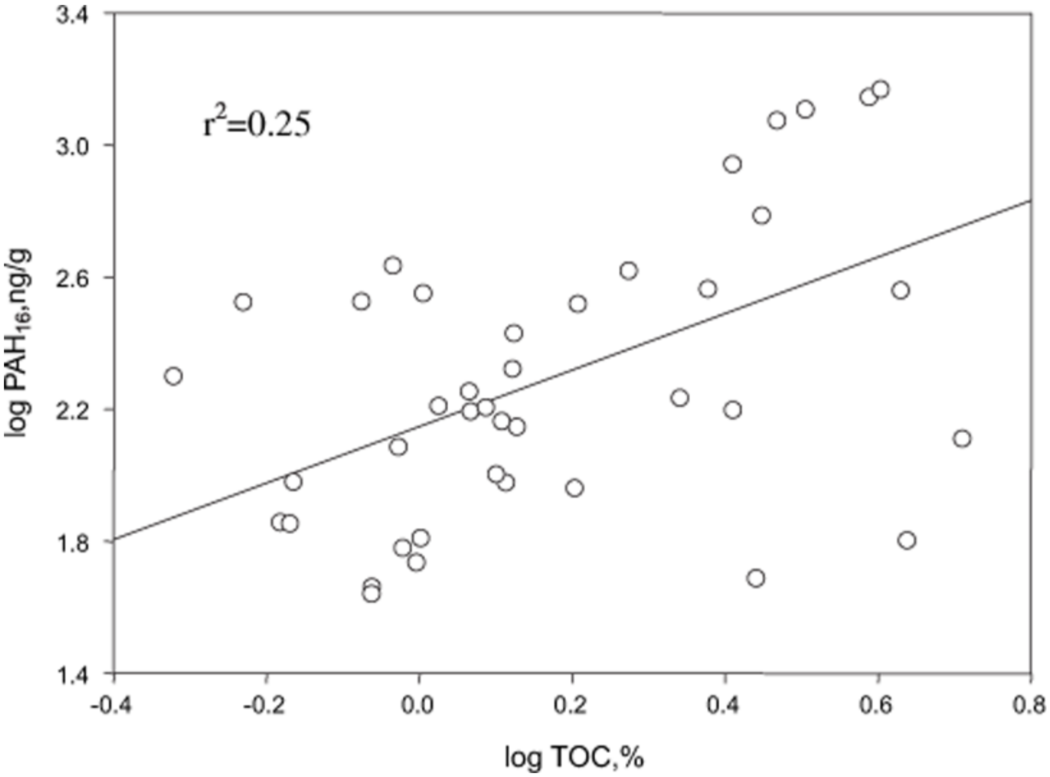

Fig. 2.

The scatter plot between soil ΣPAH_{16} concentration and TOC concentration. Both parameters are log-transformed.

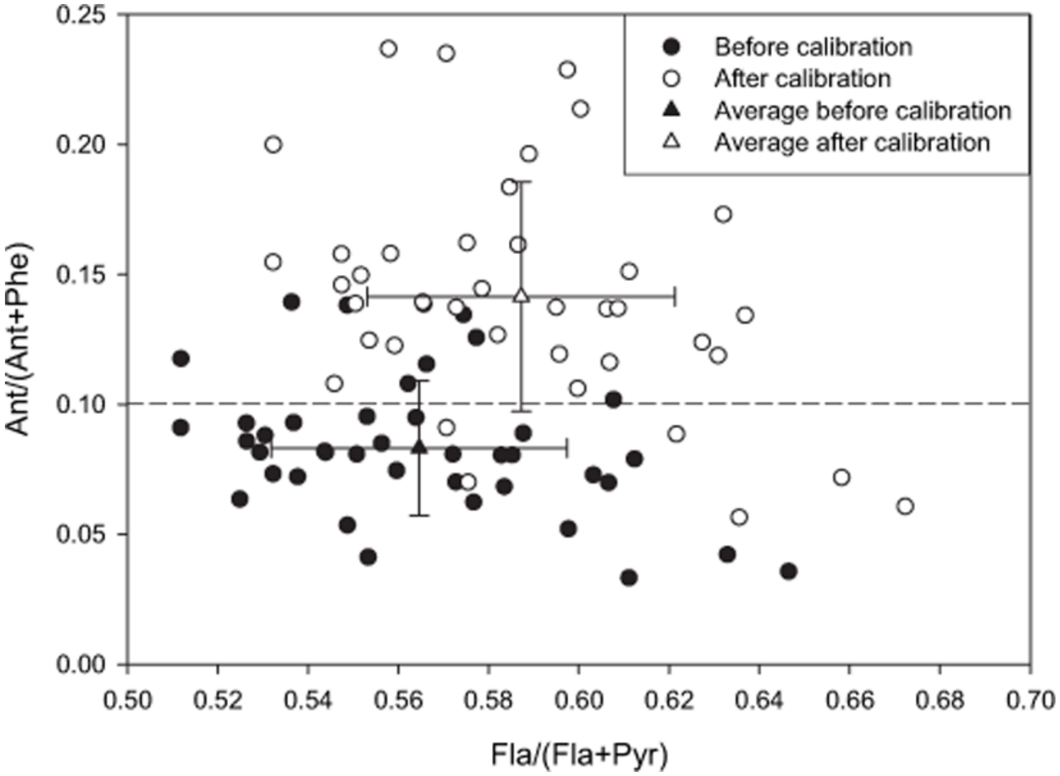

Fig. 3.

Cross plot of the Ant/(Ant + Phe) and Fla/(Fla + Pyr) ratio before and after using calibration factors.

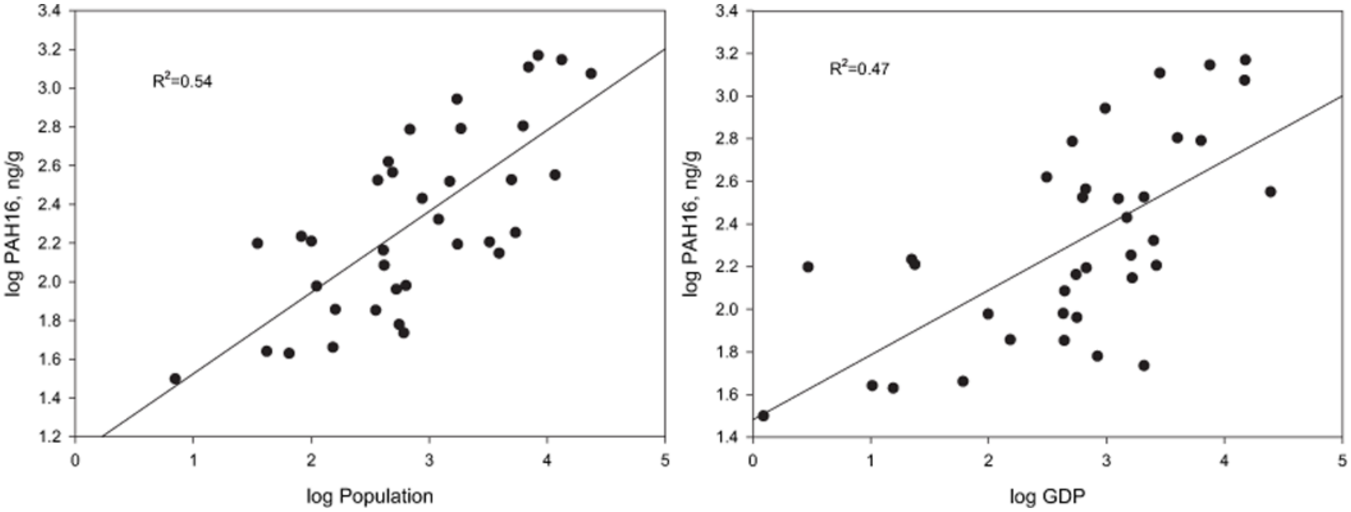

Fig. 4.

Scatter plots of soil ΣPAH_{16} concentration in rural and urban soils against village or city population density (left) and GDP (right).

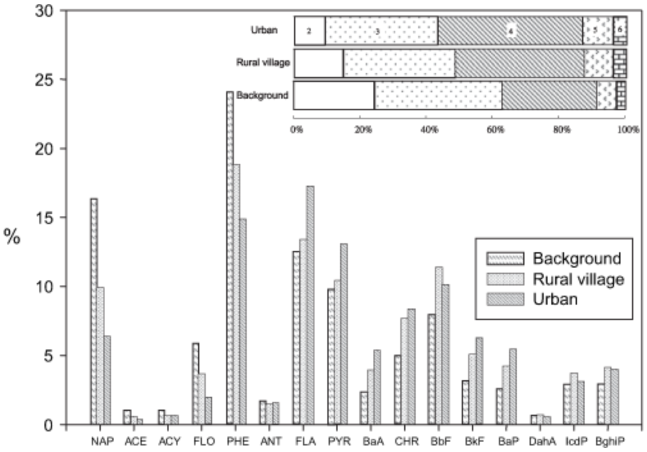

Fig. 5.

The PAH profiles for background, rural and urban locations (2: 2-ring PAH; 3: 3-ring PAH; 4: 4-ring PAH; 5: 5-ring PAH; 6: 6-ring PAH).

Table 1

PAH concentrations in soils ($n = 40$, ng/g).

	A.M.	St.d.	Min.	Max.	G.M.	Median	%
NAP	25.8	24.9	1.4	125.8	17.4	17.6	7.7%
ACE	1.7	1.7	0.3	8.4	1.3	1.1	0.5%
ACY	2.3	3.0	0.1	13.3	1.3	1.3	0.7%
FLO	8.7	6.8	1.6	28.9	6.7	6.1	2.6%
PHE	54.9	55.6	11.1	232.8	37.1	32.1	16.3%
ANT	5.4	6.6	0.4	26.4	3.2	2.9	1.6%
FLA	54.1	75.1	3.0	317.6	27.2	27.0	16.1%
PYR	41.3	56.5	1.9	235.3	21.0	20.4	12.3%
BaA	16.8	26.8	0.7	125.8	7.0	6.5	5.0%
CHR	27.2	35.0	1.9	130.3	13.5	11.7	8.1%
BbF	35.1	40.3	2.8	170.2	19.0	16.0	10.4%
BkF	19.8	26.6	0.5	114.8	8.7	7.7	5.9%
BaP	16.9	24.2	0.7	102.6	7.2	6.4	5.0%
DahA	2.4	2.7	N.D.	10.9	1.5	1.4	0.7%
IcdP	11.1	12.5	0.7	52.2	6.0	4.6	3.3%
BghiP	13.5	17.1	0.8	81.1	6.7	5.4	4.0%
$\Sigma PAH_{2\text{-ring}}$	38.5	34.7	3.4	172.9	27.6	26.8	11.4%
$\Sigma PAH_{3\text{-ring}}$	114.4	131.2	15.2	498.9	69.5	62.8	34.0%
$\Sigma PAH_{4\text{-ring}}$	140.2	180.0	9.0	667.5	70.6	61.2	41.7%
$\Sigma PAH_{5\text{-ring}}$	29.9	38.7	1.4	165.6	14.2	12.0	8.9%
$\Sigma PAH_{6\text{-ring}}$	13.5	17.1	0.8	81.1	6.7	5.4	4.0%
ΣPAH_{16}	336.4	389.0	31.6	1475.0	195.1	161.2	–
ΣPAH_{7c}	128.8	163.1	8.6	658.6	63.4	53.2	38.3%

A.M.: Arithmetic means; St.d.: Standard deviation; G.M.: Geometric means; N.D.: Under detection limit.

Table 2

Soil PAH concentration comparison to other studies.

Sites	Types	Con. (ng/g)	PAHs	Reference
Nanjing, China	Vegetable soil	22–53[a], 178[b]	15	Yin et al. (2008)
Guangzhou, China	Vegetable soil	160–3700, 1503	16	Cai et al. (2007)
Yangtze Delta, China	Agricultural soil and grassland	8.6–3881, 397	15	Ping et al. (2007)
Delhi, India	Agricultural soil	–, 830	16	Agarwal et al. (2009)
Korea	Agricultural soil	23–2830, 236	16	Nam et al. (2003)
Shunde, China	Agricultural soil	34–350, 144	16	Li et al. (2008)
Czech Republic	Arable soil	139–2436, 847	16	Holoubek et al. (2009)
Poland	Agricultural soil	18–2450, 264	16	Maliszewska-Kordybach (1996)
Poland	Agricultural soil	–, 423	16	Maliszewska-Kordybach et al. (2009a)
Poland	Agricultural soil	73–1800, 252	16	Maliszewska-Kordybach et al. (2009b)
Welsh	Rural	–, 187	16	Jones et al. (1989)
Beijing, China	Suburban and Rural	16–3884, 1347	16	Ma et al. (2005)
Tianjin, China	Urban and Rural	199–5190, 818	16	Zuo et al. (2007)
Dalian, China	Urban and Rural	219–18,727, 1104	14	Wang et al. (2007a)
Hong Kong, China	Urban and Rural	7–410, 54.6	16	Zhang et al. (2006)
Beijing, China	Urban	219–27,825, 3917	16	Tang et al. (2005)
Shanghai, China	Urban	442–17,900, 3290	16	Jiang et al. (2009)
New Orleans, US	Urban	–, 2927	16	Mielke et al. (2004)
Beijing and Tianjin	Agricultural soil and grassland	32–1475, 336	16	This study

[a] The concentration range.

[b] The arithmetic mean.

Table 3

The correlation coefficient between soil individual PAH concentration and TOC concentration, population density and GDP ($n = 40$).

	NAP	ACE	ACY	FLO	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	DahA	IcdP	BghiP	ΣPAH16
TOC	0.26	0.46^{**}	0.37^{*}	0.36^{*}	0.45^{**}	0.42^{**}	0.46^{**}	0.45^{**}	0.46^{**}	0.45^{**}	0.44^{**}	0.41^{**}	0.45^{**}	0.45^{*}	0.42^{**}	0.44^{**}	0.46^{**}
Population density	0.38^{*}	0.49^{**}	0.43^{**}	0.42^{**}	0.52^{**}	0.56^{**}	0.57^{**}	0.57^{**}	0.60^{**}	0.60^{**}	0.56^{**}	0.57^{**}	0.56^{**}	0.56^{**}	0.53^{**}	0.54^{**}	0.56^{**}
GDP	0.55^{**}	0.56^{**}	0.55^{**}	0.51^{**}	0.55^{**}	0.63^{**}	0.62^{**}	0.62^{**}	0.65^{**}	0.67^{**}	0.62^{**}	0.65^{**}	0.62^{**}	0.62^{**}	0.59^{**}	0.60^{**}	0.63^{**}

$^{**}p < 0.01$;

$^{*}p < 0.05$.

Table 4

PAH concentrations in background (B), rural (R) and urban (U) soils (ng/g).

		NAP	ACE	ACY	FLO	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	DahA	IcdP	BghiP	ΣPAH_{7c}	ΣPAH_{16}	$R_{\leq 3/\geq 4}$
B ($n = 5$)	A.M.	11.2	0.7	0.7	4.0	16.4	1.2	8.5	6.7	1.6	3.4	5.4	2.1	1.8	0.5	2.0	2.0	16.5	67.8	1.7
	St.d.	10.6	0.4	0.6	2.0	5.4	0.7	4.6	4.4	0.9	1.6	2.3	1.7	1.2	0.1	1.2	1.3	8.6	36.6	0.4
R ($n = 20$)	A.M.	19.4	1.3	1.3	7.2	36.9	2.9	26.2	20.4	7.7	15.1	22.4	9.9	8.3	1.4	7.3	8.1	71.7	195.3	1.3
	St.d.	14.5	0.8	0.8	5.1	25.8	1.8	20.3	17.2	7.3	13.8	22.0	10.6	8.4	1.2	7.9	9.1	68.2	153.3	0.4
U ($n = 15$)	A.M.	39.7	2.7	4.1	12.4	93.2	10.3	107.6	81.4	34.3	52.1	63.2	39.3	34.0	3.8	19.5	24.9	246.0	622.4	0.8
	St.d.	32.6	2.3	4.2	8.1	71.5	8.7	100.8	75.4	37.3	45.2	49.5	34.0	32.0	3.2	15.0	21.8	208.8	495.3	0.3