Characterization of PAHs Contamination in Soils from Metropolitan Region of Northern China

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Abstract The present study characterized the distribution, sources as well as carcinogenic potency of PAHs in surface soil from metropolitan region of northern China. The total PAHs in topsoil ranged from 322.6 to 23244.7 $\mu\text{g kg}^{-1}$. The mean and median concentrations of 16 PAHs were 1040.8 and 626.7 $\mu\text{g kg}^{-1}$, respectively. Source analysis revealed that pyrogenic sources played a major role at the locations and pyrogenic PAHs were mainly from incomplete combustion of coal, biomass and petroleum. The calculated mean BaP-equivalent values for individual carcinogenic PAHs were 148.4 $\mu\text{g kg}^{-1}$.

Keywords Soil · PAH · Spatial distribution · Sources

Polycyclic aromatic hydrocarbons (PAHs) are widely spread in all the compartments of the environment. Forest fires, volcanoes and microbial metabolism are the predominant natural sources. However, most of the PAHs are originated from anthropogenic activities, such as fuel spills, combustion of fuels, coal and wood (Srogi 2007). Especially in megacities, larger emissions of PAHs were

observed due to the accelerated urbanization and high-density traffic condition (Tuntawiroon et al. 2007).

Due to their stable chemical structure and hydrophobic nature, PAHs are generally found adsorbed to particulate matter in air and water, and tend to accumulate in sediment, soil or biota. Thus, although most PAHs are emitted to the atmosphere, the airborne PAHs can eventually reach the top layer of the soil to become adsorbed by soil colloids and absorbed by soil organisms (Srogi 2007). Soils could be regarded as natural sinks for PAHs. Because of the notable carcinogenic and mutagenic properties, PAHs present in the soil environment can exhibit ecotoxic effects on the development of soil organisms and create threats to the soil habitat function even at low levels. It is also of great concern because the contaminated soils can create a risk to humans through direct contact or through its introduction into the human food chain.

Megacities are considered more vulnerable with the large population and limited land resources. Therefore, it is important to evaluate the spatial distribution and apportion the sources of PAHs in soils from megacities, then to assess the potential risk of soil contamination with PAHs. The present study was carried out on a regional scale to survey the soil PAHs contamination in a mega-metropolitan region in northern China including Beijing, Tianjin and parts of the Hebei province. As we known, Beijing is the capital of the People's Republic of China. Tianjin, one of the four municipalities of China, is the largest coastal city open to the outside world in northern China. The mega-metropolitan region of Beijing-Tianjin-Hebei presently accounts for 11% of the country's gross domestic product (GDP), however, environmental pollution has become a serious problem with the rapid development of industrialization and urbanization. Although PAHs concentrations have been reported in part of this area (Zuo et al. 2007), our

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knowledge of the general contamination pattern and environmental risk in this mega-metropolitan region is still inadequate. This study presents an overview of the distribution pattern and source assignment of 16 EPA PAHs in soil samples and gives insights into the potential risk of this metropolitan region.

Materials and Methods

The study area includes Beijing, Tianjin and parts of the Hebei province, covering an area about 64,400 km² (Fig. 1). There were totally 180 soil samples were collected in July 2007 and the sampling depth was 0–20 cm. At each site, about 5 cores were bulked together to form one sample. The samples were air-dried at room temperature and were ground and sieved with a 60-mesh sieving screen. All results were reported as dried weight basis.

About 5 g soil samples were mixed with anhydrous sodium sulfate and activated copper powder. Samples were extracted by accelerated solvent extraction (Dionex ASE 300) with acetone/dichloromethane solvent (1:1/v/v). The extracts were cleaned up via silica gel/alumina column and PAHs fraction was obtained by elution with 70 mL of a mixture of hexane/dichloromethane (7:3, v/v). The samples were analyzed by GC/MS (Agilent 7890 GC, 5975 MSD) in selected ion monitoring (SIM) modes and quantified by internal calibration method. Detailed description of clean up and analysis were described elsewhere (Qiao et al. 2006). PAHs studied were naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene

(Phe), anthracene (An), 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-cd]pyrene (InP), dibenzo[a,h]anthracene (DBA), and benzo[ghi]perylene (BgP).

All data were subject to strict quality control procedures. Recovery ranged from 53.8 ± 4.9% to 117.2 ± 7.5% with a mean value of 94.0 ± 8.3% for the 16 PAHs. The detection limits were 1.7–4.9 µg kg⁻¹. Procedure blanks were run simultaneously with every set of samples and were subtracted from the analytical results.

Statistical analyses including principal component analysis among variables were conducted using the software SPSS 11.5 for Windows. Kriging interpolation and contour maps were constructed with Surfer 8.0 (Golden Software, Co., USA).

Results and Discussion

The total PAHs in topsoil of the study area ranged from 322.6 to 23244.7 µg kg⁻¹, and the mean concentration of 16 PAHs was 1040.8 µg kg⁻¹. Concentrations of individual PAHs exhibited a rather high variability with a mean coefficient of variation (CV) value of 1.8. The median value of 626.7 µg kg⁻¹ was considered more appropriate for the assessment of the mean concentration of 16 PAHs in this area because of their non-normal distribution. High molecular weight PAHs with 4–6 rings were the major fractions of the total PAHs in topsoil with an average proportion of 71%. Maliszewska-Kordybach classified soil PAHs contamination into 4 categories, namely not contaminated (<200 µg kg⁻¹), weakly contaminated (200–600 µg kg⁻¹), contaminated (600–1,000 µg kg⁻¹), and heavily contaminated (>1,000 µg kg⁻¹) (Maliszewska-Kordybach 1996). According to this classification, the concentrations obtained in this study present 46% of the samples as ‘weakly contaminated’, 37% as ‘contaminated’ and 17% as ‘heavily contaminated’. Observed median concentration of ∑16 PAHs (626.7 µg kg⁻¹) were comparable to the mean PAHs concentration of 611 µg kg⁻¹ in Tokushima of Japan (Yang et al. 2002) and the median concentration of 704 µg kg⁻¹ in urban soil of Torino, Italy (Morillo et al. 2007). The concentration was higher than those in soil from Hong Kong (median of 140 µg kg⁻¹) (Chung et al. 2007) and urban soil in Switzerland (median of 451 µg kg⁻¹) (Bucheli et al. 2004). In contrast, PAHs concentrations in soil from Glasgow, UK (median of 8337 µg kg⁻¹, mean of 11930 µg kg⁻¹, Morillo et al. 2007) were higher than those obtained in this study.

Ordinary kriging interpolation was applied to visualize the spatial distribution of PAHs in topsoil in the study area since it can provide theoretically optimal estimates without

Fig. 1 Sampling sites of surface soil in Beijing, Tianjin and the surrounding regions in China

bias and with minimal and known variance. The relatively high concentration levels were found in Tianjin and Beijing urban or peri-urban area (Fig. 2). Another hotspot located on the north of Tianjin where was associated with mining activity in the last several decades. It clearly indicates the influence of human activities on PAHs levels of soils.

To assess and reduce the environmental risk of PAHs, it is essential to identify the potential sources. Isomeric ratios of PAHs are known to provide reliable estimation of the emission sources of PAHs. $An/(An + Phe)$ and $Flu/(Flu + Pyr)$ are frequently used PAH ratios to separate petrogenic and pyrogenic sources (Yunker et al. 2002). PAHs originated from petrogenic sources are characterized by the ratios of $An/(An + Phe) < 0.1$ and $Flu/(Flu + Pyr) < 0.4$. Accordingly, the ratio of $An/(An + Phe) > 0.1$ implies the dominance of combustion. The ratio of $Flu/(Flu + Pyr) > 0.5$ indicates the source of biomass and coal combustion, while the ratio between 0.4 and 0.5 are characteristic of liquid fossil fuel (vehicle and crude oil) combustion. Furthermore, $BaA/(BaA + Chr)$ and $InP/(InP + BgP)$ are also used to distinguish between petrogenic and pyrolytic sources. Yunker et al., suggested that a $BaA/(BaA + Chr)$ or $InP/(InP + BgP)$ ratio less than 0.2 indicates petroleum source. A ratio of $BaA/(BaA + Chr) > 0.35$ accounts for combustion of coal, grass and wood, while the ratio between 0.2 and 0.35 accounts for petroleum combustion. The ratio of $InP/(InP + BgP) > 0.5$ is characteristic of grass, wood or coal combustion, from 0.2 to 0.5 indicates liquid fossil fuel combustion (Yunker et al. 2002). In this study, these molecular markers were interpreted in concert and checked for consistency to identify the possible PAHs sources of soil samples. In cross plots (Fig. 3), $An/(An + Phe)$ ratios in all soil samples are more than 0.1, and $Flu/(Flu + Pyr)$ ratios in most of soil samples are in the combustion section irrespective of

petroleum combustion or biomass & coal combustion. The ratio of $BaA/(BaA + Chr)$ ranged from 0.18 to 0.64, with 59% of the values larger than 0.35 and 41% of the values falling between 0.2 and 0.35, which suggests that the majority of PAHs in the topsoil originated from combustion. As shown in the cross plot (Fig. 3), the values of $InP/(InP + BgP)$ varied between 0.25 and 0.67, confirmed the soils were mainly suffered from mixed source of both biomass/coal combustion and petroleum combustion.

PCA was also performed to examine the sources of PAHs pollution in soils. Two factors with eigenvalues over 1 were extracted after applying the Varimax rotation and

Fig. 2 Spatial distribution of PAH concentrations for 16 PAHs ($\mu\text{g kg}^{-1}$)

Fig. 3 PAH cross plots **a** $An/(An + Phe)$ versus $Flu/(Flu + Pyr)$, **b** $BaA/(BaA + Chr)$ versus $Flu/(Flu + Pyr)$, **c** $InP/(InP + BgP)$ versus $Flu/(Flu + Pyr)$

were able to explain 89% of the total variance. PC1 was strongly correlated with the higher molecular mass compounds, including Flu, Pyr, BaA, Chr, BbF, BkF, BaP, InP, DBA and BgP. PC 2 was dominated by low ring compounds including Nap, Ace, Fl, Phe and An. The different structures of the high and low ring PAH compounds could be attributed to the different sources and physico-chemical and biological characteristics of these compounds (Agarwal 2009). The loading plot of PCA was exhibited in Fig. 4. Some researches have reported Flu, Pyr, BaA, Chr, BbF, BkF and BaP as predominant in coal combustion profiles (Larsen and Baker 2003). Both BgP and InP have been identified as typical tracers of vehicle emissions (Fraser et al. 1997). DBA predominates in gasoline engine exhaust tar (Fraser et al. 1997). Therefore, PC1 was regarded as the combined coal combustion and vehicular emission source. Fl, Phe and An are indicators for coke production. Nap accounted for the majority of the mass in coke oven, highway tunnel and gasoline engine samples (Khalili et al. 1995). Thus, PC2 was considered as coke oven sources. As shown in the cross plot of Fig. 4, Acy was separated from other compounds, suggesting other contribution sources exist. Acy has been reported to be a tracer for domestic wood combustion or vehicular emission (Jiang et al. 2009). Biomass combustion could be a possible explanation for the unidentified source since it is very common in north China to burn crop straw in the pen air after crop harvesting (Cao et al. 2008). The PCA results were consistent with the isomeric ratio analysis that coal/biomass combustion and petroleum combustion were the main contributors of PAHs accumulation in topsoil of Beijing, Tianjin and the surrounding regions.

The United States Environmental Protection Agency (USEPA) has classified seven PAHs including BaA, Chr, BbF, BkF, BaP, InP and DBA as Group B2, probable

human carcinogens. The concentrations of these seven carcinogenic PAHs were from 139.3 to 17768.8 $\mu\text{g kg}^{-1}$ and the percentage was from 24 to 76%. At present, no PAHs guideline values in soil are available in China. To assess the hazard of PAHs contaminated soil, toxic equivalency factors (TEFs) were used to quantify the benzo[a]pyrene-equivalent concentration (BaPeq). The carcinogenic potencies of individual carcinogenic PAHs were calculated by multiplying their concentration with the corresponding TEF. The total carcinogenic potency was estimated by the sum of each BaPeq. TEFs compiled by Tsai et al. (2004) were adopted to calculate BaPeq. Calculated total BaPeq concentrations varied from 35.9 to 5415.5 $\mu\text{g kg}^{-1}$. The mean and median BaPeq concentrations were 148.4 and 81.8 $\mu\text{g kg}^{-1}$, respectively. Although the highest BaPeq was even higher than that in traffic soil of India (1,009 $\mu\text{g kg}^{-1}$) (Agarwal 2009), the average or median BaPeq was lower than those in Shanghai urban soil (428 $\mu\text{g kg}^{-1}$) (Jiang et al. 2009) from China. The BaPeq was comparable to that in industrial soil (124 $\mu\text{g kg}^{-1}$) and residential soil (96 $\mu\text{g kg}^{-1}$) from Tarragona County of Spain (Nadal et al. 2004). The major contributors to BaPeq are BaP, DbA, BbF, InP and BkF, accounting for 47, 29, 8, 6 and 5% on average, respectively. The soil PAHs contamination of this study was found to be low to moderate on the global scale. The city centers or sites close to any other contamination source present higher amounts of PAHs.

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References

- Agarwal T (2009) Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi, India. *J Hazard Mater* 171:894–900
- Bucheli TD, Blum F, Desaulles A, Gustafsson Ö (2004) Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere* 56:1061–1076
- Cao G, Zhang X, Wang Y, Zheng F (2008) Estimation of emissions from field burning of crop straw in China. *Chin Sci Bull* 53:784–790
- Chung MK, Hu R, Cheung KC, Wong MH (2007) Pollutants in Hong Kong soils: polycyclic aromatic hydrocarbons. *Chemosphere* 67:464–473
- Fraser MP, Cass GR, Simoneit BRT, Rasmussen RA (1997) Air quality model evaluation data for organics.4. C2–C36 non-aromatic hydrocarbons. *Environ Sci Technol* 31:2356–2367
- Jiang YF, Wang XT, Wang F, Jia Y, Wu MH, Sheng GY, Fu JM (2009) Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere* 75:1112–1118
- Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmos Environ* 29:533–542

Fig. 4 Principal component analyses loading plot for individual components of PAHs

- Larsen RK, Baker JE (2003) Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ Sci Technol* 37:1873–1881
- Maliszewska-Kordybach B (1996) Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Appl Geochem* 11:121–127
- Morillo E, Romero AS, Maqueda C, Madrid L, Ajmone-Marsan F, Grcman H, Davidson CM, Hursthouse AS, Villaverde J (2007) Soil pollution by PAHs in urban soils: a comparison of three European cities. *J Environ Monit* 9:1001–1008
- Nadal M, Schuhmacher M, Domingo JL (2004) Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environ Pollut* 132:1–11
- Qiao M, Wang C, Huang S, Wang D, Wang Z (2006) Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environ Int* 32:28–33
- Srogi K (2007) Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. *Environ Chem Lett* 5:169–195
- Tsai PJ, Shih TS, Chen HL, Lee WJ, Lai CH, Liou SH (2004) Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station worker. *Atmos Environ* 38:333–343
- Tuntawiroon J, Mahidol C, Navasumrit P, Autrup H, Ruchirawat M (2007) Increased health risk in Bangkok children exposed to polycyclic aromatic hydrocarbons from traffic-related sources. *Carcinogenesis* 28:816–822
- Yang Y, Zhang X-X, Korenaga T (2002) Distribution of Polynuclear Aromatic Hydrocarbons (PAHs) in the Soil of Tokushima, Japan. *Water Air Soil Poll* 138:51–60
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515
- Zuo Q, Duan YH, Yang Y, Wang XJ, Tao S (2007) Source apportionment of polycyclic aromatic hydrocarbons in surface soil in Tianjin, China. *Environ Pollut* 147:303–310