POLYCYCLIC AROMATIC HYDROCARBONS IN THE TOPSOILS OF HARBIN, CHINA

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Abstract
The concentration levels of polycyclic aromatic hydrocarbons (PAHs) in 18 topsoil samples (0-20cm) collected in the City of Harbin, China in 2006 are presented. The total concentrations of the 16 PAHs ranged from 17 to 3,260 ng/g dry weight (dw) with an average of 520 ng/g dw. Large differences of the concentration levels of PAHs in topsoil were found among the samples from urban, suburban, and background/rural sites, with mean values of 50 ng/g dw for background/rural sites, 170 ng/g dw for suburban sites, and 830 ng/g dw for the urban sites. The PAH profiles were similar, with high percentages of high-molecular-weights PAHs, and dominated by 4-ring PAHs. A strong correlation was found between the PAH concentration in topsoil and the total organic carbon content of the soil. The sources of PAH in Harbin were also investigated. The results indicated that the dominant sources in this region are pyrogenic origin, such as coal and fuel combustion from domestic heating and traffic exhausts.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms.[1] PAHs emitted in the environment originate mainly from anthropogenic sources, such as oil spills, wastewater, vehicle exhaust and industrial discharge. They are formed as by-products of incomplete combustion of organic materials.[2] Due to their carcinogenic properties and acute toxicity, PAHs have been attracting much attention in recent years.[3,4,5]

Soil is one of the most important storage and transfer media for PAHs in the environment.[6] PAH concentration detected in soil correlates significantly with the corresponding levels in air and sources, therefore, PAH concentration in soil may provide important information on the environmental pollution state.[7] Some researches have been published for PAHs in soil samples from Beijing[8] and Tianjin[9]. Little information is available on PAH concentration in northeast of China, where industrialization and urbanization have been rapidly developed during the past several years. The purpose of this study is to provide information on the concentration and distribution of PAHs in topsoil collected in the City of Harbin City, one of the largest cities in this region. To our knowledge, there has not been any published information on soil concentrations and distribution of PAHs in the city.

2. Material and methods

2.1 Sampling

Harbin is the capital city of Heilongjiang Province, located at the Songhua River, and between 44°04′-46°40′ North and 125°42′-130°10′ East. The population of the city is about 3.84 million, and the urban area is about 4272 km^2. The annual mean temperature is 3.6 ^{o}C and the annual average rainfall is 523.3 mm.

Eighteen topsoil samples were collected from 18 sites within and outside of Harbin City in October 2006, among which, 10 are urban, 6 suburban, 1 rural, and 1 background. Soil sampling sites were away from pollution sources and any roads. The top (0-20cm) soil was collected using a stainless steel scoop that had been pre-washed by acetone. Five subsamples composed one sample, which was placed in a pre-washed glass flask with teflon cap and kept frozen in the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) laboratory in Harbin Institute of Technology, Harbin, where they were stored frozen (-20^{o}C) until required for extraction.

2.2 Analytical methods

Details of samples extraction and clean up are presented elsewhere[10]. 20 grams of soil were Soxhlet extracted for 24h with 100ml mix solvent (n-hexane/acetone, 1:1 v/v). The extract was then filtered through a funnel filled with anhydrous sodium sulfate and rotary-evaporated to 4 ml. The extract was passed through 10g silica gel column, eluted with 50ml mixture of hexane and dichloromethane (DCM, 1:1, v/v). The elution was

rotary-evaporated to 2 ml and then reduced to 0.2 ml under a gentler nitrogen gas flow. Samples were analyzed by GC-MS as described previously[10]. All PAH calibration and internal standards were purchased from Supelco Co. (Supelco, USA). The soil organic carbon (SOC) for each sample was measured by using a Shimadzu TOC Analyzer (Model TDC-VCPN, Kyoto, Japan).

2.3 QA/QC

All samples were spiked with a labeled recovery standard (CB 65 and 155, PAH recovery standards should be used) prior to extraction. Sample recoveries averaged for CB 65 112 ± 11% and 111 ± 12% for CB 155 in all samples. Results of blanks extracted under the same conditions were below detection limits and sample results were displayed without blank correction.

3. Results and discussion

3.1 PAH concentration and distribution

Concentrations of ∑PAHs (total 16 PAHs as priority pollutants promulgated by the US Environmental Protection Agency (EPA): NAP, naphthalene; ACY, acenaphthylene; ACE, acenaphthene; FLU, fluorene; PHE, phenanthrene; ANT, anthracene; FTH, fluoranthene; PYR, pyrene; BaA,benz(a)anthracene; CHR, chrysene; BbF, benzo(b)-fluoranthene; BkF, benzo(k)fluoranthene; BaP, benzo(a)pyrene; DahA, dibenz(a,h)anthracene; IcdP, indeno(l,2,3-cd)pyrene; BghiP, benzo(g,h,i)perylene) in surface soil for each site, shown in Figure 1, were largely different, ranged from 17 ng/g dry weight (dw) at Site SU2 to 3,260 ng/g dw at UR1, with an average of 520 ng/g dw for all 18 samples. The concentration of ∑PAHs in urban area was higher than suburban and background/rural areas, with a ratio of up two orders of magnitude. The mean concentration of the 10 urban samples was 830 ng/g dw, followed by 170 ng/g dw for the 6 suburban and rural samples and 50 ng/g dw for the 2 background/rural samples. According to the classification derived from the results of determinations of PAH concentrations in European soils[11], three urban samples (UR1, UR4, UR9) were classified as heavily contaminated (∑PAHs > 1000 ng/g), urban Site UR7 was classified as contaminated (600 ng/g < ∑PAHs <1000 ng/g), all other urban samples and one of suburban sites (SU6, with 549.9 ng/g) as weakly contaminated (200 ng/g < ∑PAHs <600 ng/g), and all the rest 6 sites can be considered as not contaminated (∑PAHs < 200 ng/g).

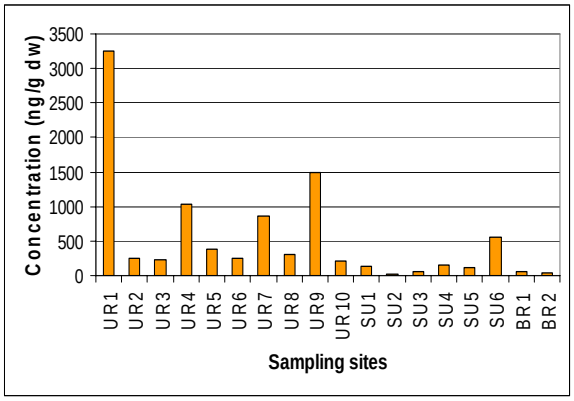

Fig. 1. Concentrations of total 16 PAHs for each sampling site. UR:urban, SU:suburban, BR:background/Rural.

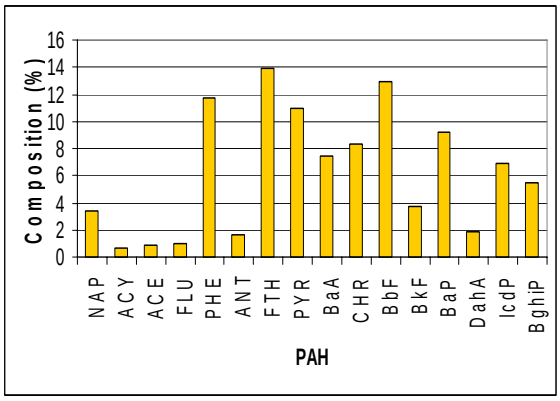

Fig. 2. Composition of PAHs in all samples.

Composition of PAH in surface soil for all sites is depicted in Figure 2, showing that, the dominant compounds in all samples were FTH (14%), BbF (13%), PHE (12%), and PYR (11%), and the carcinogenic PAHs (BaA, CHR, BbF, BkF, BaP, DahA, IcdP, and BghiP) represented 56% of the total PAH content.

Figure 3 presents the composition of PAH group by ring for urban, suburban, and background/rural samples. The similar composition pattern of PAHs indicated the same sources of PAH in this region. Although the patterns are similar, the 2-PAH is higher and the 6-PAH is lower for background/rural samples than urban and suburban samples, possibly indicating the local transport of these chemicals that lighter PAHs are atmospheric transported over longer distances more easily than heavy ones.[3,12]. The concentrations of highest molecular weight (HMW) PAHs with four to six-ring were approximately 4 times as many as those for low molecular weight (LMW)

PAHs with two to three-ring in all samples.

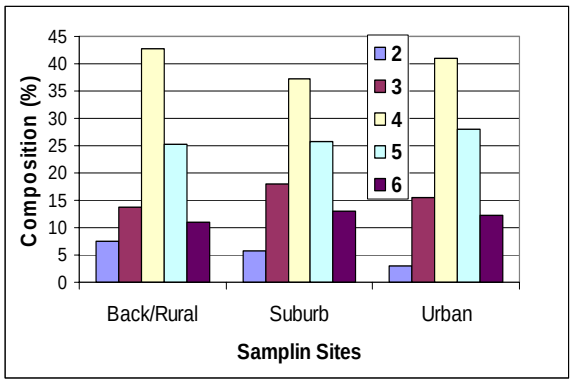

Fig. 3.Composition pattern of PAHs in topsoils by ring size.

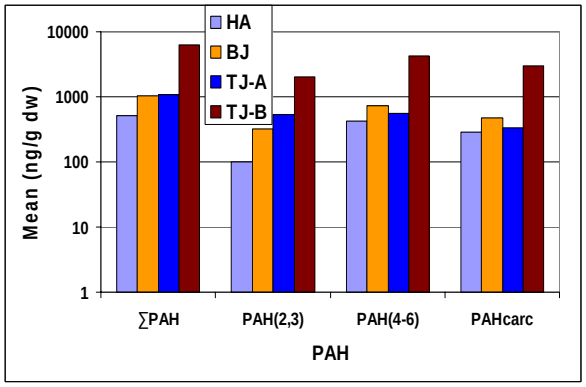

Fig. 4. Concentration for total PAHs, total 2 and 3 ring PAHs, total 4-6 ring PAHs, and total carc PAHs in topsoil for three cities of Harbin, Beijing[8], and Tianjin[9]. HA, Harbin; BJ, Beijing; TJ-A, Area A in Tianjin; and TJ-B, Area B in Tianjin.

3.2 Comparison with other cities

Only a few studies have measured PAH levels in Chinese cities. Figure 4 presents concentration for total PAHs, total 2 and 3 ring PAHs, total 4-6 ring PAHs, and total carcinogenic PAHs in topsoil for three cities of Harbin, Beijing, and Tianjin. Samples in Beijing exhibited a mean concentration of 1,350 ng/g dw ranged from 16 ng g^{-1} in rural to 3,880 ng g^{-1} in suburban soils in 2001[8], which is much higher than the average of 520 pg/g from this study. 188 samples (0–10 cm) were collected from 2 areas (A and B) in Tianjin in September, 2002[9], A is located in a less contaminated area, and B is immediately next to an urban district (less than 0.5 km) and is in the vicinity of a number of pollution sources, including large-scale coal-burning boiler and factories. The agricultural land here has been irrigated with wastewater for more than 40 years. The mean concentration of PAH16 of all samples was 820 ng/g ranging from 200 to 5,190 ng/g. The Mean concentrations of ΣPAHs in soil from the two areas were 1,080 and 6,250 ng/g, respectively, with similar pattern. Although PAH level in topsoil in Harbin were much lower than those in Beijing and Tianjin, the percentages of HMW-PAH and carc-PAH to total PAHs in topsoil of Harbin were higher than those for other 2 cities.

3.3 Regression Analysis

Organic matter content in soil is clearly an important variable that influences the concentration of POPs. Our study shows the correlation between ΣPAHs and SOC content, which is statistically significant, $p < 0.0012$ with quite strong correlation (r^2=0.46).

3.4 Sources of PAHs

The main PAH pollution sources of the area include industrial discharge, wastewater irrigation, coal burning and motor vehicle emission. Site UR1, with the highest concentration among all 18 topsoil samples, is located in an industrial area, where energy consumption, industries and metal smelting are the main sources for PAHs. The second highest concentration (1607 ng/g) occurred at Site UR9, which located in the vicinity of main sewage of the city. Higher concentration was found at UR4, which was linked to the city crossroads, and the heavy automobile traffic may be a reasonable explanation. Two background samples which were far from industries and anthropogenic activities had the lowest ∑PAHs (63.6 and 29.7 ng/g respectively).

The possible sources of PAHs may be identified by ratios of individual PAH compounds. Ratio values of LMW/HMW[13], PHE/ANT (phenanthrene/anthracene), and FTH/PYR (fluoranthene/pyrene)[14-16] have been used to distinguishing the sources of PAHs. When LMW/HMW < 1, PHE/ANT < 10 and FTH/PYR > 1, it indicates that the main source is fuel and coal combustion (pyrogenic), and when LMW/HMW >1, PHE/ANT > 15 and FTH/PYR < 1, crude oil (petrogenic) may be the major source. Some selected ratio values in this study are presented in Table 1. The results indicate that all the values of LMW/HMW were lower than 1, those of FTH/PYR were higher than 1, and all the values of PHE/ANT lower than 15 with the major less than 10,

indicating a strong pyrogenic origins of PAHs in soil of Harbin City. This is expected since that, in Harbin City, the climate is special with annual mean temperature lower than 3.6 °C, so there are six months using coal combustion for heating. The traffic exhausts has also played an important role for the residues of PAHs in soil in the city.

Table 1. Ratios of some selected PAH compounds in topsoils in Harbin City

sites	LMW/HMW	PHE/ANT	FTH/PYR	sites	LMW/HMW	PHE/ANT	FTH/PYR
UR1	0.23	12.34	1.55	UR10	0.33	7.44	1.17
UR2	0.38	9.64	1.23	SU1	0.28	6.81	1.24
UR3	0.23	4.31	1.17	SU2	0.45	10.98	1.16
UR4	0.23	5.10	1.09	SU3	0.36	12.84	1.22
UR5	0.21	8.45	1.16	SU4	0.53	8.27	1.30
UR6	0.30	7.08	1.25	RU1	0.33	10.82	1.08
UR7	0.23	6.90	1.13	RU2	0.26	7.31	1.09
UR8	0.33	8.15	1.17	BA1	0.29	13.77	1.34
UR9	0.16	5.95	1.18	BA2	0.23	13.44	1.39

Conclusions

Soil samples collected from Harbin City had moderate PAH level compared to other industrial areas worldwide. Total PAH concentrations ranged from 17.0 to 3256.2ng/g. Generally speaking, the average PAH concentration in urban sites was at least one order of magnitude higher than in the background areas. The four major PAH in all samples were phenanthrene, fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene. The PAH profile showed that HMW were the dominating group. Special PAH compounds value ratios indicated the main source of PAH in Harbin City is coal combustion and traffic exhaust.

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