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Concentration and distribution characteristics of PAHs in soil of parks in shenyang

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ABSTRACT

As the PAHs exchange, PAHs in dust and soil in a city park can reflect the pollution level of PAHs. By collecting samples of dust andsoil at different depths within eight parks in Shenyang, the concentration of PAHs in each sample was determined by indoor laboratory analysis, and then the pollution levels and the distribution characteristics of PAHs were analyzed in this paper. Especially, the distribution characteristics of ant, bap, flu, and pry in soils at different depths were analyzed. The results showed that the pollution levels of PAHs in dust, topsoil, and soil at 0-5cm depth within Wanquan Park were the highest, but there were almost no pollutants in soil at 5-10cm depth within this park. Secondly, the pollution levels of PAHs in soil of Zhongshan Park, Nanhu Park and Laodong Park were relatively high, and the concentrations of the four pollutants were all greater than those of other parks. In addition, from the perspective of the composition of PAHs pollutants, the concentration of high molecular weight PAHs was higher than that of low molecular weight PAHs. It was also found that the concentrations of pollutants in soil of parks basically decreased with the increase of depths and all the highest values were found in dust. Therefore, PAHs in soil were probably caused by substances in atmospheric dust fall from vehicle exhaust emission or fossil fuel combustion etc.

KEYWORDS

Parks; PAHs; Distribution characteristics.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are hydrocarbons containing two or more benzene rings, which take part in metabolism of organisms and human bodies. As a result, most of PAHs have a strong carcinogenicity, teratogeni city and mutagenic city, the toxicity of which grows with the increase of benzene rings[1]. PAHs have low water solubility and a high KOW (octanol water partition coefficient) value, and therefore it is easier for PAHs to be transferred from water into organisms or deposited in sediments of river. However, soil is an important carrier of PAHs and 90% of the PAHs in the environment exist in soil[2]. PAHs can easily adsorb on soil particles and have low water solubility, resulting that PAHs are relatively stable in soil and are difficult to be degraded. As a kind of hydrocarbons with a strong inertness, PAHs can be degraded mainly through photooxidation or biological degradation, but only the biological degradation of low molecular weight PAHs has made expected effects to some extent. In 1979, the US Environmental Protection Agency (EPA) issued 129 kinds of priority monitoring pollutants, including 16 kinds of PAHs. The 16 kinds of PAHs are focused on by scholars[3].

Generally, due to the relatively well-developed industry, transportation, and the relatively concentrated coal-fired heating, the pollution levels of PAHs in soil of urban areas, industrial areas as well as the surrounding areas are relatively higher than those in soil of mountains, remote suburban areas and agricultural land[4]. Studies have shown that in China the concentrations of PAHs in soil of areas far away from urban areas are far lower than those in soil of urban areas, and PAHs gradually spread to non-polluting areas from pollution sources, resulting in distribution and accumulation in a wider range of soil, which pose a serious threat to human health and survive. In addition, there are significant differences in concentrations of PAHs in soil of different functional areas in china. Wang Zhen et al[5] found that the concentrations of PAHs in soil of traffic areas, urban residential areas, suburban areas, and rural areas descended successively, and the proportions of PAHs with different number of rings showed certain regularity, mainly for human activities have impacts on PAHs pollution to some extent. In general, the concentrations of PAHs in soil decreased with increase of depths, and there is no significant difference in concentrations and compositions of PAHs in soil at depth below 40cm[6-8].

As the largest city in Northeast China, Shenyang is one of the typical old industrial bases. Due to the preferential development of heavy industry in the past and the rapid development of the city since the reform and opening up, surface dust and soil have suffered from various organic pollutions to varying degrees, among which PAHs are widely concerned for their strong toxicity. In this paper, eight major parks of Shenyang were taken as study objects and the pollution levels and concentrations of PAHs in surface dusts and soils at three different depths were analyzed, which could provide some reference for PAHs pollution control and urban planning of Shenyang.

MATERIALS AND METHODS

Study area and sample collection

Located in the south of Northeast China and the middle of Liaoning Province, Shenyang is mostly flat with mountains and hills concentrated in the southeast. Liao River, Hun River, and Xiushui River etc. flow through Shenyang. This area has a monsoon climate of medium latitudes with annual average temperature of 6.2 ~ 9.7 ℃ and annual rainfall of 600 ~ 800 mm. Affected by monsoon, rainfalls concentrate in summer and the temperature varies greatly between day and night. Shenyang has four distinct seasons: a long cold winter, a short rainy summer, a windy spring and a sunny autumn. In addition, with rapidly changing temperature, spring and autumn last a relatively short time. In order to make the samples collected typical and representative, a few sampling principles were set before sampling: first, sampling points selected should be uniformly distributed within the park and could well reflect the spatial distribution of the selected area; second, sampling points should be representative in order to meet the needs of experimental analysis; third, it is necessary to endure the number of sampling points and to control the cost of total sampling points in the budget. In March 2014, nine sampling sites of the five districts of Shenyang were selected, namely, Bainiao Park, Nujiang Park, and Beiling Park (in Huanggu District), Wanquan Park (in Dadong District), Nanhu Park and Zhongshan Park (in Heping District), Xinghua Park and Laodong Park (in Tiexi District), Qingnian Park (in Shenhe District). 36 samples were collected (including four soil layers of each park: surface dust, topsoil, soil at 0 -5 cm depth, and soil at 5-10 cm depth). In order to prevent errors due to sampling occasionality, three parallel samples of the same sampling point were collected and mixed uniformly into one storage bag, which was taken as the sample of the sampling point.

Experimental design

Experimental material preparation

Experimental reagents: methanol (HPLC grade, produced by Shandong Yuwang Chemical Factory Corporation); acetone (AR, produced by Chemical Reagent Factory of Shenyang Economic and Technological Development Zone); dichloromethane (AR, produced by Tianjin Fuyu Fine Chemical Co., Ltd.) ; acetonitrile (HPLC grade, produced by Sigma-Aldrich); standard PAHs sample, purchased from Accustandard Inc. of the United States.

Experimental apparatus: sebc bottle (Schott Duran of Germany); JJ500 Precision electronic balance (the US Shuangjie Brothers Co., Ltd); HZQ-C air temperature oscillator (Harbin Donglian Electronic Technology Development Co., Ltd.); high performance liquid chromatograph (1200series), from Agilent Technologies of the United States ; the chromatographic column is HPLC-Cartridge 250-3, LichrosphePAH (5μm).

Experimental determination

Pre-treatment of soil samples: Soil samples collected were put in the shade and dried with air drying method; discarding large plant roots and rocks, each sample was mixed uniformly and then put into a refrigerator at 0-4 ℃. 1.00g of pre-treated soil was put into a clean 100ml sebc bottle, after which 20ml of acetone, 15ml of dichloromethane and 10ml of NaCl solution (1.5g of NaCl + 10ml of water) were added into the mentioned sebc bottle with a pipette. And then the sebc bottle was put into a oscillator and taken out after 16h oscillation away from light (30 ℃, 150r / min). 10g (20ml of acetone and 15ml of dichloromethane, 35.9g totally) of upper organic phase was put into a small beaker and dried by nitrogen. And then 2ml of acetonitrile was used to enable the solution to a constant volume, after which the solution was filtered with a 0.22μm organic membrane. Soil samples under test were tested by fluorescence and UV detector. Chromatographic conditions were as follows: a) column temperature was 35 ℃; b) mobile phase was composed of acetonitrile and water; in the initial 35min, the ratio of acetonitrile was linearly increased from 60% to 100% and then maintained this ratio to run10 min; within the next 10 min, the ratio of acetonitrile decreased linearly from 100% to 60% and then maintained this ratio to run 5 min; c) flow rate was 0.5 mL·min-1; d) injection volume was 10 μL. Various PAHs were measured in their respective emission or excitation wavelengths.

QA/QC quality control

In the course of the experiment including the method blank, blank, a matrix spiked samples in parallel samples, quality assurance and quality control standard. With deuterated PAHs as internal standard addition recovery rate of samples as the relative standard deviation of each kind of 76%~101%. parallel control within 12%. The blank was not detected the target pollutants.4 PAHs the detection limit is 0.04~0.12ng/g.

RESULTS AND DISCUSSION

Concentrations of PAHs in dust of the parks

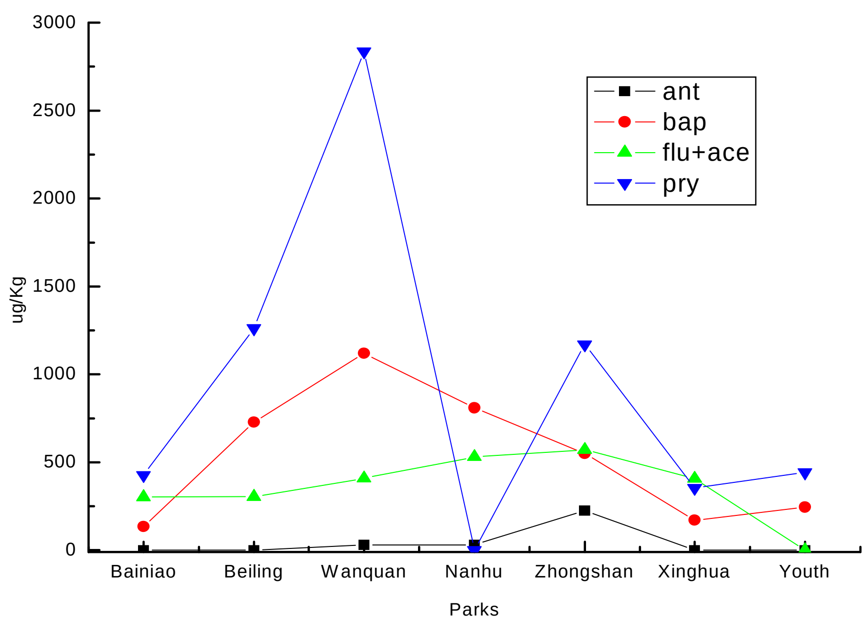

Figure 1 : Concentrations of PAHs in dust of the parks

Figure 1 shows that all 16 kinds of PAHs issued by the US EPA exist in dusts of the parks. It can be found that the order of concentrations of PAHs in dust of the parks is Wanquan Park >Qingnian Park>Bainiao Park>Zhongshan Park>Nanhu Park>Beiling Park>Xinghua Park. There is a significant difference in concentrations of different compositions, among which the concentrations of low molecular weight PAHs are relatively low, for example, ant. Some low molecular weight PAHs even are not found in part of the sampling points. The results are similar with Shanghai, which was 85.18% more than 4 ring[9]. However, there are some exceptions. The concentration of ant in dust of Zhongshan Park is 225.37ug / kg, which is rather higher compared with that of other parks. It can be reflected that the pollution sources of PAHs in these parks of different districts are significantly different due to different geographical environments. The concentrations of benzo

(a) anthracene (baa) are between 194.08 ~ 1224.21ug / kg, which are high in all parks, indicating that there are common features in pollution sources of the eight parks.

Concentrations of PAHs in topsoil

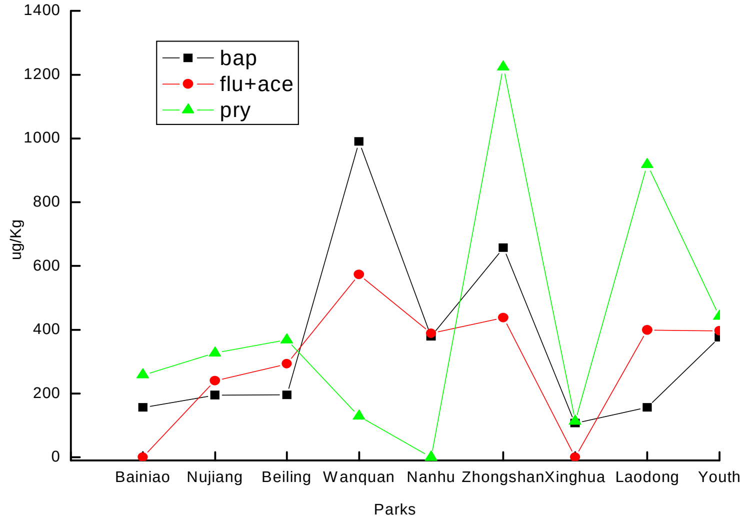

Figure 2 : Concentrations of PAHs in topsoil of the parks

Concentrations of PAHs in topsoil of the parks can be seen from Figure 2. Since background values of PAHs in soil are among 0 ~ 2000 μg/kg, there is almost no ant found in topsoil, except a little in Wanquan Park. The concentrations of other kinds of PAHs are evenly distributed. Figure 2 shows that concentrations of PAHs in topsoil of Wanquan Park, Zhongshan Park and Laodong Park are relatively high. In addition, the concentrations of the four pollutants in samples of Wanquan Park are significantly higher than those of other parks. Wanquan Park is located in Dadong District where many industries are distributed. Zhongshan Park and Laodong Park lie in areas with dense population and traffic. Although densely populated other parks (such as Beiling Park, Nanhu Park, Qingnian Park, and Zhongshan Park) are, those parks boast relatively independent and closed areas and are not next to major transport roads, so the accumulated concentrations of PAHs are relatively low, around 500 μg/kg. In addition, with the largest area, Beiling Park can bear large amount of PAHs, which also a reason for its low concentration of PAHs. The concentration of PAHs was lower than 2.5 μg/g (the average concentration of Shanghai[10]). And the concentration of PAHs was similar with 0.682.5μg/g (the average concentration of Shenzhen[11]).

Concentrations of PAHs in soil at 0-5 cm depth

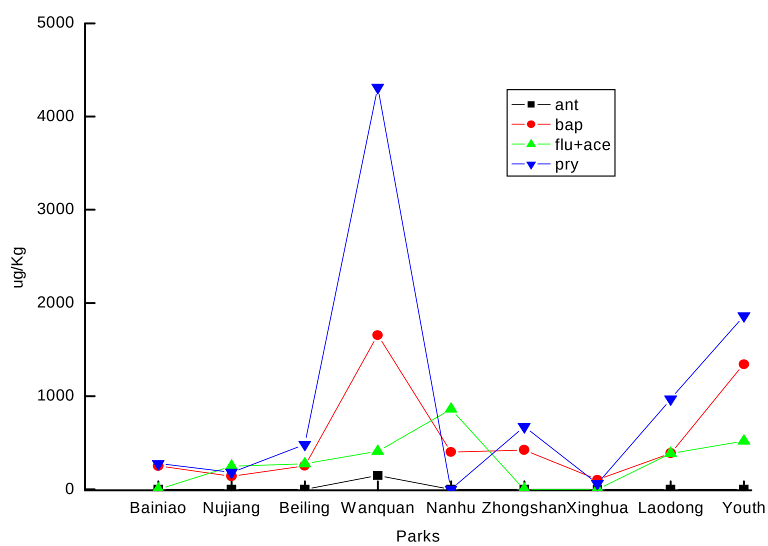

Figure 3 : Concentrations of PAHs in soil at 0-5 cm depth of the parks

As can be seen from Figure 3 there is almost no ant in soil at 0-5 cm depth of the parks, while the concentrations of pry (the maximum, 971.8739) and flu (the maximum, 573.4614) bap (the maximum, 989.8723) are distributed evenly. The concentrations of other three kinds of PAHs in Nanhu Park, Zhongshan Park and Laodong Park are all higher than those in other parks. Since Zhongshan Park and Laodong Park are located in areas with dense population and traffic, there are more pollutants in topsoil, which are transferred to subsurface soil through transportation or survival activities and excrement of animals.

Concentrations of PAHs in soil at 5-10 cm depth

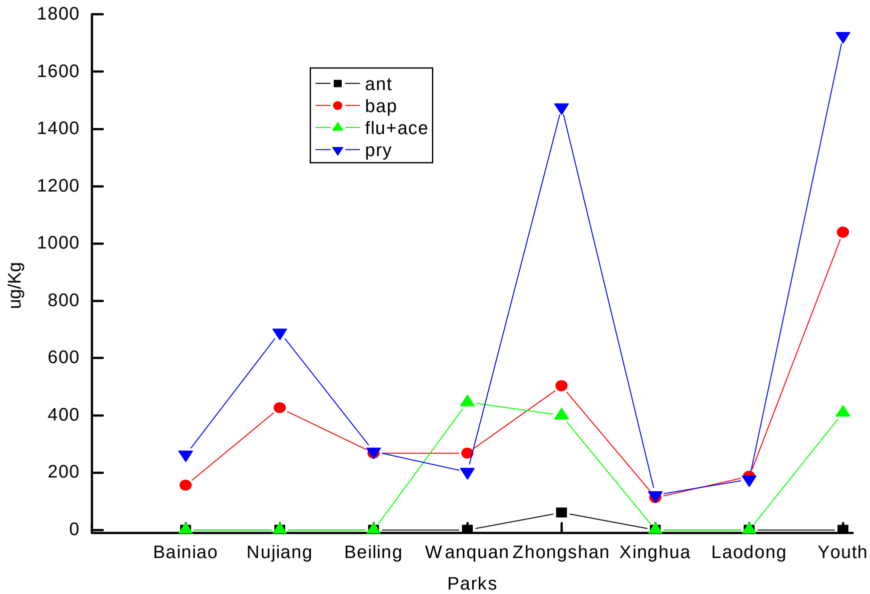

Figure 4 : Concentrations of PAHs in soil at 5-10 cm depth

As can be seen from Figure 4 the concentrations of PAHs in relatively deep soil are significantly low. However, the concentrations of bap and pry in Zhongshan Park are distinctly higher than those in other parks, probably due to transportation of pollutants in topsoil and subsurface as well as pollution caused by industrial wastewater discharges. However, except small amount detected in Nanhu Park and Zhongshan Park, no flu are found in other parks. The causes of PAHs pollution were similar with the Fang's study, the pollution source were industry and traffic[12].

Evaluation of pollution level of PAHs in surface soil

Currently the single factor index method is widely used to evaluate the pollution level, which can effectively express the influence degree of a single factor. For instance, Hankanson (1980) used this method to evaluate the influence degree of sediments. The formula is as follows:

$$\mathrm{C}^i{}_f = C^i / C^i{}_n \quad (1)$$

Where $C^i{}_f$ represents the pollution coefficient of i, a component of PAHs;

C^i refers to the actual concentration of i;

$C^i{}_n$ is the reference value for evaluation of i.

In this paper, the Canadian agricultural soil remediation standards are taken as reference values (Annokkee, 1990). According to the Canadian agricultural soil remediation standards, the concentration limits of ant, flu, pry and bap in agricultural soil are 0.1 ug/g. Hankanson used $C^i{}_f$ to represent pollution level of individual pollutants and put forward the corresponding relationship between the value of $C^i{}_f$ and pollution level, which has been widely used in researches. $C^i{}_f < 1$ represents low pollution level; $1 \le C^i{}_f < 3$, moderate pollution level; $3 \le C^i{}_f < 6$, relatively high pollution level ; $C^i{}_f > 6$, high pollution level.

The single factor indexes of each pollutant in dust of the parks can be seen from TABLE 1. The concentrations of ant are between 0 and 7.05(average, 3.02) and there is one sampling point at high pollution level, two at relatively high pollution level and others at moderate or low pollution level; The concentrations of pry are between 0 and 12.62(average, 6.45) and there are three sampling points at high pollution level, three at relatively high pollution level and one at low pollution level; The concentrations of bap are between1.36 to 8.09 (average, 4.29) and there are two sampling points at high pollution level, one at relatively high pollution level and others at moderate pollution level; The concentrations of flu are between1.94 to12.24 (average, 5.74) and there are four sampling points at high pollution level and others at moderate pollution level.

CONCLUSIONS

(1)There are anthracene, fluorene, pyrene, and benzopyrene in almost all soil of parks in Shenyang. The concentrations of high molecular weight PAHs, Anthracene and fluorine in surface soil are significantly higher than those in deep soil; located in Dadong District where many industries are distributed, Wanquan Park is at the highest pollution level, the concentration of pyrene in Wanquan Park is much higher than that in other parks.

(2)Concentrations of PAHs in different soil layers within the park are also somewhat different. Concentration of PAHs in dust are significantly higher than that in other soil layers, probably due to vehicle exhausts, industrial waste discharges or barbecues by surrounding residents.

(3)From the perspective of the spatial distribution of the eight parks, Parks that located in industrial areas and densely populated areas in city had higher concentrations of PAHs.

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