



Polycyclic Aromatic Hydrocarbon Distribution in Soil and Their Ecological Risk Evaluation in Zhengzhou, China

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH), as a primary organic pollutant in soil, is highly stable in soil and does not degrade easily. Thus, it accumulates and may penetrate deeper soil, which will cause long-term pollution of soil and underground water. To study PAH concentration distribution in soil in Zhengzhou, China, ecological risk evaluation of PAHs in soil was implemented. In this study, 30 soil samples from different places in Zhengzhou were collected in August 2015. Concentration levels and distribution characteristics of PAHs in the soil samples were analysed, and ecological risk evaluation of PAH pollution in soil was conducted. Results indicated that among the 30 soil samples collected, the content scope of 16 PAHs under priority control of the US Environmental Protection Agency was 436.37-4,784.13 $\mu\text{g}\cdot\text{kg}^{-1}$ with a mean value of 3,096.71 $\mu\text{g}\cdot\text{kg}^{-1}$. Detection rates of monomers were high, and not all benzo[k]fluoranthene (BkF) and dibenzo[a,h]anthracene were detected. All dibenzo[a]pyrenes with high carcinogenicity were detected with a content scope of 436.37-4,784.13 $\mu\text{g}\cdot\text{kg}^{-1}$ and a mean value of 23.01 $\mu\text{g}\cdot\text{kg}^{-1}$. A total of 27 soil samples exhibited severe PAH pollution, which indicated that overall soil pollution level in Zhengzhou was considerably severe. Only two samples were within ERL-ERM (effect range-low, effect range-median). However, the PAH contents of most samples were higher than ERM, indicating a high ecological risk of soil PAHs in Zhengzhou. Results will provide indispensable scientific basis for government sectors and relevant environmental protection departments to formulate a reasonable control scheme in determining the total amount of soil pollution and to implement human health protection measures.

INTRODUCTION

As an important chemical compound among persistent organic pollutants prevalent in nature, polycyclic aromatic hydrocarbon (PAH) is a chemical compound with stable properties formed through the connection of two or more benzene rings. PAH, an environmental pollutant with strong carcinogenicity, is a cancerogenic substance found predominant in nature. As one of the most poisonous and harmful organic pollutants in the environment, PAHs have drawn significant attention because of their durability and potential carcinogenicity. PAHs have thus far been found nearly among all environmental media. PAHs in nature were originally derived from spontaneous fire and plant decomposition. However, incomplete combustion of fossil fuels and timbers has become an important source of PAHs in environmental media in this modern time. As a source and sink of PAH migration and conversion, soil has become a research hotspot.

Zhengzhou, the provincial capital of Henan Province, China, is a large city and economic center with high urbanization level and continuously increasing demand for en-

ergy sources. Numerous enterprises focused on chemical engineering production, such as chemical plants, steelworks, dockyards, electroplate factories, accumulator plants, paper mills, textile mills, and pharmaceutical factories, are distributed around Zhengzhou City. Although these chemical enterprises significantly contribute to the urban construction of Zhengzhou, they will inevitably cause environmental pollution in Zhengzhou. Moreover, dense population and heavy traffic aggravate the accumulation of organic pollutants and harm human health and the ecological environment. Therefore, soil in Zhengzhou is taken as the research object. The PAH content in the soil samples was determined to measure the PAH pollution level in Zhengzhou, as a reference for scientific method and basis for determining PAH sources and pollution regulation in Zhengzhou.

STATE OF THE ART

PAHs distribution in soil and their pollution risks have been investigated in foreign research. Greenberg analysed the concentration levels of 15 urban and rural PAHs in air for two years in New Jersey, USA, and conducted a compara-

tive analysis of urban PAH concentration levels during summer and winter; results show that PAH concentration was higher in winter than in summer (Greenberg et al. 1967). Brown detected the concentration of dust on urban road surface and heavy metals in suspended matter in gutterways during rainstorm; the analysis of source features of PAHs revealed that PAH minutia features of the two were similar, and pollution sources of the two were identical (Brown et al. 2006). Dahle studied PAH concentration and spatial distribution in bottom sediments between Norway and Russia and evaluated the degree of influence of PAHs on humans in these areas (Dahle et al. 2006). Amaraneni studied the distribution of pesticides and heavy metals in water bodies and deposits in shrimp ponds surrounding lakes and wetlands in India and evaluated their effects on humans (Amaraneni 2006). Olivella analysed PAH content in rainwater in northern Italy and those in Maggiore lake water; findings show that rainwater was the main source of PAHs in Maggiore lake water (Olivella 2006). Bourotte compared PAH content between urban soil and natural forest soil in Sao Paulo and found that PAH concentration in urban soil was 4.5 times of that in forest soil, whereby high PAH pollution with a significant amount of contribution came mostly from industry and transportation (Bourotte et al. 2009). Agarwal studied PAH concentration level, distribution characteristics, and potential toxicity in roadside soil of major communication lines in New Delhi; results indicated that PAHs in the research area were derived mainly from motor vehicle exhaust emission and coal combustion (Agarwal 2009). Maliszewska-Kordybach studied pollution level, distribution characteristics, and PAH sources in farmland soil in Poland; results indicated that PAHs in farmland soil in Poland were derived mostly from coal combustion (Maliszewska-Kordybach et al. 2009). Orecchio studied PAH pollution in the soil of a botanical garden beside one waste coal gas production field in Palermo, Italy, and evaluated pollution risks generated to the environment (Orecchio 2010). Von studied PAH distribution and sources in surface soil in five different places in Kelang Valley, Malaysia; results indicated that all PAHs in the research area were derived primarily from pyrolysis, combustion of petroleum and biomass, industry, and non-point source pollution (Von et al. 2012). On domestic research, Liu analysed PAH concentration levels, alternative distribution, migration, and their possible sources in the middle and lower reaches of the Yellow River in China (Liu et al. 2001). Wang analysed PAH distribution and composition in overlying deposits in Kiaocho Bay of Qingdao, China (Wang et al. 2006). Li J analyzed PAH concentrations in air in Guangzhou, China, and deemed that PAH concentration in particulate matters in winter was high (Li et al. 2006). Deng analysed PAH

contents in water and suspended matters for 12 months in Xijiang River in Guangdong Province and analyzed their effects on the environment (Deng et al. 2006). Wang analyzed PAH distributions in Bohai gulf and its neighbouring sea areas in China (Wang et al. 2015). Zhang analyzed PAH distribution in surface deposits on the coast of Weihai City, Shandong Province, China, and determined their hazard degree (Zhang et al. 2016). These studies show that in recent years, the improvement in the collection of environmental data on PAHs in various countries has enriched the research achievements on PAH distribution and their pollution risk. Most studies indicate that PAHs are prevalent in the environment and become rich in soil and bottom mud. At present, soil organic matters can turn the soil as the main storage and transfer station for PAH-like chemical compounds by absorbing and restoring PAHs. Moreover, with the rapid development in industry and agriculture as well as the large-scale application of fossil fuels, many PAH pollutants are emitted in the air, and PAHs emitted from urban areas diffuse in the atmosphere and move with airflow. Some PAHs in air will deposit nearby (urban areas or suburbs) through dry and wet deposition action, and then enter and pollute soil, water bodies, deposits, and organisms. Therefore, by analysing the concentration levels and distribution features of PAHs in soil in Zhengzhou, China, the main sources of PAHs within the research area were identified, and ecological risk evaluation on PAHs was conducted. Results will provide an indispensable scientific basis for government sectors and relevant environmental protection departments to formulate a reasonable control scheme of soil pollution to implement human health protection measures.

MATERIALS AND METHODS

Sample collection: Zhengzhou has a vast territory. To guarantee the reliability of coverage and data analysis of collected soil, 30 soil samples were collected from two different places in each area, among 6 municipal districts (Zhongyuan District, Erqi District, Jinshui District, Huiji District, Guancheng District, Shangjie District) under the jurisdiction of Zhengzhou City, 5 county-level cities (Gongyi City, Xinzheng City, Dengfeng City, Xinmi City, and Xingyang City), 1 county (Zhongmu County), and 3 national-level development zones (Zhengzhou New District, Zhengzhou High and New Tech Development Zone, Zhengzhou Comprehensive Bonded Zone).

Sample preprocessing: After soil samples were freeze dried, and stone and plant roots were removed, sufficient amount of samples were taken to determine soil organic matters. Residual samples went through a 60-mesh steel sieve after grinding and were then used for PAH determination.

A total of 20 g sieved samples were taken and extracted using accelerated solvent extractor ASE300 (DIONEX, USA). Extraction agents selected were acetone and dichloromethane (1:1, volume ratio). Extraction conditions were as follows: extraction pressure was 10,342.14 kPa, static circulation was conducted three times, heating temperature was 100°C, volume ratio between the two solvents in rapidly washed samples was 60%, and the time for nitrogen to purge and collect extracted solution was 60 s.

Acetone and dichloromethane were washed in a receiving flask in three separate times, and extract liquors were gathered. DryVap full-automatic quantitative concentrator (LabTech, USA) was used to concentrate the solution to 2-3 mL, and 15 mL n-hexane was added for solvent conversion. The solution was then continuously concentrated to 2-3mL, after which silica gel and aluminium oxide chromatographic column were used for purification. Dichloromethane was used for wet packing of chromatographic column, being successively anhydrous sodium sulphate, neutral alumina, silica gel, quartz sand, and glass wool from top to bottom. The volume ratio of silica gel to aluminium oxide in the chromatographic column was 2:1.70 mL of eluent (volume ratio of dichloromethane to n-hexane was 3:7), which was used to wash chromatographic column. After the concentrated liquor was added into the chromatographic column, 15 mL n-hexane was used, the leachate was removed, 70 mL of eluent was added, and the eluent was collected. Before the eluent was added, the liquor level of the chromatographic column was kept above the anhydrous sodium sulphate, and flow velocity was maintained at approximately 2 mL/min. DryVap was used to concentrate the eluent to 2-3mL; 15 mL n-hexane was added for solvent conversion. The concentration was then continued. The liquor was accurately quantified to 0.9 mL, and 100 µL of internal standard was added. The analysis was done on a computer.

All organic solvents (acetone, n-hexane, and

dichloromethane) used in the experiment were at pesticide residue level and purchased from German Merck Corporation. Quartz sand, anhydrous sodium sulphate, and aluminium oxide were purchased from Sinopharm and ignited in muffle for 4 h under 450°C. Silica gel (Sinopharm) was excited for 16 h under 130°C. Glass wool, at pesticide residue level, was purchased from C.N.W. Corporation and ignited in muffle for 8 h under 350°C.

Sample testing: Samples were determined using a gas chromatograph-mass spectrometer (Agilent 7890AGC, USA) equipped with a CTC automatic sampler. The chromatographic column selected was HP-5MS quartz capillary column. The sampling method was unsplit stream sampling with sampling size being 1 µL, temperature at injection port at 300°C, temperature of ion source at 150°C, and temperature of transmission line at 280°C. Standard samples included 16 PAHs under priority control as stipulated by the US Environmental Protection Agency (US-EPA), specifically naphthalene (Nap), acenaphthenyl (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indenoindene [1,2,3-cd] (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP). These 16 PAHs under priority control were quantified.

RESULTS AND DISCUSSION

Content characteristics of PAHs in soil in Zhengzhou: The PAH content and content levels of different monomers among the 30 soil samples collected in Zhengzhou are shown in Fig. 1. The content scope of the 16 PAHs under the priority control of EPA was 436.37-4,784.13 µg.kg⁻¹ with mean value of 3,096.71 µg.kg⁻¹.

The detection rates of monomers were high, and not all BkF and DahA were detected, as shown in Table 1. BaP with

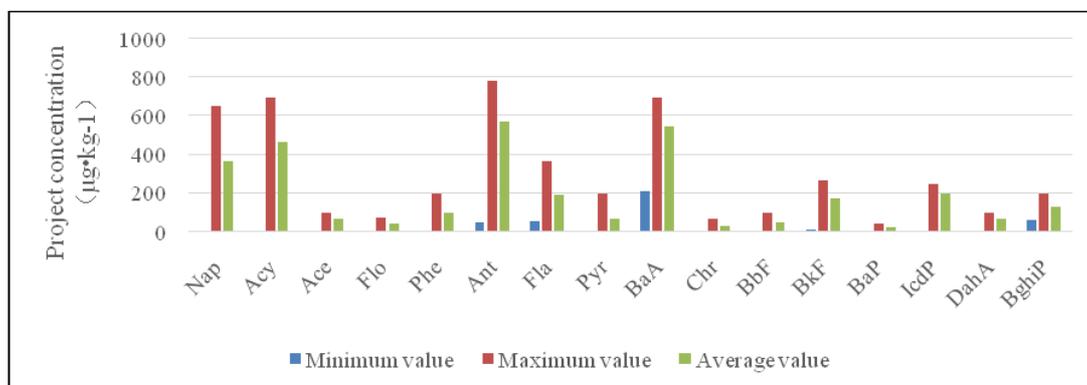


Fig. 1. The PAH content and content levels of different monomers among the 30 soil samples.

Table 1: PAH concentrations in soil samples in Zhengzhou.

Name	Detection rate (%)
Naphthalene (Nap)	100
Acenaphthenyl (Acy)	100
Acenaphthene (Ace)	100
Fluorene (Flo)	100
Phenanthrene (Phe)	100
Anthracene (Ant)	100
Fluoranthene (Fla)	100
Pyrene (Pyr)	100
Benzo[a]anthracene (BaA)	100
Chrysene (Chr)	100
Benzo[b]fluoranthene (BbF)	100
Benzo[k]fluoranthene (BkF)	98.6
Benzo[a]pyrene (BaP)	100
Indenoindene [1,2,3-cd](IcdP)	100
Dibenzo[a,h]anthracene (DahA)	98.4
Benzo[g,h,i]perylene (BghiP)	100

high carcinogenicity were detected with content range of 2.36-45.68 $\mu\text{g.kg}^{-1}$ and mean value of 23.01 $\mu\text{g.kg}^{-1}$. At present, no soil quality standard for PAHs in China has been developed. However, the Netherlands government has developed a set of standards about the evaluation and governance of PAHs and stipulated that PAH content in unpolluted soil is 20-50 $\mu\text{g.kg}^{-1}$. According to this standard, the highest average PAH content in farmland soil in Zhengzhou has exceeded 60 times of the upper limit in this standard. In the literature (17), Maliszewska-Kordybach studied agricultural soil in Poland and divided soil PAH pollution into four levels, namely, no pollution ($< 200 \mu\text{g.kg}^{-1}$), slight pollution (200-600 $\mu\text{g.kg}^{-1}$), medium pollution (600-1,000 $\mu\text{g.kg}^{-1}$), and serious pollution ($> 1,000 \mu\text{g.kg}^{-1}$)

(Maliszewska-Kordybach 1996). With a reference to this standard, 27 soil samples collected in Zhengzhou belonged to PAH serious pollution, which indicated that the overall soil pollution level in Zhengzhou is considerably severe.

Ecological risk evaluation of soil in Zhengzhou: China currently lacks an environmental quality standard for PAHs in soil. Therefore, with reference to the soil quality standard formulated by the US EPA National Center for Environmental Assessment, the concentration levels of 16 PAHs in soil in Zhengzhou were analyzed in this study. Table 2 shows that only two samples were within ERL-ERM. However, the PAH contents of most samples were higher than ERM, indicating that the ecological risk of soil PAHs in Zhengzhou is considerably high.

CONCLUSIONS

As one of the most poisonous and harmful organic pollutants in the environment, PAHs have drawn significant attention because of their durability and potential carcinogenicity. PAHs have thus far been found nearly among all environmental media. PAHs in nature were originally derived from spontaneous fire and plant decomposition. However, incomplete combustion of fossil fuels and timbers has become an important source of PAHs in the environmental media in the modern times. As a source and sink of PAH migration and conversion, soil has become a research hotspot. A total of 30 soil samples were collected in different places in Zhengzhou in August 2015. The concentration levels and distribution characteristics of PAHs in the soil samples were analyzed, and ecological risk evaluation of PAH pollution in soil was conducted. Results indi-

Table 2: Distribution of PAHs in soil.

Item	Type standard		Number of samples satisfying $< \text{ERL}/\text{ea}$	Number of samples within ERL-ERM /ea	Number of samples satisfying $> \text{ERM}/\text{ea}$
	ERL	ERM			
Naphthalene (Nap)	160	2,100	0	1	29
Acenaphthenyl (Acy)	44	640	0	0	30
Acenaphthene (Ace)	16	500	0	0	30
Fluorene (Flo)	19	540	0	0	30
Phenanthrene (Phe)	240	1,500	0	0	30
Anthracene (Ant)	85.3	1,100	0	0	30
Fluoranthene (Fla)	600	5,100	0	0	30
Pyrene (Pyr)	665	2,600	0	1	29
Benzo[a]anthracene (BaA)	261	1,600	0	0	30
Chrysene (Chr)	384	2,800	0	0	30
Benzo[b]fluoranthene (BbF)	-	-	0	0	30
Benzo[k]fluoranthene (BkF)	-	-	0	0	30
Benzo[a]pyrene (BaP)	430	1,600	0	0	30
Indenoindene [1,2,3-cd](IcdP)	-	-	0	0	30
Dibenzo[a,h]anthracene (DahA)	63.4	260	0	0	30
Benzo[g,h,i]perylene (BghiP)	-	-	0	0	30

cated that among the 30 soil samples collected in Zhengzhou, the content scope of 16 PAHs under the priority control of US-EPA was 436.37-4,784.13 $\mu\text{g.kg}^{-1}$ with mean value of 3,096.71 $\mu\text{g.kg}^{-1}$. Detection rates of monomers were high, and all BaP with high carcinogenicity were detected with content scope of 436.37-4,784.13 $\mu\text{g.kg}^{-1}$ and mean value of 23.01 $\mu\text{g.kg}^{-1}$. The PAH contents of most samples were higher than ERM, which indicated that ecological risk of soil PAHs in Zhengzhou is considerably high. This paper emphasized the analysis of PAH distribution and their ecological risks in soil in Zhengzhou City. Therefore, in-depth studies should be conducted on seasonal variation in soil environment, extraction of optimized PAHs, separation and analysis methods, reduction of uncertainty in risk evaluation using multiple risk evaluation methods, and establishment of a database of the residual characteristics of PAHs over the years in Zhengzhou City.

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